Study of a dental cobalt-base alloy used in prosthetic dentistry. part 2: electrochemical properties

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ABSTRACT

The dental alloys for frameworks destined to strengthen prostheses as bridges must be not only mechanically resistant, but also corrosion resistant. After having characterized its microstructure and its mechanical and thermophysical properties in the first part of this work, the same dental cobalt-base alloy was here tested in corrosion. Mounted as working electrode in a three-electrodes cell containing a {9g/L NaCl; pH=7.4} aqueous solution simulating saliva heated to human body temperature, this cobalt alloy was subjected to Stern-Geary, Tafel and cyclic polarization experiments. Added to the open circuit potential evolution over two hours, these electrochemical tests demonstrated that the alloy passivated rather rapidly and thereafter well behaved in corrosion. The obtained polarization resistances were very high, and the determined corrosion current densities very low. They were of the same levels as for nickel-base alloys characterized in similar artificial saliva.
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INTRODUCTION

In prosthetic dentistry metallic alloys are used to mechanically reinforce bridges and other prostheses replacing natural teeth. They ensure an important mechanical role since metallic frameworks allows bridges ((for example) resisting the intense cyclic flexural solicitations involved by mastication. But the two main parts of the metallic assemblage, the parent alloys as well as the pre- and overall post-solder alloys, are additionally exposed to the buccal milieu and, consequently, they are in contact with more or less aerated saliva. They must be then resistant against aqueous corrosion to pre-vent possible mechanical weakening of the framework but also to avoid the loss of metallic ions which may results from corrosion[1], phenomenon depending of different parameters such as the electrolyte nature, its pH, the aeration conditions[2-5] and the consequences of which may be dangerous[6].

Among the dental alloys used in this field there are alloys based on noble metals such as gold, platinum or palladium and silver (American Dental Association[7]). But there are also must cheaper alloys displaying high mechanical strength too, and possibly also high resistance against corrosion. These "predominantly base" alloys can be based on nickel or on cobalt, and they

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contain high quantities of chromium which is favourable to the development of a protective passivation layer.

With about 25 wt.%Cr in their composition some nickel-base alloys, such as the Pisces Plus (61.5Ni-22.0Cr-11.2W-2.6Si-2.3Al, in wt.%) and the 4ALL (61.4Ni-25.7Cr-11.0Mo-1.5Si, in wt.%)[8] may be very resistant against corrosion, even in various media simulating saliva[9-12]. The alloys based on cobalt may be resistant, as the "Vitallium" alloy[13]. Furthermore some alloys belonging to this second family of "predominantly base" alloys can be more resistant than nickel-base alloys[14]. The present work concerns another dental cobalt-base alloy, the dSIGN30 one. After having characterized its microstructure and its mechanical and thermo-physical properties[15] this is here its behaviour in corrosion in a solution simulating saliva which will be studied in this second part.

EXPERIMENTAL

The studied alloy

The chemical composition of the so called dSIGN30 which was studied here, is reminded in TABLE 1 (commercial data). In fact measurements performed in Energy Dispersive Spectrometry gave a little different results[14].

TABLE 1 : Chemical composition of the dSIGN30 alloy (commercial data); all contents in weight percent[12]

Co	Cr	Ga	Nb	Mo	Si	B	Fe	Al	Li
60.2	30.1	3.9	3.2	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0

Its microstructure, reminded in Figure 1, is composed of a dendritic matrix of solid solution of cobalt containing the main part of chromium, and of precipitates of two types: the first ones rich in niobium and molybdenum, and the second one rich in chromium.

