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COMPARATIVE STUDY ON THE CORROSION BEHAVIOR OF TI METAL, Ti-6Al-4V AND CO-CR-W ALLOYS IN ARTIFICIAL SALIVA

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ABSTRACT

Open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were used to examine the corrosion behavior of Ti, Ti-6Al-4V and CoCrW in artificial saliva containing different NaF concentrations. Also, the effects of saliva pH and immersion time of the studied materials in the test solution were taken into consideration. The corrosion resistance of the three materials was found to decrease with increasing fluoride concentration and increased as pH increased. As the immersion time of the materials in 0.005 M NaF increases their passivity increase in the order CoCrW > Ti > TAV. Anodization of the electrodes led to increase the passivity but did not change the electrodes behavior in saliva at different pH values.

Keywords: Ti, Ti-6Al-4V, CoCrW, saliva, fluoride, passivation

1- INTRODUCTION

Titanium and titanium alloys have been used in medical and dental applications in consequence of their low density, high specific strength, appropriate mechanical properties, low elastic modulus, good biocompatibility and super corrosion resistance in body fluids [1, 2]. The corrosion resistance of Ti and its alloys is due to the formation of an insoluble titanium oxide layer [3]. The corrosion behavior of Ti and Ti-6Al-4V alloy in artificial saliva containing fluoride ions was studied [4-11]. Decrease in corrosion resistance and less tendency for passivation was observed as F⁻ ions concentration increased and pH decreased.

Cobalt-chromium alloys have extensive applications in prosthetic dentistry due to their low weight and excellent mechanical properties, such as high hardness, strength, resistance to tarnish and high temperature and also good resistance to corrosion. The leaching of metal ions from the Co-Cr-Mo alloy in the solution was dependent both upon the nature of the solution and the duration of the immersion [12]. The behavior of Co-Cr-Mo alloy in artificial saliva at different temperatures and pH values, and containing fluoride (1500 ppm) was studied [13]. Addition of fluoride did not affect the alloy corrosion whereas the alloy

dissolution increased with increasing temperature and increased as a function of pH in the range 3.4-11.4 but in acid solution stable molybdenum oxides were formed. Also the effect saliva pH and fluoride content on the electrochemical stability of Co-Cr-Mo alloy was studied [14-17]. Sodium fluoride addition or decreasing the pH led to a marked decrease in corrosion resistance of Co-Cr-Mo dental alloy in artificial saliva. The aim of the present work is to investigate the influence of pH and fluoride ions content of artificial saliva on the corrosion of titanium metal, Ti-6Al-4V and Co-Cr-W alloys. Also, the effects of immersion time, of the test materials in the artificial saliva containing F⁻ ions, and the anodic passive film, on the test materials, on the corrosion rate were examined. The study was carried out using open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy.

2. EXPERIMENTAL PROCEDURE

Pure titanium (99.9%), Ti-6Al-4V (TAV) and Co-Cr-W (CoCrW) alloys of the compositions shown in Table 1 were fixed into glass tubes of appropriate internal diameters with epoxy resin leaving surface areas of 0.315 cm² for titanium with density 4.51g/cm³, 0.503cm² for TAV alloy with density

Table 1: Composition of the studied materials

	N	C	O	Fe	V	Al	Ti	Ti-6Al-4V
	0.035	0.038	0.106	0.180	3.85	5.70	90.091	(Wt %)
	Si	Mn	Fe	Nb	Mo	W	Cr	Co-Cr-W
	1	1	1	1	2.5	8	24	61
								(Wt %)

4.51g/cm³ and 0.594 cm² for CoCrW alloy with density 5.5 g/cm³. Prior to immersion in the electrolyte, the electrodes were abraded using successively grades emery papers down to 2000 grit, then rubbed with a soft cloth until they acquired a mirror-bright surface and washed with doubly distilled water. The electrolytic cell was an all glass double jacket three electrode cell. A platinum sheet was used as an auxiliary electrode. All potential were measured and reported against a saturated calomel electrode as a reference electrode. The Fusayam a artificial saliva [18] with the composition: 0.4 g NaCl, 0.4 g KCl, 0.795 g CaCl₂.2H₂O, 0.690 g NaH₂PO₄.H₂O, 0.005 g Na₂S.9H₂O, 1.0 g urea was prepared from analytical grade chemical reagents and doubly distilled water. Saliva containing different concentrations of fluoride ions was prepared using NaF addition. The pH of the saliva was adjusted to different values using dilute HCl or NaOH solutions. The measurements were carried out in naturally aerated solutions at 25 °C. The open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy measurements were carried out using the electrochemical workstation 1M6 zahner elektrik (Me β technik, Germany). For impedance measurements the input signal was usually 10 mV peak to peak in the frequency domain 0.1-105 Hz.

