

Corrosion characterisation of brazing Ag₅₉Cu₃₁Pd₁₀ alloy for potential dental applications

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ARTICLE INFORMATION :

<https://doi.org/10.56801/MMD25>

Received: 11 March 2024

Accepted: 21 March 2024

Type of paper: Research paper



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ABSTRACT

This research addresses the corrosion behaviour of the Ag-based alloy with Pd as the component in three different corrosion environments: standard physiological saline solution (SS; 0.9% NaCl), Ringer's solution (RS), and Fusayama's artificial saliva (AS) at 37 °C. The examination has a primary goal to evaluate the suitability of the alloy as dental material and is used following the electrochemical methods: open circuit potential (OCP), linear polarisation resistance (LRP), and Tafel extrapolation from the potentiodynamic measurement, which is a broad interval of anodic potential. Chemical analysis of the RS after recording a polarisation curve was also a significant part of the study. The results showed OCP values from 35 mV to 65 mV and polarisation resistance values (Rp) in the interval from 8.5 up to 19.3 kΩ·cm². The most corrosive solution was RS, and the least was AS. The corrosion current density in AS was close to 1 μA·cm⁻². Although the alloy, in AS particularly, has a relatively high Rp value and OCP close to the Ag alloys with a higher content of noble metals, it has low breakdown potential, which directly led to its classification as an unstable dental material for permanent use. The concentrations of the metals in RS were at ppb levels for Ag, tens of ppb for Pd, and 0.64 mg dm⁻³ for Cu. Regardless of the unsatisfactory corrosion characteristics for the application, the paper showed good potential for the Ag-Cu-Pd system as a brazing filler for dental use and as an adequate control for similar studies.

Keywords: silver brazing alloy, dental application, corrosion, isotonic solutions, artificial saliva.

1. Introduction

Depending on the specific needs, brazing is a unique kind of joining process for intricate parts of components made of both similar and dissimilar combinations of materials. Because this method's connecting area is extremely thin, it requires a precise joining technique with the proper heat input to produce a nearly net-shaped component. In this regard, a proper brazing filler alloy provides particular qualities such as sufficient wetting, low thickness, a narrow melting zone, prevention of intermetallic formation, and a restricted amount of stress development at the joint interface (Roy R.K., and Ghosh M., 2022). Brazing's main benefit in contemporary production is its ability to create strong bonds, with parent materials that are similar or completely different with negligible alteration of the contact materials (Way M. et al., 2020).

Because of their moderate melting points, good wetting and spreading qualities, and good thermal and electric conductivity and corrosion resistance, Ag-based brazing filler metals are the most

appropriate for joining metals such as copper, iron, stainless steel, and hard alloys (Ntasi A., et al., 2019).

Many orthodontic appliances (brackets, hyrax appliances, headgear, space maintainers, and others) are made by joining dissimilar metallic parts (Ntasi A., et al., 2014; Veljković M.F. et al., 2023) and due to their properties, Ag brazing alloys are extensively utilized in the manufacture. Commercially available Ag brazing alloys are ternary or multi-component alloys based on the Ag-Cu system, where other components are zinc, palladium, indium, tin, or nickel (Wataha J.C. et al., 2000). It has been revealed that these systems are the best substitute for the AgCuZnCd-series filler metals, which were the most widely used in the past. However, the application of Cd-containing filler metals has been restricted (Commission Regulation (EU), 2011) due to the high toxicity of Cd.

Concerns about the possible harmful biological effects of heavy metal ions released through corrosion and/or wear mechanisms are always present when a metallic material is introduced to the aggressive environment of the human mouth.

In brazed joints, where multiple parent materials, filler metal, and possibly interfacial phases are involved, corrosion can be especially

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complicated. In certain situations, the presence of different materials in contact, often in hard-to-observe areas, creates an environment that is susceptible to high corrosion rates, which are frequently difficult to detect.