The electrode

A cut part of dSIGN30 was partly sawed and the denuded extremity of a plastic-gained copper wire was stick in the slot. The alloy and the not gained part of the copper wire were embedded in cold resin (Araldite CY230 and HY956) to isolate these metallic parts from the solution when the electrode will be immersed, except of course a main face of dSIGN30. The surface of the emerging alloy was measured using a simple office scanner and the Adobe Photoshop CS software of Adobe. This led to 0.284 cm². This Working Electrode (WE) will be associated with an Auxiliary Electrode (AE) (also called counter electrode) and a Reference Electrode (RE). The second electrode (AE) was a platinum one and the third electrode a Saturated Calomel Electrode (SCE).
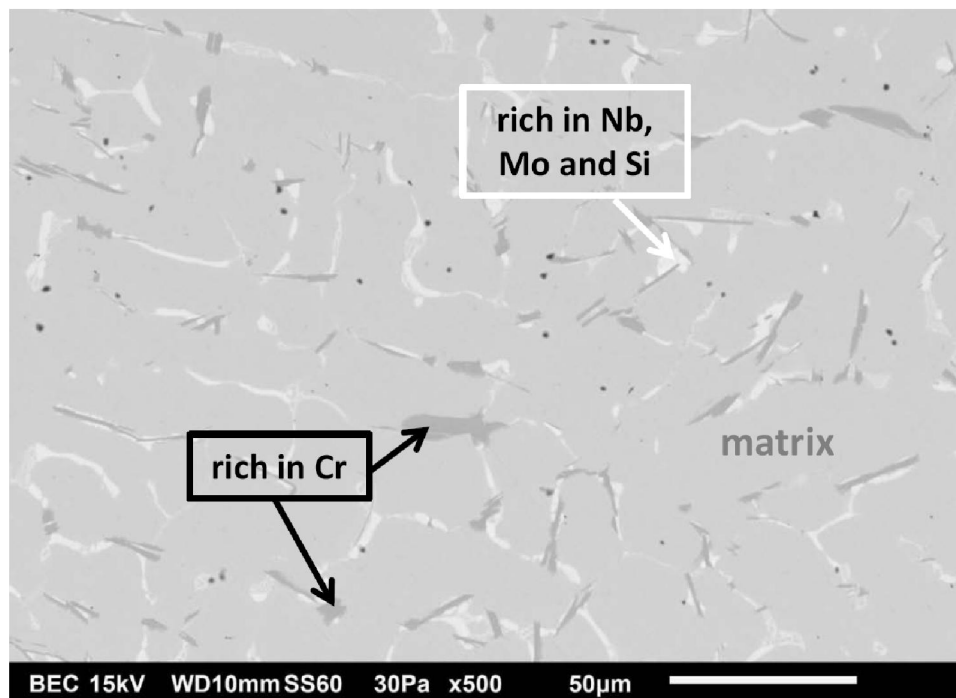
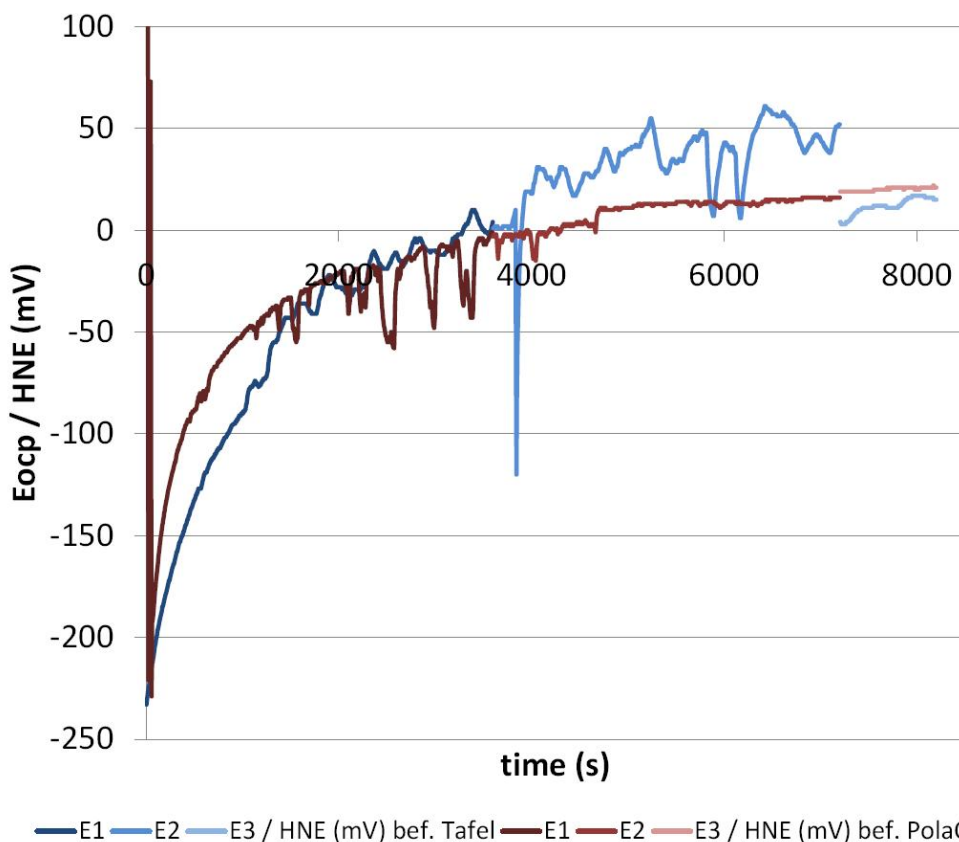**Figure 1 : The as-cast microstructure of the dSIGN30 alloy[15]**