3. RESULTS AND DISCUSSION

3.1. Effect of fluoride ions

The effect of fluoride ions on the corrosion behavior of Ti metal, Ti-6Al-4V and Co-Cr-W alloys in saliva was studied at different concentrations ranging from 0.005 M to 0.1 M and pH 6.34. The electrochemical impedance spectroscopy spectra were recorded for the test

materials at the open circuit potential after 1 h of immersion in the solution. Nyquist plots of the three materials are shown in Fig.1a-c. All the diagrams are characterized by abroad capacitive loops except Ti in 0.1 M NaF,

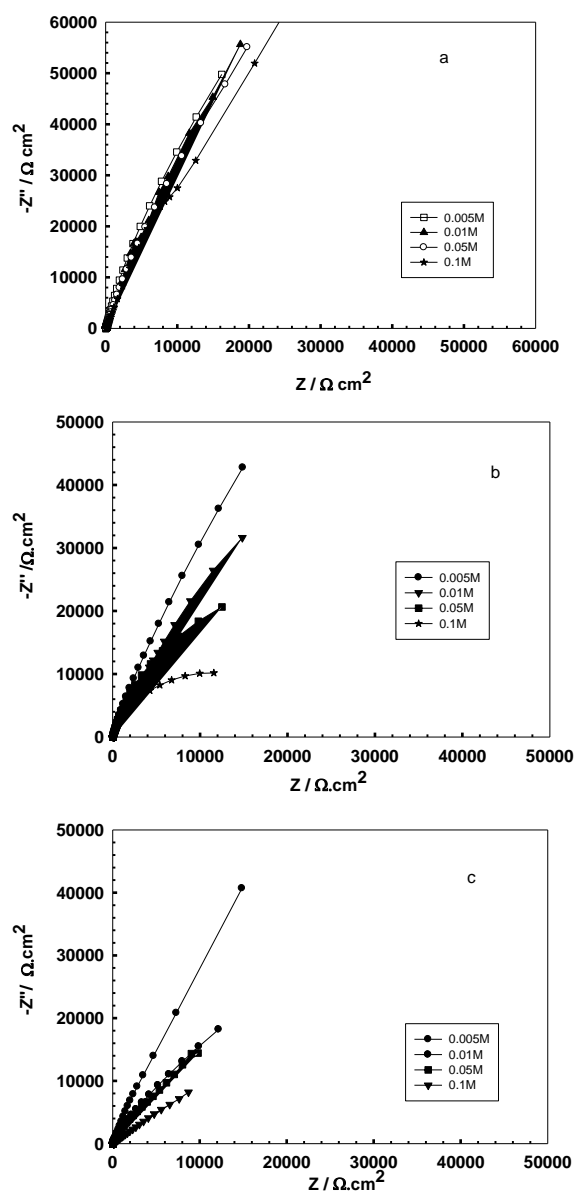


Figure 1: Nyquist plots of (a) CoCrW, (b) Ti and (c) TAV in artificial saliva containing different NaF concentrations ranging from 0.005 to 0.1 M.

indicating better film stability. In general, the surface is covered with oxide film, whose size decreases as fluoride ion concentration increases. These results reveal a decrease in the corrosion resistance of the three used materials with increasing F- ions concentration. This was observed previously for Ti [6, 11], for Ti-6Al-4V [10], for Co-Cr-Mo [17] and for SLMedCoCrW where F- ions slightly accelerated the corrosion of this alloy by changing the composition of the passive film, thereby reducing the protectiveness of the film [19]. The corrosion resistance of the three electrodes is in the order Co-Cr-W > Ti > Ti-6Al-4V as shown in Fig. 2 for the different fluoride concentrations. Also, the bode plots in Fig. 3 conform the results in Fig. 2. Titanium showed a much better corrosion resistance than Ti-6Al-4V alloy in artificial saliva [4].

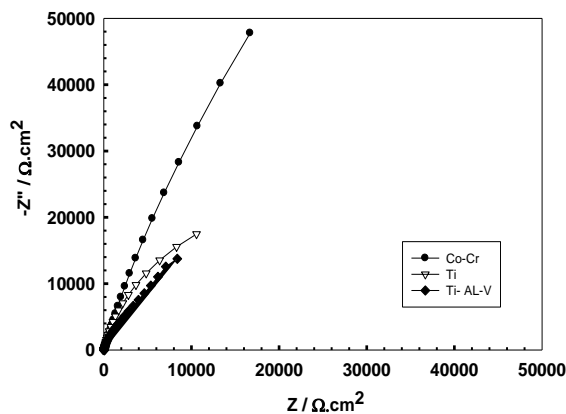


Figure 2: Nyquist plots of CoCrW, Ti and TAV in artificial saliva containing 0.05 M NaF

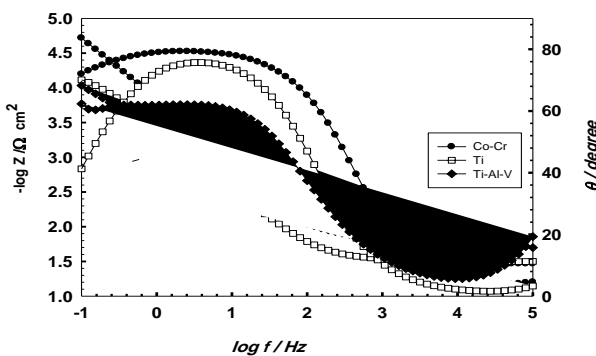


Figure 3: Bode plots of CoCrW, Ti and TAV in artificial saliva containing 0.1 M NaF.