Testing of brazed joints is typically done on a case-by-case basis because the combination of different materials presents the risk of generating galvanic couples, which could drive accelerated corrosion in aqueous environments. When common filler metals based on silver are brazed onto stainless steel, such as AgCuZnSn, the interfacial bonding layer dissolves when exposed to moisture in service, so interfacial corrosion becomes a significant issue. As a result, corrosion issues need to be addressed comprehensively in both the assembly and operating environments. From the biocompatibility perspective, the corrosion of materials points toward that some of the elements can impact the surrounding tissues (Wataha J.C. et al., 2000). When dental alloys interact with oral fluids, metal ions are released, which may cause an adverse response in the organism (Hwang C. et al., 2011). Because of this, knowledge regarding the corrosion behavior of a dental alloy is crucial from a practical standpoint.

The Ag-Cu systems exhibit superior corrosion resistance in chloride solutions compared to less expensive copper alloys. Unfortunately, seawater causes corrosion, particularly in the form of dezincification of these alloys, which are resistant only to high silver contents (above 43% for the Ag-Cu-Zn system). It should be noted that this resistance is conditional and insufficient at high electrode potentials (Way M. et al., 2020; Dimitrijević P.S. et al., 2015) where porous surface films are formed.

Using 42% nickel-iron alloy as the parent material, the silver-copper eutectic and three variations containing 5%, 10%, and 25% palladium were studied (Perrz E., 1989). The Pd-free alloy was found to have stress corrosion pits and tunnelling, whereas the Pd-rich alloys had none of these characteristics. The author has concluded that the molten brazing alloy's uptake of Fe caused a reduction in the penetration of grain boundaries in the parent metal as Pd increased.

The corrosion resistance of dental alloys containing or based on palladium has been investigated in numerous authors (Tufekçi E. et al., 2022; Manaranche C. and Hornberger H., 2007; Stéphane et al., 2006; Joska L. et al., 2005; Joska L. et al., 2005; Joska L. et al., 2008; Sarantopoulos D. M. et al., 2011). Results shown in (Grgur B. et al., 2021), based on the EDS, SEM and ICP-MS analysis, have shown that all alloys containing noble metals (gold, platinum and palladium) possess high corrosion stability, both at open circuit potentials and under anodic polarizations. According to their research, dental alloys of chemical composition with 25-60 wt.% of noble metals are in the second group ranked by corrosion stability and labelled as stable alloys. They should have $I_{0.3}$ between $2 \mu\text{A cm}^{-2}$ to $5 \mu\text{A cm}^{-2}$ and E_p between 0.3 V to 0.6 vs SCE.

Ag-Pd alloys exhibit good resistance to corrosion, as confirmed by (Stéphane et al., 2006). The authors report that the studied alloys have R_p values that fall between those of the noble alloy and the base metal alloy, and that their OCP values are among the highest for dental alloys. These findings suggest that the alloys exhibit noble electrochemical behavior and good corrosion protection. This agrees with the American Dental Association (ADA) classification system, which classifies Ag-Pd alloys as semi-noble prosthodontic alloys (Wataha C.J., 2022). Previous research of the authors (Dimitrijević P.S. et al., 2018), has shown that in comparison to Ag-Cu-Zn, the Ag-Cu-Pd alloy showed a more positive OCP, -195.5 and -5.3 mV versus SCE, respectively (in 3.5% NaCl solution), indicating a higher level of corrosion resistance in the palladium-containing alloy.

Also, a passive layer is formed as an efficient protection against saliva influence in this type of alloy. The equilibrium composition calculation results presented in (Joska L. et al., 2008) indicate that both palladium and silver may oxidize within the range of relevant potentials, resulting in the formation of both complex and insoluble compounds of both components. Nevertheless, complex soluble species are in equilibrium

at excessively low concentrations ($<10^{-6}$ mol-dm⁻³ for AgCl₂⁻ and $<10^{-13}$ mol-dm⁻³ for PdCl₃⁻, both at +350 mV vs SHE potential) so that they hardly could be detected at lower (anodic) potentials, for instance, at the free corrosion potential or after LPR measurement. However, the previous does not exclude the dissolution of both alloy components at highly non-equilibrium conditions (higher potentials) and film formation at the surface of the alloy, primarily AgCl.

