

Short Communication

Corrosion Stability of Metallic Materials in Dentistry as Studied with Electrochemical Impedance Measurements

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The corrosion susceptibility of selected metallic materials frequently employed in prosthetic dentistry has been examined with electrochemical methods. Results have been compared with data derived from breakthrough potential measurements performed with these materials before. Mostly agreement and/or close correlation were found, discrepancies are discussed and tentatively assigned to the different experimental conditions.

Keywords: Palladium-based alloy, non-precious metal alloys, dentistry, corrosion, electrochemical impedance measurements

1. INTRODUCTION

Alloys of precious, semi-precious or non-precious metals have been used in the manufacturing of removable and fixed prosthetic dentistry for a long time. Among them, the latter materials corrode easily. This limits their application despite their sometimes attractive mechanical properties. Because of the ,any local as well as general biological effects of corrosion products containing a variety of potentially toxic metals, this *in vitro* corrosion constitutes a major drawback [1]. However, more recently regulations and laws aimed at a reduction of costs in health care have reinvigorated the interest in less expensive alloys. A large number of alloys of the various types named above is currently

available [2]. In the absence of any regulatory procedure (according to the knowledge of the authors and as confirmed by a recently rekindled public discussion of the perceived lack of oversight for “medical products” including these materials in Germany, see also [2]) employed to evaluate in comparative studies the stability of these materials against corrosion, studies of this property seemed to be desirable. The situation is further complicated by the growing number of materials used in dentistry (e.g. cements, adhesives, filling materials) as well as food constituents previously not encountered. In addition, processing parameters (method of casting, temperature control during casting) may influence corrosion stability.

We had studied the corrosion stability of a selection of palladium-based and cobalt- and nickel-based non-precious metal alloys in artificial saliva. Because corrosion of metallic materials in the mouth is almost exclusively an electrochemical process [3], we have employed in previous studies of the corrosion of metallic materials used in dentistry an electrochemical method [4 - 14]. Cyclic voltammetry (CV) or similar techniques with an electrolyte solution as similar as possible to natural saliva proved to be particularly helpful and relatively easy to perform [15 - 18].

The experimental results and thus the comparability (and compatibility) between various studies, unfortunately depend strongly on the experimental conditions, in particular the composition of the electrolyte solution [16, 19], the sample pretreatment and the scan rate. The latter parameter has been examined in investigations of the corrosion behavior of alloys of semi-precious metals or with low precious metal content with cyclic voltammetry with widely varying scan rates, results have been reviewed elsewhere [20]. Low scan rate CV has been shown to be a method giving results strongly correlated with those of other, in particular *in vivo*, studies of corrosion behavior (see e.g. [21]), although the sample under investigation is away from the electrochemical equilibrium, i.e. at the spontaneously established rest potential. In the present study, we have used a synthetic saliva solution composed of various salts as suggested by Meyer [22]. A very similar solution has been described first by Swartz and others [23] and modified later by Fusayama and others [24]; it is now generally known as Fusayama saliva. Its properties are similar to those of natural saliva. Ringer's solution (0.8 %wt. NaCl, 0.02 %wt. KCl, 0.02wt. % CaCl₂, 0.1 %wt. NaHCO₃ in water), frequently used in corrosion studies, shows an artificially enhanced chloride corrosion (see e.g. [25]). Nevertheless, the corrosion products formed *in vivo* and in Ringer's solution are very similar with those formed at dental amalgams [26]; similar comparability studies for other materials and alloys are absent. Engel has reviewed differences in results and further arguments in favor of Fusayama saliva by [20]. The low scan rate of 1 mV·s⁻¹ (= 60 mV·min⁻¹) chosen in our earlier studies resulted in long duration of experiments leaving this approach somewhat unattractive. In addition, exposure of the samples to electrode potentials possibly far away from the electrode potentials commonly encountered in daily use *in vivo* may result in data possibly not characteristic of the corrosion behavior under actual conditions. Inspired by a recently provided review of experimental methods in corrosion research [27], we have reexamined selected samples of our previous studies assumed to be representative with electrochemical impedance measurements with the aim of relating corrosion susceptibilities derived from breakthrough potential E_B (corresponding to thermodynamic system properties and not related to breakdown potentials as discussed in detail elsewhere [27]), as reported in previous studies with corrosion currents obtained from impedance measurements (corresponding to kinetic system properties).