Fig. 4 represents a two-time constants equivalent electrical circuit for fitting the EIS spectra obtained here. A circuit with two time constants was used for a two-layer structure film [20, 21]. The passive film on Ti [6] and TAV alloy [10, 22] consists of a barrier-like inner layer and a porous outer layer and the same suggested circuit here was used. In the circuit, the components are as follows, R_s solution resistance, C_p and R_p capacitance and resistance of the porous layer and C_b capacitance and R_b resistance of barrier layer. Since there is a deviation between real capacitance and pure capacitance therefore, simulation of the impedance spectra can be performed by replacing the capacitance C , with a constant phase element (CPE). The impedance of CPE is described by the following expression [23]:

$$Z_{CPE} = \frac{1}{Q(j\omega)^\alpha} \quad (1)$$

Where Q is the frequency independent real constant of the CPE which is identical to the idealized capacitance at $\omega = 1$, ω is the angular frequency ($\omega = 2\pi f$ rad s⁻¹), $j = \sqrt{-1}$, and α is the coefficient related to deviation which varies between 1.0 for a purely capacitive behavior associated with a perfectly smooth surface and 0.5 for a porous electrode [24].

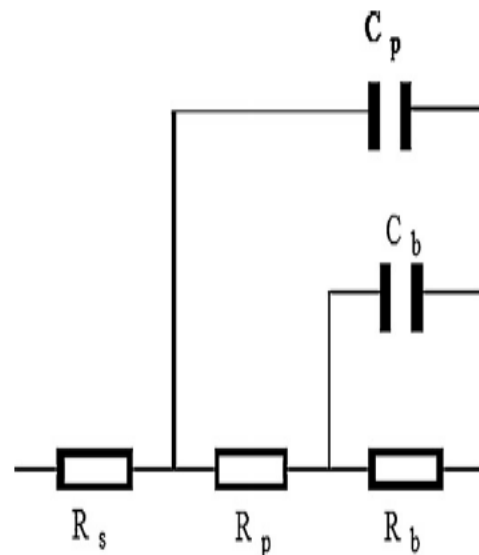


Figure 4: Equivalent electrical circuit used to fit the impedance spectra of CoCrW, Ti and TAV.

The fitted characteristic parameters for the three used materials are given in Table 2. From this Table it is obviously that the resistance values of the inner barrier layer, R_b , are significantly larger than the resistance values of the outer porous layer, R_p . This reveals that the protection provided by the passive film is predominantly owing to the barrier layer. Both R_b and R_p are in the order $\text{Co-Cr-W} > \text{Ti} > \text{Ti-6Al-4V}$ and decrease with increasing of F^- ions in the saliva indicating that the protectiveness of the passive film on the three investigated materials decreases due to its dissolution. The passive film is mainly composed of TiO_2 on Ti [9, 25] and TAV alloy [9], and of chromium oxides on CoCr alloy [26, 27].

The potentiodynamic polarization was measured after the steady state potential was reached for the three used materials in the artificial saliva containing different F^- ions concentrations (0.005 M-0.1 M) and the results

are shown in Fig.5a-c. The Tafel region is followed by a wide constant current plateau which corresponds to passivity region. This indicates the ability of the three electrodes to grow oxide layer on their surfaces which causes the potential of the electrodes to increase in the positive direction. Polarization parameters, including corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a) and Corrosion Rate (C.R) are listed in Table 3. From Fig.5 it is clear that the cathodic and anodic branches are shifted to higher current density region while E_{corr} is shifted to more negative potential with increasing F^- ions concentration. Also from Table 3, it can be seen that i_{corr} increases as fluoride concentration increases for three materials. This indicates a decrease in the corrosion resistance of the tested materials and the loss of passivity due to thinning the primary

Table 2: Electrochemical parameters obtained from the EIS data for CoCrW, Ti and TAV in artificial saliva containing different NaF concentrations ranging from 0.005 to 0.1 M.

α_2	C_b ($\mu\text{F.cm}^{-2}$)	R_b ($M\Omega.\text{cm}^2$)	α_1	C_p ($\mu\text{F.cm}^{-2}$)	R_p ($k\Omega.\text{cm}^2$)	R_s ($\Omega.\text{cm}^2$)	Conc.Of Na F(M)	Alloys
0.89	42.1	33.8	0.88	260	7.1	64.1	0.005	Co-Cr-W
0.92	43.6	30.7	0.89	262	6.8	66.3	0.01	
0.87	44.2	28.6	0.87	272	6.1	68.4	0.05	
0.88	48.1	23.6	0.89	278	5.5	70.11	0.1	
0.86	49.1	30.1	0.9	330	6	43.7	0.005	Ti element
0.90	51.1	28.4	0.91	350	5.8	46.1	0.01	
0.89	52.4	25.2	0.88	378	5.4	47.9	0.05	
0.88	52.7	22.5	0.88	400	5.1	49.89	0.1	
0.89	55.9	20.1	0.87	411	5.6	34.9	0.005	Ti-6Al-4V
0.88	56.2	19.3	0.89	422	5.3	36.1	0.01	
0.87	57.6	18.2	0.90	430	5.1	37.2	0.05	
0.91	58.2	17.1	0.88	450	4.9	38.34	0.1	

Table 3: Electrochemical parameters calculated from the potentiodynamic polarization curves for CoCrW, Ti and TAV in artificial saliva containing different NaF concentrations ranging from 0.005 to 0.1M.

