COMPARISON OF THE BEHAVIOR OF A NEW DENTAL CoCr MoNbZr ALLOY WITH AND WITHOUT INCORPORATED Ag

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Abstract. *The electrochemical stability of CoCr based alloys is due to the passive oxide film grown on their surface, but it is to notice the aspect of ion release in their working time in this paper a new CoCrMo dental alloy alloy with small amount of niobium and zirconium (6% Nb and 0.8% Zr respectively) is modified by incorporation Ag on its surface. This paper aims to compare the ion release from CoCrMoNbZr in Tani Zuchi artificial saliva at various periods of time before and after Ag nanoparticles incorporation by pulselectrodeposition. The surface analysis reveled that Ag are nanoparticles with 100 nm average diameter. The ion release determination with inductively plasma mass spectrometer (ICP-MS established that after Ag incorporation the surface is more protective and Zr release decreased significantly. Electrochemical tests in artificial saliva Tani Zuchi sustain the ICP-MS determination which indicate better performance of alloy CoCr MoNbZr after Ag incorporation.*

Keywords: CoCr alloy, electrochemistry, ion release, nanoparticles, artificial saliva.

1. Introduction

CoCr based alloy are increasingly present in the dental restoration works being much cheaper than noble metals, resistant to corrosion in various bioliquids with acid and alkaline ph and having remarkable mechanical properties and biocompatibility as well [1-4].

The electrochemical stability due to the passive oxide film grown on their surface [5] is a recommendation for stability and biocompatibility, but it is to

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notice the aspect of ion release in their working time [6,7]. In this idea introducing in CoCrMo alloy composition small amounts of other elements with superior properties from the point of view of electrochemical stability in oral cavity environment and biological performance, was successfully finalized with elaboration and characterization of a new dental alloy [8,9] with small amount of niobium and zirconium (6% Nb and 0.8% Zr respectively). Both are very resistant metals to corrosion on a large pH domain. Furthermore, Zr improves mechanical properties as well [10], even when the two elements are added in relatively small quantities. The beneficial effect of Nb and Zr is due to the enrichment of the passive oxides stratum with Nb_2O_5 and ZrO_2 making alloys very stable [9] in bioliquids at various pH and high biocompatible. Nowadays due to bacterial attacks which are more and more aggressive and can generate serious concerns for environmental human health there is a continuous expansion of investigations for developments to guarantee better antibacterial effect of used biomaterials. In this context incorporation of Ag in the surface of the new alloy could be a good idea. The release of metal ions during corrosion may lead to several possible consequences, including serious damage to patient health [11], allergies, oral lesions, Metal ion concentration increases significantly in the saliva of patients with a metal dental prosthesis [12]. The oral environment is an ideal place for corrosion because of the presence of saliva, acid bacterial plaque, changes in pH and temperature related to food or beverage intake, and the action of different drugs [13,14]. This present paper aims to compare the corrosion and ion release in artificial saliva Tani Zucchi at various period of time from the alloy CoCrMoNbZr before and after Ag nanoparticles incorporation in the surface in pulselectrodeposition. The ion release determination with inductively plasma mass spectrometer (ICP-MS) established that after Ag incorporation which is known for its antibacterial activity [15] the surface is more protective and Zr release decrease significantly. Such conclusion is sustained with corrosion kinetic parameters values as well.

2. Materials and methods

2.1. Materials

The new alloy CoCrNbMoZr alloy was obtained by vacuum melting using the semi-levitation method, as presented in previous papers [6,7] and has the composition in Table 1:

Table 1 Composition of new alloy CoCrNbMoZr

Element	*wt.%*								
	Co	*Cr*	*Mo*	*Mn*	*Si*	*C*	*N*	*Nb*	*Zr*
CoCrNbMoZr	60	26.5	4.5	0.8	1.0	0.4	0.2	6.0	0.8

The artificial saliva Tani-Zuchi was prepared after a recipe existing in literature [16]: 1.5 g/L KCl, 1.5 g/L $NaHCO_3$, 0.5g/L NaH_2PO_4, 0.5 g/L KSCN and 0.9 g/L lactic acid.