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Figure 2 : Evolution of the open circuit potential of the dSIGN30 alloy during the first two hours of immersion

The used electrolyte and the apparatus

The solution chosen for simulating saliva was a {9g/L NaCl}-containing solution the pH of which was adjusted at 7.4. This solution was heated then maintained at 37°C with a Julabo F32 apparatus.

The experiments were performed using a Versa Stat potensiostat from EG&G Princeton Applied Research driven by the 352 software.

The electrochemical experiments

The experiments which were run were a 2 hours - long immersion during which the variations of the Open Circuit Potential (E_{ocp}, or free potential) were recorded, aiming to know in which state – active or passive – the alloy is, and also if there is change during the immersion (from active to passive or the contrary: depassivation). Every 60 minutes a linear polarization between E_{ocp}-20mV up to E_{ocp}+20mV at 10mV/min was performed in order to get values of the polarization resistance Rp according to the Stern-Geary method. A Tafel experiment from E_{ocp}-250mV up to E_{ocp}+250mV was thereafter applied, with a scanning rate of 10 mV/min, in

order to specify the values of I_{corr} and E_{corr} (corrosion density of current and corrosion potential) as well as the ones of the anodic and cathodic Tafel coefficients β_a and β_c. Also after a 2 hours-long E_{ocp} recording during which to Stern-Geary runs were also realized, a cyclic polarization run was carried out with scanning of the applied potential from E_{ocp} – 150 mV up to E_{ocp} + 1.225 V at 1 mV / s (i.e. 60 mV / min) to see whether the alloy is able to get passive and whether this eventual passive state remains stable when the applied potential decreases.

RESULTS AND DISCUSSION

The open circuit potential over 2 hours

The evolution of E_{ocp} with time is shown in Figure 2 with the three successive curves plotted together, from the data recorded before the Tafel experiment. In the same graph the corresponding three successive curves obtained in the same conditions but before the cyclic polarization experiment are added. One can see that, in both cases, the potential increases from an initial low

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value (between -250 and -200 mV / HNE) characteristic of an active state, to a much higher potential (between +0 and -50 mV / HNE) characteristic of a passive state. These increases are initially fast but they decelerate before stabilizing. One can point out that the two global curves are not exactly superposed but they are close to one another.

The polarization resistances

During the two hours before the beginning of the Tafel experiment two liner polarizations were performed over a small potential interval centred on the running E_{ocp}. At t=1 hour and at t=2 hours this leads to polarization resistances which are Rp_{T1}=248 k$\Omega \times$ cm² and Rp_{T2}=266 k$\Omega \times$ cm². The same two linear polarizations were also performed during the two hours before the start of the cyclic polarization run. At t=1 hour and at t=2 hours this leads to polarization resistances which are Rp_{CP1}=124 k$\Omega \times$ cm² and Rp_{CP2}=124 k$\Omega \times$ cm². Despite that these four values were not the same they were all very high and characteristic of a passive state.

The tafel experiment

The obtained Tafel curve is plotted in Figure 3, with the first part of the cyclic polarization curve.

The Tafel curve is situated at a rather low level in current density, this suggesting very low corrosion current density (I_{corr}). The Tafel determination effectively led to very low value of I_{corr} (88 nA/cm²) and a corrosion potential E_{corr} of about +30 mV/HNE. The Tafel
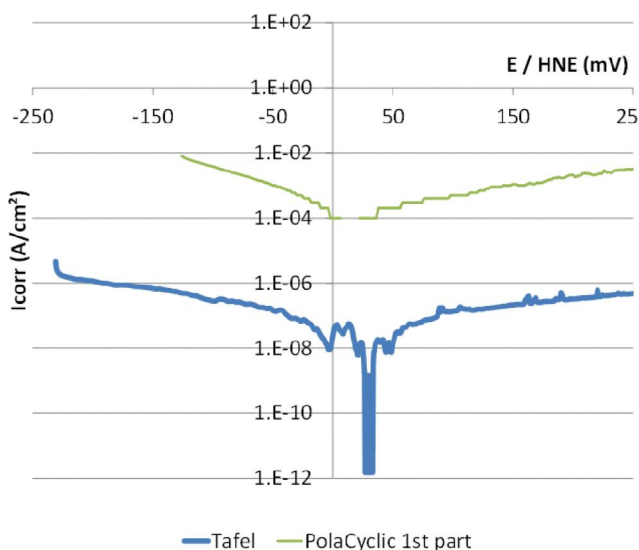