C.R (mm/y)	β_a (mV.dec^{-1})	β_c (mV.dec^{-1})	I_{corr} ($\mu\text{A.cm}^{-2}$)	E_{corr} (V)	Conc.Of Na F (M)	Alloys
0.017	24.1	-40.6	0.518	-0.180	0.005	Co-Cr-W
0.031	49.9	-47.4	1.99	-0.220	0.05	
0.052	90	-70.6	3.98	-0.250	0.1	
0.027	98.5	-49.9	1.584	-0.230	0.005	Ti element
0.054	128	-91.1	3.162	-0.260	0.05	
0.086	179	-104	5.014	-0.275	0.1	
0.036	185	-71.8	2.52	-0.225	0.005	Ti-6Al-4V
0.057	243	-98.4	3.96	-0.260	0.05	
0.092	365	-105.2	6.31	-0.280	0.1	

oxide film layer by chemical dissolution. This phenomenon was observed previously for Ti [6, 28], TAV [10, 29] and for CoCrW [19]. The values of i_{corr} follow the order TAV > Ti > CoCrW, see Table 3. This means that the material with the best corrosion resistance in the artificial saliva containing different F ions concentrations is CoCr alloy, followed by Ti metal and finally TAV alloy. There fore the potentiodynamic polarization results are in good agreement with those of EIS measurements.

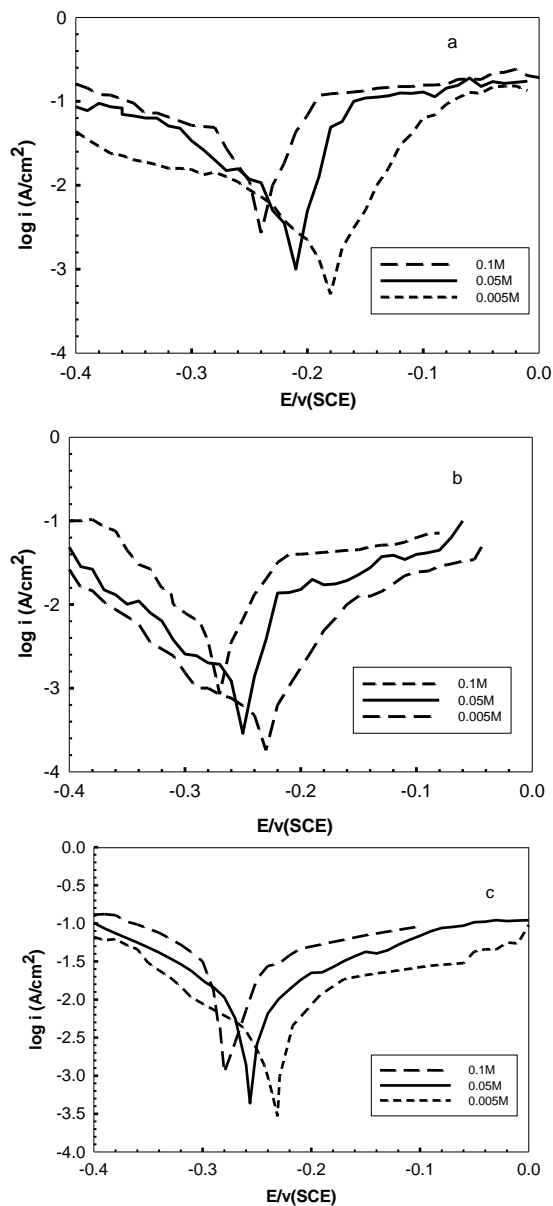


Figure 5: Potentiodynamic polarization of (a) CoCrW, (b) Ti and (c) TAV in artificial saliva containing different NaF concentrations ranging from 0.005 to 0.1 M.

3.2. Effect of saliva pH

3.2.1. Effect of saliva pH before anodization

To examine the effect of pH of the artificial saliva on corrosion behavior of the three tested materials, EIS measurements were carried out at the open circuit potential after 1 h immersion in the test solution of different pH values (2-11). The impedance results of the three materials: CoCrW, Ti and TAV are expressed in the form of Nyquist plots as shown in Fig.6a-c. The results in this Fig. reveal that for all the electrodes, the diameter of the capacitive semicircle increases as pH increases. The equivalent circuit in Fig.4 was used for fitting the EIS spectra at different pH and the fitting parameters are given in Table 4. In this Table the values of R_p and R_b increase with pH and are of the order CoCrW > Ti > TAV. In Previous studies, the impedance measurements indicated that the resistance of the surface film on Ti [4, 6] and on TAV [4, 5] increased as the pH increased and its value for Ti is greater than that for its alloy [4]. Increasing of saliva pH helps in growth the pre-immersion oxide film on the metallic material, thus its corrosion resistance increases. The passivity of this film is highest for CoCrW and is the lowest for TAV. This is very clear from the comparison between the impedance results for the three electrodes in saliva at pH 4 as shown in Figure 7.