2.2. Electrodeposition of Ag nanoparticles Firstly 20 mL of an aqueous solution of silver nitrate; with a final concentration of 0.25 mM, and 0.25 mM trisodium citrate was prepared. While stirring vigorously, 0.6 mL of 10 mM NaBH4 was added to the solution. Following this the silver nanoparticles were potentiostatic electrodeposited in puls onto CoCrNbMoZr alloy as a working electrode. The deposition was performed in a cell with three electrode the other two electrodes being Pt as auxiliary electrode and - Ag/AgCl, KCl the reference. After electrodeposition the samples were washed with deionized water.

2.3. Surface analysis

The morphological texture of the Ag nanoparticles on CoCrNbMoZr alloy surface was studied using scanning electron microscopy (SEM) Scanning Electronic Microscopy (SEM) analysis performed on field-emission scanning electron microscope – Hitachi FE-SEM S4800.

2.4. Electrochemical stability

The corrosion behavior alloys without and with Ag incorporation was evaluated artificial saliva type Tani-Zuchi. All experiments were performed using an AutoLab PGSTAT 12 EcoChemiepotentiostat/ galvanostat. A conventional three-electrode electrochemical cell as well as for electrodeposition was used for evaluation of kinetic parameters.

The polarization behavior of alloys electrode was studied by potentiodynamic method when the electrochemical polarization was started about 30 minutes after the working electrode was immersed in saliva and conducted in a potential range of -0.6 V to 0.6 V vs. Ag/AgCl with a scan rate of 2 mV/s.

2.5. ICP-MS analysis

ICP-MS analysis was performed in the static immersion condition in accordance with JIS T 0304 standard [17]. The concentrations of metals released into solutions were determined in ppb (ng/mL). The calibration curves were obtained using standard multi element with concentration 10mg/L. Liquid samples were introduced with a peristaltic pump in nebulizer in-situ with the specific system for samples and after this reaching plasma with a high temperature as 6000 K, were changed into steam phase and transported to ICP-MS for quantitative elemental analysis in solution. The coated and uncoated samples were incubated in saliva solution at 37^0C without stirring. At predetermined time, the coating specimen was withdrawn and the resulting solution was measured by ICP- MS to determine the amount of released ions. After each measurement, the saliva solution was renewed. Metal concentration was measured in a clean room and the solutions for measurement were prepared on a clean bench (class 100). The analytical detection limits under these conditions were all below 0.05 ng/mL. 12 CoCrNbMoZr samples (6 unmodified and 6 with incorporated Ag) were analyzed and elements of interest have been: Co, Cr, Mo, Nb, Zr, Mn si Si. As blank artificial saliva Tani-Zuchi was used. The time periods for ions release determination represents medium time being as following: 3, 7, 14, 32, 40, 65, 130 days and the instrumental conditions are outlined in Table 2.

Table 2. ICP-MS equipment and operating conditions

ICP-MS instrument	**Perkin Elmer SCIEX ELAN DRC-e**
Plasma conditions	
Rf power and Plasma gas flow	1500 W and 15 L.min^{-1} respectively
Aerosol gas flow	1.2 L. min^{-1}
Mass spectrometer settings	
Resolution and Dweel time	Normal and 500 msrespectively
Sweeps/reading and Points/spectral peak	5 and 1 respectively
Readings/replicate	400

3. Results and discussion

The Ag nanoparticles electrodeposition and incorporation in surface under an applied potential of-350mV vs. Ag/AgCl in 500 pulses of 4 milliseconds is presented in Fig1.

Top-view of morphology of CoCrNbMoZr alloy with silver nanoparticles incorporated is presented in Fig. 2 at two different magnifications. As can be seen the deposition is relatively uniform and has average dimensions of Ag nanoparticles around 100 nm, based on value between 70-150 nm.