The research presented in this paper investigates the corrosion behavior of the Ag₅₉Cu₃₁Pd₁₀ alloy in two physiological saline solutions and artificial saliva. This study aims to fill the gap between the research of less corrosion-resistant AgCuZn alloys with similar silver content and more noble alloys with higher palladium and lower copper contents. It has additional goals, consisting of an assessment of the use in dentistry applications of the alloy and an evaluation of the difference between osmolar solutions and artificial saliva and their capability to be a replacement for the latter or an appropriate control in the studies with the dental use of similar alloys.

2. Materials and methods

The alloy sample was prepared by the ingot metallurgy method using high-grade (99.97%+) base metals (silver, copper, and palladium) and silver-copper eutectic alloy (Ag₇₂Cu₂₈) produced from the same metals. The sample was subjected to the annealed process described elsewhere (Dimitrijević P.S. et al., 2018). The specimen's chemical composition was determined by an X-ray Fluorescence (XRF, Niton XL3t-950).

Open circuit potential (OCP), linear polarisation resistance (LPR), polarisation curves and linear sweep voltammetry (LSV) were the electrochemical methods conducted in this study, with a classical three-electrode electrochemical cell setup. The electrochemical cell was filled with 330 cm³ of solution before every test. This test system was thermostated using an appropriate bath of 10 dm³ volume (8 dm³ of water) with temperature control.

The Gamry Interface 1000™ potentiostat-galvanostat was used for electrochemical measurements. The authors collected data using Gamry Framework software (version 6.25) and analysed raw data using Echem Analyst (v. 6). The area of the working electrode was 0.50 cm². A platinum sheet with a surface of 2.00 cm² was the counter electrode. A saturated calomel electrode (SCE) was the reference electrode, completing the electrochemical cell setup. All potentials reported in this paper are against this reference electrode system (+0.241 V versus standard hydrogen electrode, SHE). The pH meter was WTW 3110.

The following solutions were corrosive media: standard physiological solution (SS; 0.9% NaCl), Ringer's solution (RS; 8.6 g/dm³ NaCl, 0.33 g/dm³ CaCl₂ and 0.3 g/dm³ KCl) and artificial saliva (AS; Fusayama-type). The isotonic solutions were pharmaceutical products (Hemofarm, Serbia) with pH of 5.069 and 5.380, respectively. Since they are unbuffered solutions, the values were as expected and under the specifications for the products (4.5-7 for SS and 5-7 for RS, as stated on the product's label). AS was unmodified Fusayama's solution with the following composition (g/dm³): NaCl 0.400; KCl 0.900; CaCl₂ 0.684 (equivalent to CaCl₂·H₂O 0.795); Urea 1.000; NaH₂PO₄ 0.690. All chemicals were p.a. quality, measured using a precise digital balance KERN EG 620-3NM (readability 1 mg, reproducibility 1 mg, linearity ± 3 mg), and dissolved in Millipore grade ultrapure water (electrical resistivity of ≈ 18 MΩ·cm). After preparation, it had pH=5.542. Chemical analysis of the solution was conducted on an Agilent 7900 ICP-MS instrument.

The metal sample was Polytetrafluoroethylene (PTFE) wrapped and ground with a series of SiC papers up to #2500 and further polished using a series of diamond pastes up to the size of 1.0 μm. The experiments were performed at a temperature of 37 ± 1 °C. The duration of the OCP experiment was one hour. LPR potential limits were set standardly at ± 20 mV related to the OCP and with a potential change rate of 83.3 μV·s⁻¹ (this slow rate was chosen because of low currents near OCP, which are under 50 nA and with a high noise influence). Tafel extrapolation was

performed in the area of ± 100 mV from OCP in polarisation curves, again because of the extreme anode slopes immediately after the OCP (the short potential interval of apparent Tafel region for this system). A potential change rate of 0.333 mV·s⁻¹ was applied to record polarisation curves, and the potential range was from -0.300 V, with respect to OCP, up to $+1.00$ V, with respect to the reference electrode (SCE). All potentials below are against SCE.

The chemical analysis of the sample is given in the table below.

Table 1. The chemical composition of the alloy (wt. %).