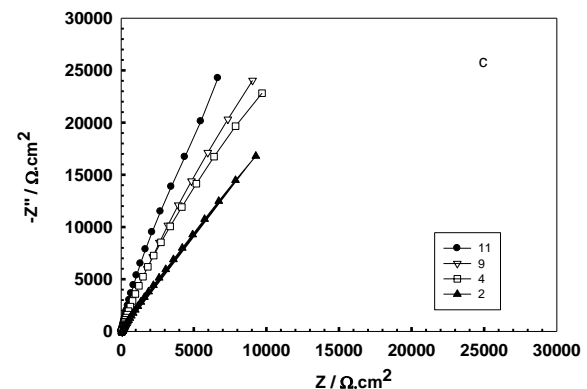


Figure 6: Nyquist plots of (a) CoCrW, (b) Ti and (c) TAV in artificial saliva at different pH values.

Potentiodynamic polarization was measured after the open circuit potential of the material was reached the steady state in saliva of differentp H and the results are given in

Table 5. These results reveal that i_{corr} decreases while E_{corr} shifts to less negative value as pH increases indicating thickening of the passive film on the examined material. A similar results were observed before for Ti [4,6] and TAV [4,5] whereas the corrosion current density for Ti is lower than that of its alloy [4]. At any pH CoCrW has a low current density while TAV has the highest one and Ti is between them. This is illustrated in Fig.8 which includes a comparison between the polarization results for the three materials in saliva at pH 4. Increasing of the passive film protectiveness with pH follows the order CoCrW > Ti > TAV. And in Fig.9, the Corrosion Rate decreases as pH

increases and follows the order TAV > Ti > CoCrW.

3.2.2. Effect of saliva pH after anodization

The EIS spectra of the three investigated electrodes were measured in saliva at different pH values after anodic polarization at 0.5 V for 15 min. The results of these measurements are shown in Table 6 which show that the behavior of tested materials in saliva of different pH values is the same before and after the anodization, i.e. the resistance increases as pH increases and follows the order CoCrW > Ti > TAV, see also Table 4 for comparison. This means that the formation of anodic oxide film

Table 4: Electrochemical parameters obtained from the EIS data for CoCrW, Ti and TAV in artificial saliva at different pH values.

α_2	C_b ($\mu F.cm^{-2}$)	R_b ($M\Omega.cm^2$)	α_1	C_p ($\mu F.cm^{-2}$)	R_p ($k\Omega.cm^2$)	R_s ($\Omega.cm^2$)	pH	Alloys
0.89	45.33	25.2	0.88	300	5.1	70.79	2	Co-Cr-W
0.92	43.09	34.8	0.89	280	6.3	63.09	4	
0.87	41.92	44.9	0.89	265	7.4	58.88	9	
0.89	40.58	53.4	0.88	255	8.5	56.23	11	
0.86	53.52	18.35	0.89	420	4.2	51.28	2	Ti element
0.90	50.21	27.3	0.89	403	5.7	50.11	4	
0.89	49.87	36.4	0.87	400	6.8	43.65	9	
0.90	47.34	45.7	0.89	313	7.7	39.81	11	Ti-6Al-4V
0.91	68.72	16.2	0.84	480	3.1	32.35	2	
0.95	64.63	20.6	0.88	478	4.9	35.11	4	
0.91	63.57	30.3	0.89	465	5.9	30.11	9	
0.90	60.31	35.9	0.87	450	6.7	24.54	11	

Table 5: Electrochemical parameters calculated from the potentiodynamic polarization curves for CoCrW, Ti and TAV in artificial saliva at different pH values.

C.R (mm/y)	β_a (mV.dec-1)	β_c (mV.dec-1)	I_{corr} ($\mu A.cm^{-2}$)	E_{corr} (V)	pH	Alloys
0.0380	57.1	-181.2	0.794	-0.163	11	Ti-6Al-4V
0.0445	213	-108	1	-0.196	9	
0.1720	49.4	-47.4	3.16	-0.230	6.34	
0.3880	354	-96.2	25	-0.312	4	
0.6790	374	-88.4	125	-0.345	2	
0.0110	110	-32.1	0.012	-0.159	11	Ti element
0.0140	140	-55.9	0.076	-0.17	9	
0.0400	179	-104	0.158	-0.25	6.34	
0.2570	153	-79.7	7.8	-0.27	4	
0.3880	242	-194	19.9	-0.291	2	
2.0000e-4	112	-37.9	0.001	-0.11	11	Co-Cr-W
1.0000e-3	132	-117.1	0.005	-0.151	9	
2.0000e-3	365	-105.2	0.02	-0.179	6.34	
0.1300	370	-143.5	6.3	-0.200	4	
0.2900	410	-167.9	15.8	-0.211	2	

on the studied materials does not change their trends in the test solutions but the passivity of the surface becomes greater than before the anodization as shown from Fig.10. The