Ions release from modified and unmodified surface of CoCrNbMoZr alloy is presented in Table 3 and table 4 respectively.

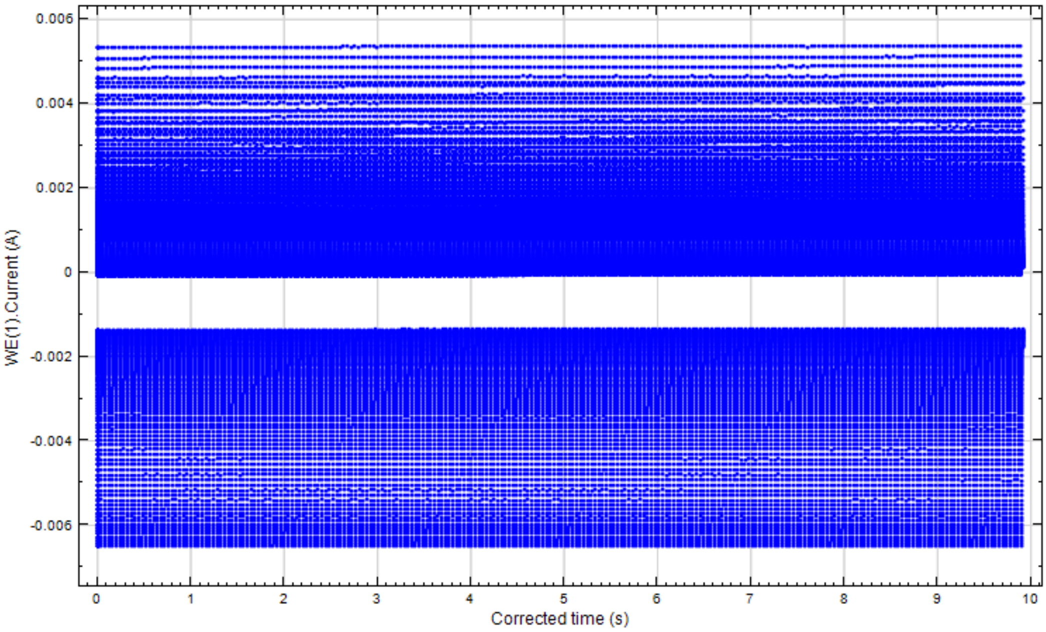

Fig.1. Ag nanoparticles potentiostatic electrodeposition

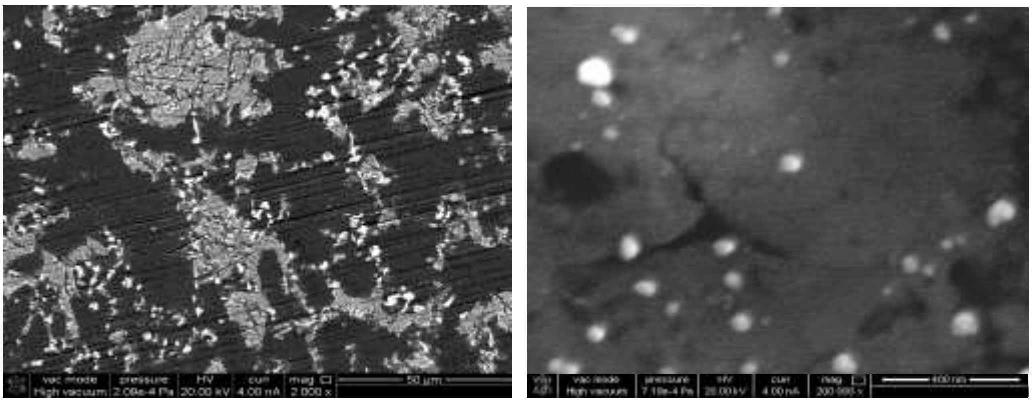

Fig.2 Top-view of morphology of CoCrNbMoZr alloy with Ag nanoparticles

Table 3. Ions release unmodified surface of CoCrNbMoZr alloy

Element	*CoCr unmodified -Concentration (ppm)*						
	3 days	*7 days*	*14 days*	*32 days*	*40 days*	*65 days*	*130 days*
Co	0.000	0.000	0.000	0.000	0.000	0.000	1.121
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.076
Mo	0.000	0.000	0.000	0.000	0.000	0.000	0.006
Nb	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Zr	0.004	0.005	0.014	0.029	0.029	0.071	2.147
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Si	0.000	0.000	0.000	0.000	0.000	0.000	0.000