Alloy	Ag	Cu	Pd
Ag59Cu31Pd10	58.7	31.2	10.1

The composition above is according to the PD 105 alloy in EN 1044:1999 standard and allowed tolerances in the same standard (Dimitrijević P.S. et al., 2018).

3. Results and discussion

The corrosion resistance of the silver brazing alloy was tested using several methods. The starting method is OCP measurement, which is the predecessor for the other tests used in this study. Figure 1 shows the OCPs of the alloy in three different but similar solutions.

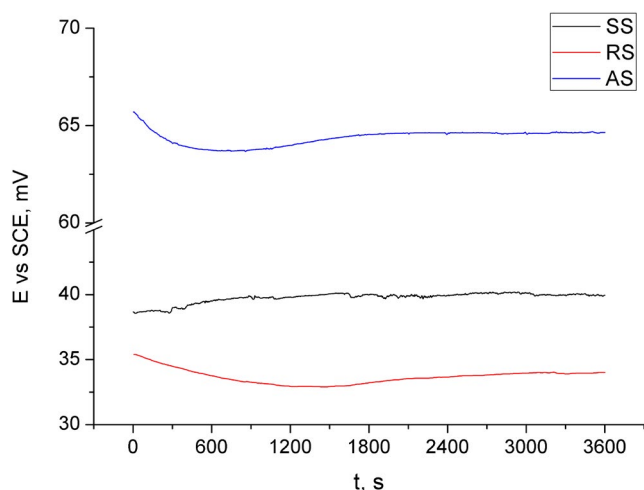


Fig. 1. The OCP curves for Ag59Cu31Pd10 alloy in different corrosion environments at 37 °C. The corrosion solutions were: SS, RS and AS with a time interval for the test of 3600 s (one hour).

The break at the ordinate axis in Figure 1 from 45 mV to 60 mV was applied with the aim of providing more detailed OCP curves since they were stable with only ± 2 mV through the whole duration of the experiments, and with the respect that OCP for AS had significantly different, more positive, value than for the other two solutions (~ 25 mV) that had very close values.

Except for the curve for SS, the other two had similar shapes with smooth lines and a slight decrease of the value at the start with a slow logarithmic increase afterwards. The parabolic decreasing part of the curve indicates the eventual dissolution of the thin (micro or nano) oxide film at the surface of the alloy despite the sample being freshly polished and protected in a nonpolar solvent (petrol ether) during the manipulation. The SS had a rough curve with a small but steady increase in value. The absence of the oxide film could not be confirmed just by the shape of the curve, mainly due to the very stable values of OCP.

Although OCP value is not a precise measure of corrosion rate or a strong indication of the difference between different corrosion environments, Figure 1 suggests that the alloy is the most resistant in AS and that the RS is slightly more corrosive than SS with the same osmotic pressure.

It should be noted that OCP values are above equilibria for CuCl formation and even at higher potentials than the peak for the CuCl formation at potentiodynamic polarisation for the same and similar alloys in chloride solutions (Dimitrijević P.S. et al., 2018). It implies that the reverse reaction of Cu to Cu(I) oxidation, followed by CuCl forming, is the main reaction at the OCP (at a very slow rate). The OCP for SS and RS are almost equal with the formation of AgCl since a reaction:



has equilibrium potential that follows next Nernst equation (Hung H. and Payer J., 2011):

$$E = -15 - 59.2 \log |\text{Cl}^-| \text{ (mV vs SCE)} \quad 2$$

Since the concentration (approximate activity) for the SS is 154 mmol·dm⁻³, the equilibrium potential is at about 33 mV, which is very near the OCP for the solution. The same can be applied to the RS, and even AS is not that far from these two solutions. This indicates the possibility that reaction (1) proceeds during the OCP conditions, but at an extremely slow rate.

After stabilisation of the OCP (practically after an OCP test), LPR measurement was followed. Figure 2 shows the results of the measurements of LPR using a doubly slower scan rate than standard to obtain more precise data.