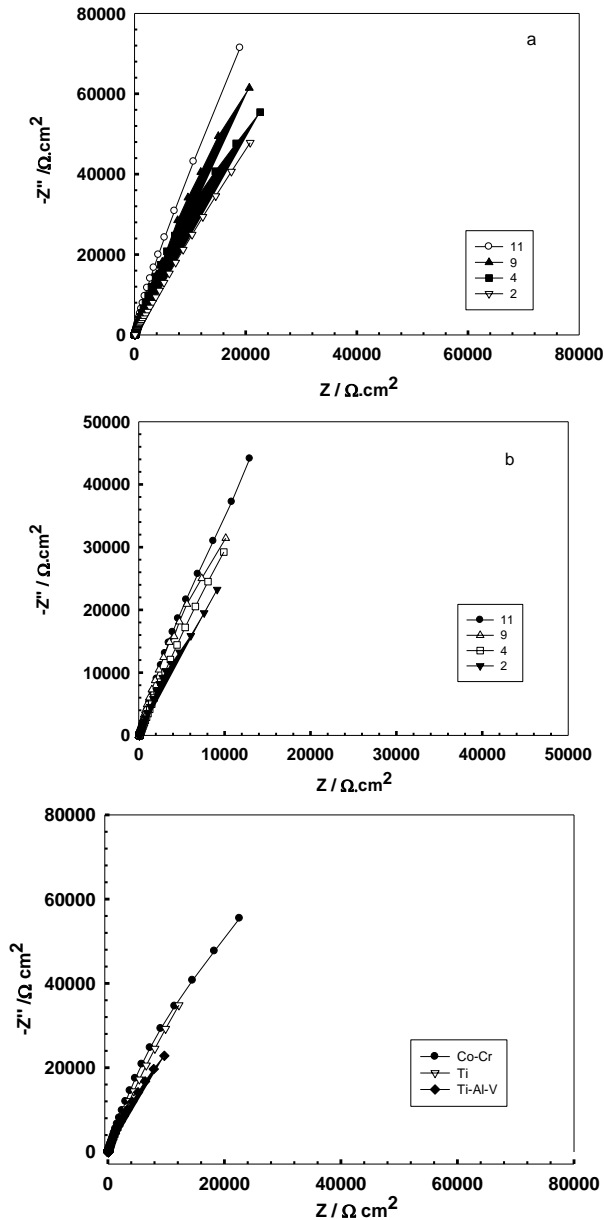


Figure 7: Nyquist plots of CoCrW, Ti and TAV in artificial saliva at pH 4.

3.3. Effect of immersion time

The three used materials were immersed in the artificial saliva containing 0.005 M NaF at pH 6.34 for different time intervals: 3, 10 and 17 days. The variation of the open circuit potential with time is shown in Fig. 11. It is clear from this figure that the pre-immersion (air formed) oxide film is not sufficient to

impart complete passivity to the studied materials here, as the potential changes rapidly at first with the time till one hour towards more noble values then the change becomes very slowly and finally a steady state is reached. The ennobling of the metallic materials potential with time indicates film repair and healing. The increasing of the open circuit potential of Ti [4,6],TAV [4,5] and CoCrM [13,17] with time in saliva containing F- ions was observed mostly in neutral solutions.

EIS spectra of the three materials were measured over different periods of time in the artificial saliva containing 0.005 M NaF at pH 6.34 and the results are given in Fig.12a-c. As can be seen from this Fig., the diameter of the capacitive semicircle increases with increasing the immersion time. Also the fitting parameters obtained from the EIS data are presented in

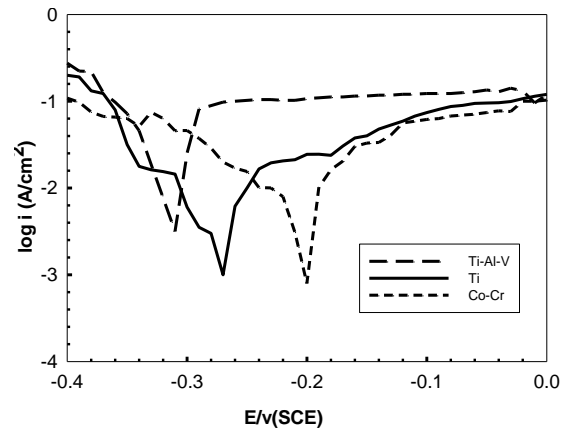


Figure 8: Potentiodynamic polarization of CoCrW, Ti and TAV in artificial saliva at pH 4.