The data from Table 3 indicate that despite the high level of heavy metals as Co and Cr in the alloy it is not ions release from such elements until the last period of analyzed time, respectively 130 days. Heavy metals are elements that cannot be metabolized by the body and thus are bio-accumulative. It follows that their concentration can be aggressive over time, taking into account that such metals are specifically aggressive for teeth and stressors for oral health. In the research field of influence of environmental factors on health, heavy metals' impact in oral health proved to be a topical approach, taking into account particularly their strong negative influence and their accumulation in time, in various structures [17-19]. Regarding Zr the release amount appears relatively fast after 3 days and is increasing over the time, but this element is supposed to be one of the less toxic elements of the system.

Table 4. Ions release from surface of CoCrNbMoZr alloy with Ag incorporated

Element	*CoCr+Ag-nanoparticles Concentration (ppm)*						
	3 days	*7 days*	*14 days*	*32 days*	*40 days*	*65 days*	*130 days*
Co	0,000	0,000	0,000	0,000	0,000	0,000	0,576
Cr	0,000	0,000	0,000	0,000	0,000	0,000	0,032
Mo	0,000	0,000	0,000	0,000	0,000	0,000	0,002
Nb	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Zr	0,000	0,000	0,000	0,000	0,000	0,004	0,078
Mn	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Si	0,000	0,000	0,000	0,000	0,000	0,000	0,000

In the case of samples having surface with nanoparticles incorporated it is to mention firstly that very small amount of Zr are released after 65 days. It is the amount release after 3 days in the case of untreated alloy. Regarding heavy metals as Co and Cr the amounts released is only after 130 days and seems to be aroubd half of the release at the same time from the unmodified alloy.

This observation is a very interesting one taking into account that corrosion rate for both modified CoCrNbMoZr alloy is much smaller compared to unmodified alloy as can be seen in table 5 with kinetic parameters in Tani Zuki saliva. In Table 5, i_{corr} is current density and K_g, P, are corrosion rate as gravimetric and respectively penetration index.

Table 5. The kinetic parameters in saliva of CoCr NbMoZr with and without Ag incorporated

Electrolyte	*Material*	*Tafel slope method*				*Polarization resistance method*	
		E_{corr}, mV	*i_{corr}, $\mu A\ cm^{-2}$*	*K_g, $gm^{-2}h^{-1}$*	*P, mm $year^{-1}$*	*R_P, $K\Omega$*	*i_{cor}, $\mu A\ cm^{-2}$*
Artificial saliva	CoCr	-247	1.127	0.01279	0.01435	44062	1.013
	CoCr+Ag	-102	0.86	0.00988	0.01108	52860	0.767

The data from Table 5 indicate clearly a more protective behavior for the samples with Ag nanoparticles incorporated sustaining the smaller ions release in this case. It is to mention that the new alloy with Nb and Zr as was compared with classical CoCr alloy presents a better behavior in oral cavity.

Conclusions

In the research field of influence of environmental factors on health, heavy metals' impact in oral health proved to be a topical approach, taking into account particularly their strong negative influence and their accumulation in time, in various structures. CoCr based alloys with small amount of Nb and Zr has better performance and could be promoted for dental restorative works. Based on experimental data of our paper we can promote that incorporation of Ag nanoparticles it will be an improvement as well. The electrochemical kinetic data indicate clearly a more protective behavior for the alloy with Ag nanoparticles electrodeposited sustaining the smaller ions release in this case.

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