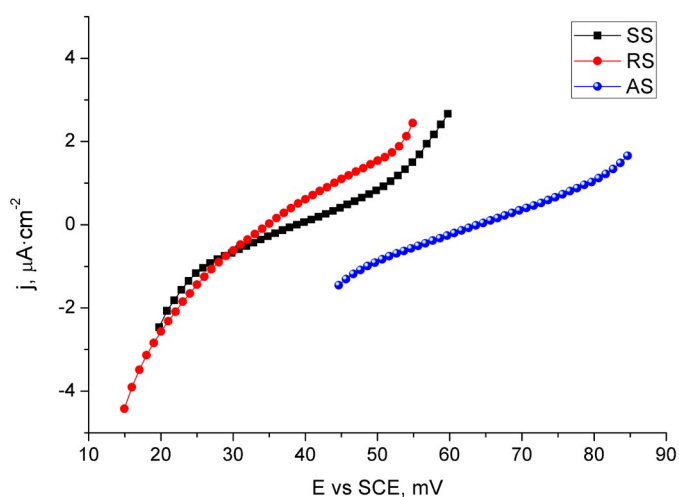


Fig. 2. LPR method for determination of corrosion current density of Ag59Cu31Pd10 alloy at 37 °C in SS, RS and AS

The LRP method reveals precise data connected to corrosion rates. It is clear that AS is the weakest corrosion environment and that the difference between this and the other two solutions is larger than between these. Since the graph is given with potential at abscissa (like the variable in measurement), the slope of the linear part of the curve is lower for the higher polarisation resistance (R_p). The LPR method not only confirms a assumption from the OCPs that the corrosion rate is higher in RS than in SS and that the difference is not as negligible as suspected.

The corrosion current densities for all three solutions are shown below (Table 2) because they need values for the Tafel's slopes. Nevertheless, values of the R_p strongly indicate the corrosivity of all tested solutions, which is in the following order (from the most severe to the mildest): RS (~ 8.5 k Ω ·cm²), SS (~ 12.0 k Ω ·cm²) and AS (~ 19.3 k Ω ·cm²).

Finally, it should be stressed that linear behaviour did not correspond to the entire measured interval of potentials (± 20 mV). For the SS, it was just about ± 10 mV, and even shorter (± 7 mV) for the RS and just a bit wider (± 12 mV) for the AS.

The polarisation curves, shown in Figure 3 for all three test solutions, provide additional parameters that can be used to determine the corrosion current densities. They were used for the Tafel extrapolation method, which has been performed only in limited potential intervals.

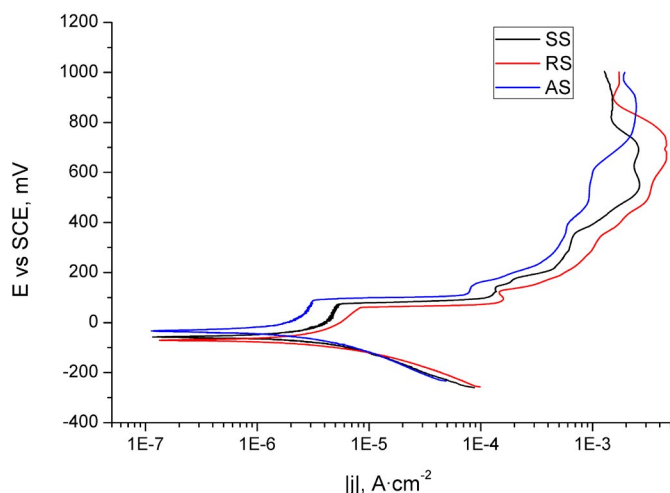


Fig. 3. Potentiodynamic polarization curves for Ag59Cu31Pd10 alloy in SS, RS and AS at temperature of 37 °C. From -0.3 V vs OCP to $+1.0$ V vs SCE

The studied alloy did not show passivation area in any of the tested solutions. It is evident that potential monotonously rises to about $+500$ mV. Areas of nearly constant current arise at all potentiodynamic curves. At potentials of about 0.49 V to 0.54 V, and even with a wide minimum at 0.63 V for the SS. The curve for the AS has two of such areas, the second at higher potentials from about 0.75 V to 0.9 V. All these features at the curves resemble to the areas of limited current and are probably related to the corrosion anodic film reactions, mainly formation but also its desintegration. Such films are porous, and parallel reactions could occur during the anodic polarization (Dimitrijević P.S. et al., 2018) this will be further discussed in relation to Figure 3.