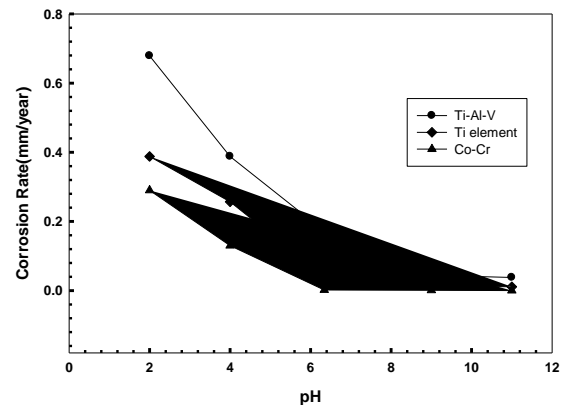


Figure 9: Corrosion Rate of (a) CoCrW, (b) Ti and (c) TAV in artificial saliva at different pH values.

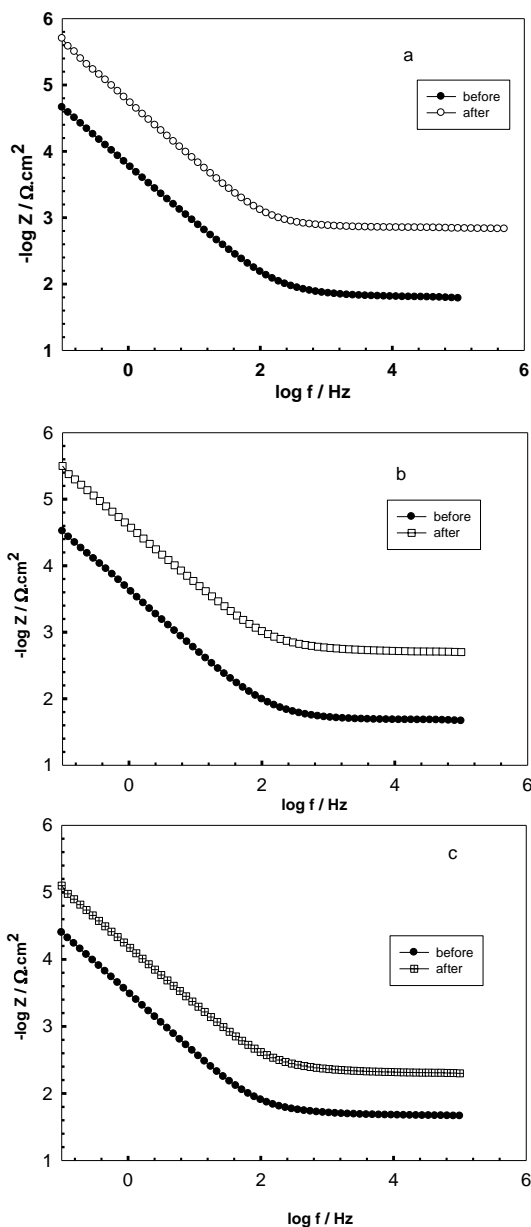


Figure 10: Bode plots of (a) CoCrW, (b) Ti and (c) TAV before and after anodization in artificial saliva at pH 9.

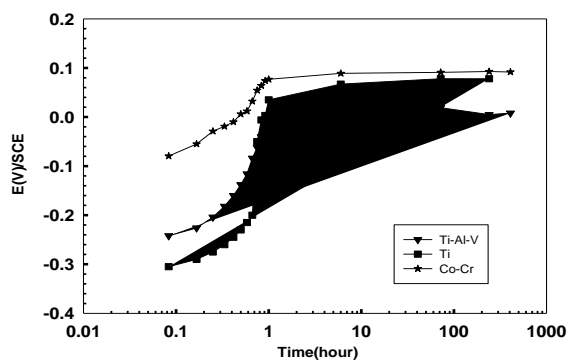


Figure 11: Variation of the open circuit potential of CoCrW, Ti and TAV with time in artificial saliva containing 0.005 M NaF at pH 6.34.