Impedance measurements are well established in corrosion research [27 - 30]. Compared to slow scan voltammetry aimed at determining breakthrough potentials E_B or to get Tafel plots, they have a major advantage: They are executed at the open circuit potential with the system in electrochemical equilibrium. Nevertheless they have been employed in studies of metallic materials in dentistry only infrequently: Cailean and others [31] have examined one Co-Cr and one Ni-Cr alloy in contact with a 3 %wt. NaCl solution (see also for results obtained with Rondelli saliva [32]). Results indicate growing layer of passivation products, corrosion rates were not reported. Mareci and others studied the corrosion behavior of five nickel-based alloys in acidified Fusayama saliva [33]. Poor stability was found. Results related to further non-precious metal alloys have been reported elsewhere by Mareci and others [34]. In a study of three non-precious metal alloys, increased corrosion was observed in acidified and in fluoridated artificial saliva [35]. Corrosion enhancing effects of various bleaching agents on alloys of the WIRON family has been studied by Ameer and others [36]. Localized corrosion of nickel-based alloys in acidified artificial saliva has been studied by Mareci and others [33]. Details of alloy composition on corrosion susceptibility were found. Saji and Choe have observed no influence of casting procedure and consequent differences in microstructure of Co-Cr and Ni-Cr alloys on their corrosion behavior [37, 38]; this agrees with earlier observations with palladium-base alloys [4, 5]. Sufficient corrosion stability of Ni-Cr alloys for practical applications with only small variations between the examined products has been noticed with impedance measurements by Liliana and others [39]. Mareci and others have compared Ag-Pd and Co-Cr alloys [40]. Liu and Duh reported on impedance investigations of TiAlN films on nickel-base alloys [41]. The corrosion of copper-based alloys in various modified artificial salivas has been examined [42]. Impedance measurements have been applied together with open-circuit potential measurements in corrosion studies of selected amalgams [43].

Mueller and Hirthe have examined a silver-palladium alloy with impedance measurements [44]. Three palladium-base alloys have been examined with various electrochemical techniques [45, 46]. The similarity of the obtained corrosion data was attributed to the high palladium content. Advantageous effects of a small titanium addition to a silver-palladium alloy in various artificial salivas have been reported [47].

In this study, we have examined a set of representative alloys already studied before with slow scan CV with electrochemical impedance measurements to verify comparability of data and rankings of corrosion susceptibility.

2. EXPERIMENTAL

Taking into account the results of an earlier study (see Fig. 3 below) we have selected representative palladium-base and non-precious metal alloys already investigated with slow scan cyclic voltammetry before [4 - 578914, 48]. Their actual composition as reported in Table 1 was determined using electron beam microanalysis EPXMA (CAMECA SX 100).

The alloys were cast into samples of various shapes including cylindrical rods for electrochemical studies (length 40 mm, diameter 5 mm) using casting procedures discussed elsewhere

[4, 5] and identified as having only insignificant influence on the corrosion behavior. Non-precious metal alloys were casted using centrifugal casting with protective gas blanket after melting in an open flame and vacuum pressure die casting with protective gas after melting in a resistance-heated furnace under inert gas, for palladium-base alloys in addition centrifugal casting after melting in an induction furnace (high frequency heating) and vacuum pressure casting after melting in a resistance-heated furnace were employed.

Before electrochemical measurements, the samples were polished with abrasive paper (wet paper, type 240, 320, 400 and 600), cleaned in an ultrasonic bath and rinsed with acetone and ultrapure 18 M Ω water (Seralpur Pro 90 C). Subsequently they were connected to a sample holder fitted with a tapered joint. A conventional electrochemical H-cell with a corresponding tapered joint and cell compartments for a platinum sheet counter electrode and a saturated calomel electrode (SCE) acting as a reference electrode separated from the main compartment by glass frits was used; for further details see [4, 5].

Table 1. Composition of studied alloys¹ (Mass percent/%, data provided by manufacturers for comparison)

Palladium-base alloys							
alloy	Pd	Ag	Cu	Pt	Sn	In	Fe
Pd1	57.8	30.0	-	-	6.0	4.0	-
P2	56.5	25.6	6.2	-	3.2	12.1	-
Pd3	57.2	34.5	-	6.7	-	1.4	4.7
Non-precious metal alloys							
alloy	Ni	Cr	Mo	Si	-	Ce	
Ni1	57.1	23.8	12.6	2.1	-	0.13	-
<i>by manufacturer</i>	61	26	11	1.5	-	-	-
	Co	Cr	Mo	Si	W	Ce	
Co1	61.8	22.8	8.2	1.1	4.5	0.1	-
<i>by manufacturer</i>	61	25	7	1.5	5	-	-
	Co	Cr	Mo	Si	Fe	Mn	
Co2	33	30.5	5.2	1.1	29.6	0.4	-
<i>by manufacturer</i>	33	30	5	1	29	1.5	-

A Fusayama synthetic saliva containing 0.4 g KCl, 0.4 g NaCl, 0.69 g NaH₂PO₄·H₂O, 0.005 g Na₂S·9H₂O, 0.795 g CaCl₂·H₂O and 1 g urea per dm³ dissolved in 18 M Ω water was used as electrolyte solution; its pH was 4.7 - 5.00. All chemicals were of analytical purity, they were used as received. The solution was saturated with pressurized air filtered with activated carbon. The cell was immersed in a water bath kept at 37 °C. The solution was saturated with pressurized air instead of nitrogen or argon before every measurement in order to keep the composition of the electrolyte solution as similar as possible to the *in vivo* situation.