The only actual peak in all three corrosive environments is at about $+100$ mV (95 to 125 mV, depending on the solution). It corresponds to the reaction $\text{Ag} + \text{Cl}^- \rightleftharpoons \text{AgCl} + e^-$ as discussed earlier, considering that these were potentiodynamic conditions. This peak is the most pronounced for the RS and the least for AS, where it is more in the form of the shoulder at the polarisation curve. Finally, corrosion potentials in polarisation curves are about 0.1 V lower than the OCP values, which is unusual but a common feature for similar alloys in physiological solutions (Hung H. and Payer J., 2011).

Tafel extrapolation was performed in a short anodic area with carefully chosen intervals; otherwise, the software was giving a warning that the anodic slope was too high and that the curves did not follow the Butler-Volmer equation (Lukács Z., and Kristóf, T. Et al., 2022), probably due to the formation of passivation film, which was also evident by the manual analysis of the curves. This passivation area is very short and could be the initial step in the mixed Ag and Cu film. Immediately, after a very steep area in all curves just under the peak at the diagram, it is very characteristic of this system. It is affected by the formation of the porous CuCl/AgCl film at the surface of the alloy, which was discussed above in relation to Figure 1. Furthermore, it is also a typical behaviour of the polarisation curve for pure copper in chloride solutions, where an abrupt increase in current density, at about 40 mV vs SCE, was explained by the start of pitting corrosion (Arjmand F. and Adriaens A. 2012). In that sense, potentials between 60 and 90 mV in the polarisation curves should be treated as active dissolution (breakdown)

Table 2. The corrosion parameters obtained by OCP, LPR and Tafel methods, for Ag59Cu31Pd10 alloy in three different corrosive environments.

Corrosive solution	OCP, mV	R_p , $\text{k}\Omega\cdot\text{cm}^2$	LPR j_{corr} , $\mu\text{A}\cdot\text{cm}^{-2}$	β_a , $\text{mV}\cdot\text{dec}^{-1}$	β_k , $\text{mV}\cdot\text{dec}^{-1}$	B, mV	Tafel I_{corr} , $\mu\text{A}\cdot\text{cm}^{-2}$
SS	39.95	11.96	2.127	157.1	-93.4	25.43	2.230
RS	34.01	8.498	3.695	173.5	-124.0	31.40	3.545
AS	64.58	19.27	1.189	125.8	-90.9	22.91	1.232

potentials. Parameters from Tafel extrapolation are given in Table 2, although anodic Tafel slopes should be approached cautiously and with reserve.

The LPR method's j_{corr} values were calculated using the Geary-Stern equation (Porcayo-Calderon, J. et al., 2015). For a proportionality constant (B) in Table 2, Tafel slopes from Tafel extrapolation were used to obtain its value. The LPR corrosion current (density) is then the quotient of it and R_p , which was determined as a reciprocal value of the slopes from Figure 2. Tafel extrapolation confirms corrosion rates from LPR methods, within about $\pm 5\%$ (higher values, except for the RS).

Generally, those values of j_{corr} are not too high. They are acceptable for many technical applications because they correspond to the corrosion rates (in $\mu\text{m}/\text{year}$): 85.8 , 49.4 and 27.6 for RS, SS and AS, respectively. It was calculated for pure copper (as the less resistant metal in the alloy) and oxidation from metal state to Cu(I), which is less favourable than Cu to Cu(II) corrosion. The actual situation is probably better since the primary reactions are not the dissolution of the metals (mainly copper) but the formation of corrosion film.