Figure 3 : The Tafel curve (thick blue line), and the first part of the cyclic polarization curve (thin green line)

determination was also carried out on the low potential part of the E-increasing cyclic polarization curve: corrosion current density of about 0.1 mA / cm² (i.e. much more than for the Tafel experiment) and corrosion potential of about +20 mV/HNE.

The Tafel characterization also led to cathodic and anodic Tafel coefficients of about 198 mV / decade and 302 mV / decade respectively.

The cyclic polarization run

The E-increasing part and E-decreasing part of the cyclic polarization curve are plotted together in Figure 4. One can see that no passivation plateau is present in the E-increasing part of the curve, maybe because the alloy was already passivated before the cyclic polarization part of the experiment. There is a progressive increase in current when the applied potential exceeded the corrosion potential, with additionally a final increase before reaching E_{ocp}+1.225V. The latter high currents are probably related to the oxidation of the solution (solvent's wall) itself ($H_2O \rightarrow O_2$), to add to the probable start of transpassivation (re-oxidation of $Cr^{III}(OH)_3$ or $Cr^{III}_2O_3$ into Cr^{VI} species. The resulting enrichment of the solution in dissolved O_2 is probably responsible of the highest currents measured during the E-decreasing part of the cyclic polarization experiment for the same potentials as in the E-increasing part. Notably the new corrosion current (about 10mA/cm²) is much higher than the initial one while the new corrosion potential (about -20 mV/HNE) is slightly lower than the initial one (about +10mV/HNE): this let think that the passivation scale was deteriorated by the exposure to very high potentials at the end of the E-increasing part).

General commentaries

The present dental cobalt-base alloy seems thus rather resistant against corrosion in the buccal milieu, as proven by these electrochemical experiments realized in a solution simulating saliva. The Stern-Geary runs as well as the Tafel runs, which gave very high values of polarization resistances and very low values of corrosion currents respectively, showed that the alloy was certainly already passivated when these experiments were carried out. This was also confirmed by the absence of passivation plateau in the potential-increasing part of the cyclic polarization curve. The evolution of

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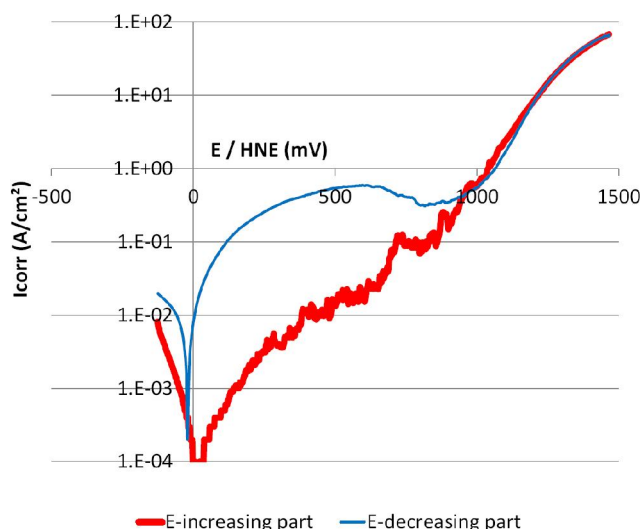
Figure 4 : The obtained polarization curve (E-increasing part in thick red line and E-decreasing part in thin blue line)

the open circuit potential during the 2 hours free immersion probably revealed the progressive fast then slow establishment of the protective passivation layer over the alloy. However the time necessary for that was obviously not much lower than these two hours. But the first polarisation resistances which were recorded (at t = 1 hour) show, by their already very high values, that passivation was probably already realized after one hour of immersion.

CONCLUSIONS

The dSIGN30 dental cobalt-base alloy, which already appeared as rather mechanically resistant as suggested by its high values of hardness[15], appeared here additionally very corrosion resistant. The values of Rp and I_{corr} are comparable to the ones earlier[16] measured for nickel-bas alloys in the same {9g/L NaCl; pH=7.4} solution at 37°C. However the solution simulating saliva was here rather simple and one can think potentially useful to confirm with additional electrochemical experiments in other artificial saliva, such as the Fusayama's one.

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