Electrochemical impedance measurements were performed on a potentiostat IVIUMSTAT Electrochemical Interface in the frequency range 100 kHz to 10 mHz, with 5 data points per frequency

¹ Alloy tradenames and manufacturer's names withheld on publishers request.

decade at sine wave amplitude of 10mV. Measurements were repeated five times per sample. For data handling, in particular for fitting of the obtained impedance data, software Zsimpwin was used. A Randles-type circuit (Fig. 1) was assumed as has been reported elsewhere for similar materials [45] with a constant phase element Q instead of a simple double layer capacitance.

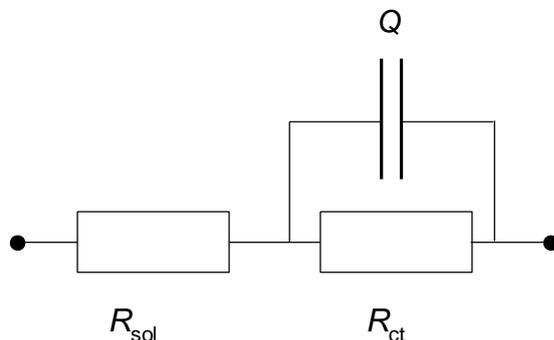


Figure 1. Equivalent circuit used in impedance measurements.

3. RESULTS AND DISCUSSION

Measurement of the spontaneously established open circuit potential (OCP), i.e. the corrosion potential, did not yield useful data in case of the palladium-based alloys [2, 5, 40, 49]. The presumably very low anodic current of the rather noble alloy naturally limited the cathodic current due to dioxygen reduction; these very small currents resulted in slow establishment of any potential.

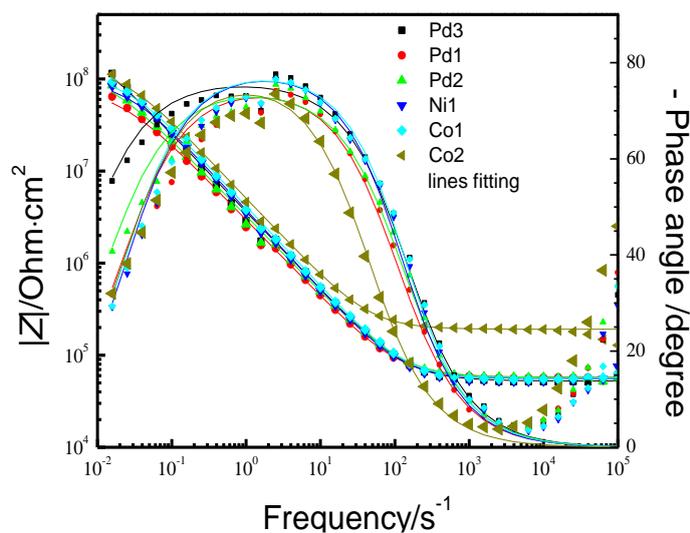


Figure 2. Results of impedance measurements; symbols: measured data points, lines: result of fit and simulation.

Presumably rapid formation of surface layers and poorly defined conditions at the metal/solution interface further contributed to a significant electrode potential drift resulting in

meaningless data. OCP measurements over extended periods of time as reported elsewhere [40, 49] were not attempted. Impedance measurements were instead started soon after sample immersion after the potential fluctuations immediately after immersion had abated. To examine reproducibility the sequence abrasive treatment – cleaning – immersion – impedance measurement was performed five times with every sample. Results are displayed in Fig. 2.

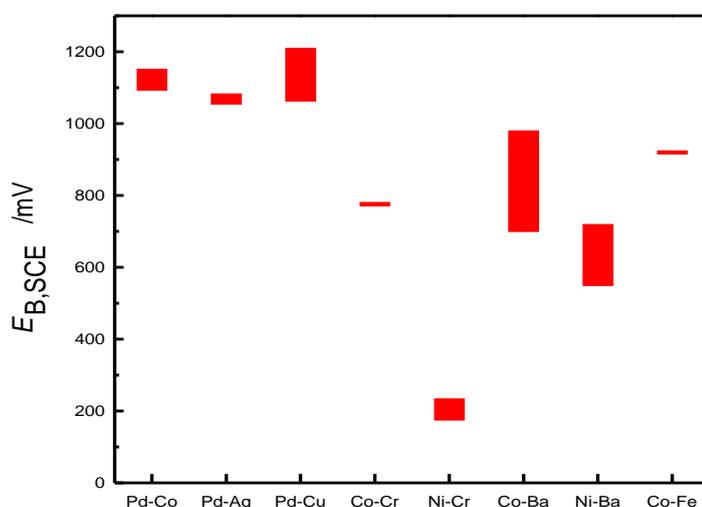


Figure 3. Breakthrough potentials of alloys studied in artificial saliva [13].