Nevertheless, the alloy did not fit the general requirements ($j_{\text{corr}} < 1 \mu\text{A}\cdot\text{cm}^{-2}$) (Krupa D. Et al., 2004) for the (permanent) biocompatible material in any of the tested solutions. However, the material was close to the maximum allowed value in AS. Additionally, it has much better characteristics than Ag-Cu-Zn alloys with similar Ag content (55-59%), even the two that had 2% of Sn or Ni (Ntasi A. Er al., 2014). The Ag-Cu-Zn-Ni alloy from that research, with the best results among them, had $j_{\text{corr}} = 7.5 \mu\text{A}\cdot\text{cm}^{-2}$ in RS at ambient temperature, which is double the value (or more, concerning the temperature) of the investigated alloy, and others were far worse.

Furthermore, the values of OCPs were comparable with commercial alloys with much higher noble metal content (some of the silver types), and R_p was just moderately lower than those alloys (40 - $82 \text{ k}\Omega\cdot\text{cm}^{-2}$) or pure silver ($\sim 40 \text{ k}\Omega\cdot\text{cm}^{-2}$) (Joska L. Et al., 2005; Grgur B. Et al., 2021) as discussed above. It should be stressed here that regardless of the precise Tafel parameters presented in Table 2 and significantly higher j_{corr} values than the alloys with a high noble metal content, the graphic determination of Tafel gradients at j_{corr} about $1 \mu\text{A}\cdot\text{cm}^{-2}$, especially when is much lower ($< 100 \text{ nA}\cdot\text{cm}^{-2}$), could scatter results and make them inappropriate for interpretation (Manaranche C. and Hornberger H., 2007). Typical values of Tafel parameters ($B \sim 17.4$ mV) would give considerably lower j_{corr} than in Table 2 (0.90 ; 1.45 ; $2.05 \mu\text{A}\cdot\text{cm}^{-2}$, from the smallest to the largest). Despite these minor differences in j_{corr} , they would raise questions about additional tests for this alloy.

The chemical analysis results, shown in Table 3, further complicate the evaluation of the appropriation of the alloy to be used as a biomaterial.

Table 3. Chemical analysis of the RS after recording the polarisation curve

Metal	Cu	Pd	Ag	Total
Concentration ($\text{mg}\cdot\text{dm}^{-3}$)	0.64	0.049	0.005	0.694
Realisation $\text{mg}\cdot\text{cm}^{-2}\cdot\text{day}^{-1}$	11.4	0.87	0.09	12.4
Realisation from j_{corr} , $\text{mg}\cdot\text{cm}^{-2}\cdot\text{day}^{-1}$	0.0569	-	-	0.0569

Note: The calculation for j_{corr} realization was simplified by neglecting the sub μg levels of Ag and Pd (at the corrosion potential) and taking Cu as the only dissolution of the metallic species.

The RS was chosen as the representative due to its highest corrosion influence on the alloy and that the current densities were the highest in the polarisation curve, as detailed shown above (Figure 3.). Although the recording lasted only, one hour for the whole polarisation, and about 2780 s after appearance of breakdown potential at the curve or 3210 s after the anodic part of the curve (taken in calculation), severe corrosion conditions were something like an accelerated test of the leaching of the metals in the environment. The concentrations of the metals were extremely low, which indicates a higher stability of the alloy than other tests suggest. The Ag was \leq from the value shown in Table 3 and close to the solubility of AgCl, further implying that the film formation of AgCl and CuCl were the main reactions in the system. The Pd was present in the solution in a chloride complex form but had an insignificant concentration. Only Cu had a concentration near the ppm level, partly as Cu(I) soluble chloride complexes and mostly as Cu(II) soluble species.

The metal ions release was relatively low, considering the high anodic potentials and was more than 200 times higher than the one calculated by Faraday's law from j_{corr} , which could be considered moderate, even a little higher than alloys with a high noble metal content (Manaranche C. and Hornberger H., 2007). On the other side, it is far less (for areas up to 1 cm², joints are usually much smaller) than allowed by consuming drinking water (2.0 mg·dm⁻³) (Directive (EU), 2020).

Regardless of all the above, specific and more rigorous requirements for dental materials (e.g. ADA) classify it as nonstable (group III) material for dental applications. The main problem with the alloy is its low E_p value, which is located at only half of the minimum +0.3 V respect to corrosion potential. By this, the study confirmed that silver alloys with a limited content of noble metals (<25%) can hardly fit the group II ADA classification requirements.

The results led to the rejection of the starting hypothesis (that the alloy could be an adequate dental material). Despite the negative results, research has demonstrated that silver brazing alloys have the potential to be joint materials in dentistry. The lower content of copper and higher content of palladium and (or) silver in the alloy would be beneficial, and the standard PD 101-104 alloys (Ag54Cu21Pd25, Ag52Cu28Pd20, Ag65Cu20Pd15, and Ag67.5Cu22.5Pd10), or similar, are promising candidates and would be tested in future research. In particular, they are complementary with Ag59Cu31Pd10 and could complete (together with PD 106, Ag68.5Cu26.5Pd5) the Ag-Cu-Pd system with a detailed analysis.

The increase in Pd content is the easiest way to enhance corrosion resistance. However, then the temperature of solidus/liquidus rises, which is an unwanted characteristic that limits the materials that could be successfully brazed. This is why metals that lower the melting point of brazing would be helpful and In is very promising (Ntasi A. Et al., 2019) but with the disadvantage of softening alloy, confirming the complexity of the process of choosing the most suitable brazing material.

Finally, research confirmed that AS is less corrosive than isotonic saline solutions and, thus, more appropriate and closer to natural conditions for dental materials. Even unchanged, Fusayama's solution proved to be a better replacement for real-life dental conditions, and the more advanced artificial salivas would be even more beneficial (Duffó, G.S. and Quezada Castillo, E., 2004).

4. Conclusion

The high-silver ternary brazing alloy from the Ag-Cu-Pd system (Ag59Cu31Pd10) was tested as an excellent filler metal for joint dissimilar materials for corrosion resistance in two physiological solutions and AS. It was considered as an auxiliary material with possible use for joining other metal and ceramic materials that are in use in dentistry. The following conclusions are made:

1. The OCP method gave a good insight into the order of corrosion resistivity, which was confirmed by other methods. The higher value of OCP was in AS, and the lowest was in RS.

2. The LPR demonstrates the short linear part in the curves.

Polarisation resistance values for SS, RS, and AS were 8.498 kΩ·cm², 11.96 kΩ·cm² and 19.27 kΩ·cm², respectively.

3. Linear polarisation curves in a wide area of anode potentials (up to +1.0 V) showed breakdown potential at very low potentials: 60 mV, 73 mV and 92 mV. This disqualifies the studied alloy as a stable dental material. There were no pas-sive areas on these curves.

4. Tafel extrapolation gave the corrosion current densities in all three solutions and the parameters needed to determine them by the LPR method. The j_{corr} were (in μA·cm⁻²) 3.62, 2.18, 1.21 (the average of these two methods) for the RS, SS, and AS, respectively. The worst result was nearly triple higher than the best one (the lowest). These have shown that small changes in solution composition could almost double j_{corr} .

5. The results of the chemical analysis of RS after recording the polarisation curve showed ppb levels for Ag and Pd and ppm levels for Cu. The concentrations were lower by one order of magnitude from Cu to Pd and Ag. Calculated as metallic ion release, it was moderately high for such severe corrosion conditions. The Cu release taken from the j_{corr} could be near both sides of the limits to induce adverse biological effects, depending on the classification/regulative.

6. The j_{corr} values are insufficient to confirm the alloy classification in biocompatible materials. Furthermore, low break-down potentials at about +0.15 V from the corrosion potential on the polarisation curves (consequently with very high $I_{o,3}$ parameters, a few tens of times larger than the requirement) definitely classify the alloy as an unstable (group III by ADA) dental material.

7. Although physiological solutions are not an exact replacement for natural saliva and are worse than basic/simple artificial salivas, they have two significant advantages over them; one is that they could serve as superb control. More importantly, they are more corrosive and provide a good safety factor in evaluating whether an alloy is suitable as a dental material.

Acknowledgments

This work was financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, contracts number: 451-03-66/2024-03/200052, 451-03-65/2024-03/200135 and 451-03-66/2024-03/200287.

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