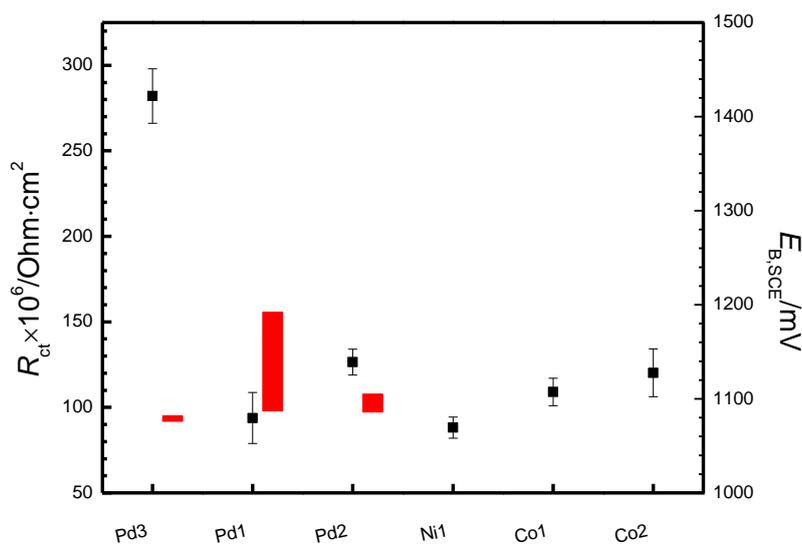


Figure 4. R_{ct} values of alloys studied in this work, red bars indicate range of breakthrough potential E_B of palladium-base alloys from [48] not published before.

Values of breakthrough potentials E_B obtained for some of the alloys studied here already re-

ported elsewhere are shown in Fig. 3 for comparison. Palladium-base alloys (Pd-Co, Pd-Ag, Pd-Cu), some older cobalt-chromium (Co-Cr) and nickel-chromium (Ni-Cr) and the currently used non-precious metal alloys (Cobalt-base and Nickel-base) studied here are included. The displayed bars show the range between the lowest and the highest value of recorded breakthrough potentials. No statistical data treatment was applied.

Fig. 4 shows the obtained values of charge transfer resistance R_{ct} , they correspond to the rate of corrosion with smaller resistances indicating faster corrosion. A direct transformation of R_{ct} into j_{corr} is possible according to

$$j_{corr} = \frac{R \cdot T}{n \cdot F \cdot A \cdot R_{ct}} \quad (1)$$

with electrode surface area A and the other symbols with common meaning. Because of the presence of several metals in all alloys with possible different stoichiometries of their respective corrosion reactions identification of the number of transferred electrons, n remains ambiguous; we have refrained from doing it. Error bars display results after applying the common “trimmed means” procedure.

A comparison of Fig. 4 with data from the preceding Fig. 3 shows values of E_B of palladium-silver alloys closely relate with those of the single palladium-silver alloy previously studied [4, 5]. The impedance data closely correspond to those reported before by other researchers with three typical high-palladium alloys [45]. They suggest the following conclusions: Nickel-base alloy Ni1 shows the lowest values of R_{ct} and of E_B , respective values for the cobalt-base alloy Co1 are higher. R_{ct} of the iron-containing alloy Co2 is only slightly better than that of Co1, whereas values of E_B suggested a larger difference.

The close agreement of the values of E_B for palladium-silver alloy does not completely correlate with the impedance results. Alloy Pd3 shows a significantly higher R_{ct} implying a much larger corrosion resistance. In the absence of results obtained with other methods, this discrepancy cannot be explained. Mueller and Hirthe examined only one palladium silver alloy with linear potential scan and impedance experiments but did not compare the corrosion rates [44]. Vasilescu and others condensed their comparison of data from various methods into “good corrosion stability” [50].

As indicated above, impedance measurements performed *in vitro* under spontaneously established electrochemical conditions without forcing possibly unrealistically high electrode potentials as in slow scan cyclic voltammetry on the electrode may provide more realistic corrosion susceptibility information. This should apply to all materials; the discrepancy observed here cannot be explained currently.

4. CONCLUSIONS

Electrochemical impedance measurements performed with selected palladium-base alloys and non-precious metal alloys yielded results that confirm the very few previously reported data on these materials, showing similar relative rankings of corrosion susceptibility, as previously reported measurements of breakthrough potentials with much shorter experiment durations.

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