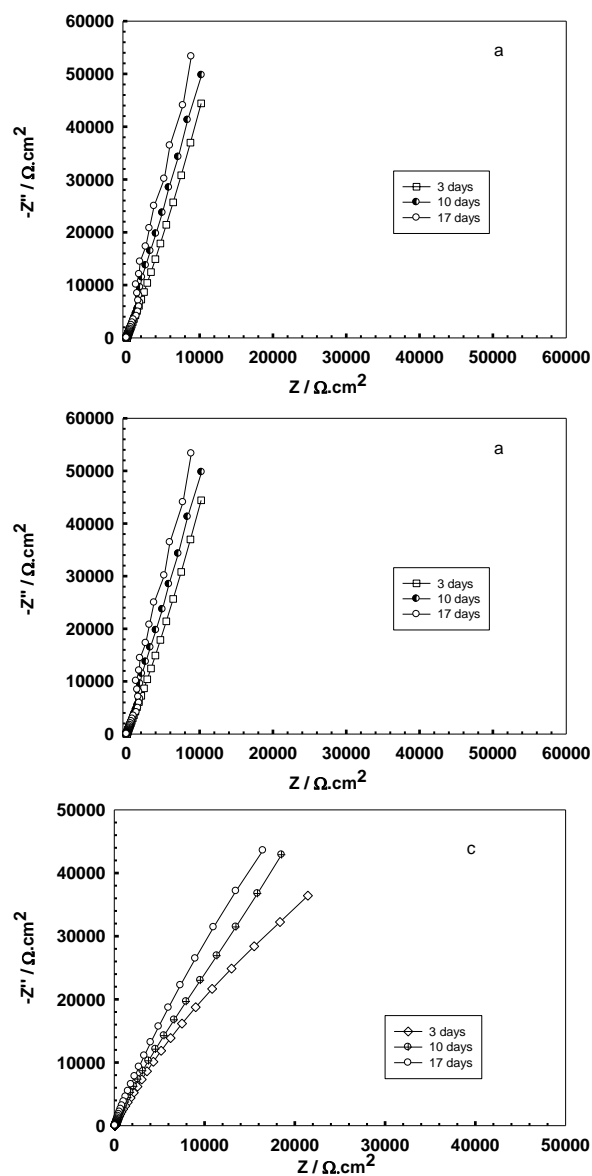


Figure 12: Nyquist plots of (a) CoCrW, (b) Ti and (c) TAV in artificial saliva containing 0.005 M NaF at pH 6.34.

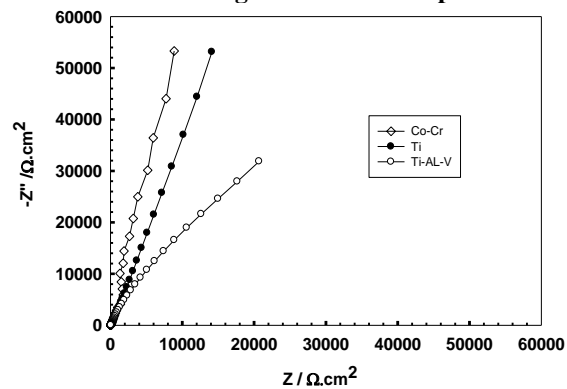


Figure 13: Nyquist plots of CoCrW, Ti and TAV after immersion for 17 days in artificial saliva containing 0.005 M NaF at pH 6.34.

Tables 6: Electrochemical parameters obtained from the EIS data for CoCrW, Ti and TAV after anodization in artificial saliva at different pH values.

α_2	C_b ($\mu F.cm^{-2}$)	R_b ($M\Omega.cm^2$)	α_1	C_p ($\mu F.cm^{-2}$)	R_p ($k\Omega.cm^2$)	R_s ($\Omega.cm^2$)	pH	Alloys
0.89	36.39	44.9	0.88	247	16.3	75.79	2	Co-Cr-W
0.90	32.11	54.7	0.89	239	27.5	66.09	4	
0.86	30.82	68.8	0.89	219	39.8	57.88	9	
0.89	30.08	77.2	0.87	207	56.1	59.23	11	
0.96	48.62	36.5	0.89	367	14.8	58.20	2	Ti element
0.90	46.31	45.9	0.87	314	28.6	49.18	4	
0.99	45.80	58.1	0.86	306	36.7	47.68	9	
0.95	44.37	68.6	0.87	301	49.3	44.81	11	
0.94	59.75	25.8	0.85	471	12.9	36.05	2	Ti-6Al-4V
0.97	54.37	36.9	0.80	462	24.7	39.18	4	
0.90	51.54	46.8	0.87	440	31.7	37.13	9	
0.91	50.67	58.6	0.81	431	46.5	34.94	11	

Table 7: Electrochemical parameters obtained from the EIS data for CoCrW, Ti and TAV after immersion for different periods of time in artificial saliva at pH6.34.

α_2	C_b ($\mu F.cm^{-2}$)	R_b ($M\Omega.cm^2$)	α_1	C_p ($\mu F.cm^{-2}$)	R_p ($k\Omega.cm^2$)	R_s ($\Omega.cm^2$)	Times	Alloys
0.89	42.1	33.8	0.88	260	7.1	64.1	An hour	Co-Cr-W
0.91	41.2	34.3	0.89	254	7.2	62.78	3 days	
0.89	39.4	38.7	0.88	252	7.3	56.77	10 days	
0.89	37.9	49.4	0.88	246	7.6	51.34	17 days	
0.86	49.1	30.1	0.9	330	6	43.7	An hour	Ti element
0.91	50.21	31.3	0.89	293	6.1	42.32	3 days	
0.89	47.1	33.1	0.87	286	6.3	41.45	10 days	
0.90	45.2	38.6	0.85	255	6.8	38.25	17days	
0.89	55.9	20.1	0.87	411	5.6	34.9	An hour	Ti-6Al-4V
0.91	51.3	23.3	0.89	333	5.9	32.18	3days	
0.94	49.4	28.7	0.86	326	6	29.19	10 days	
0.91	47.5	32.4	0.87	310	6.3	22.87	17 days	

4. CONCLUSION

*The corrosion resistance for the three studied materials increases with decreasing F-ions content and increasing pH of the artificial saliva.

*Anodic polarization of the used materials leads to thickening of the passive film on their surfaces and hence improves the corrosion resistance.

*Increasing the immersion time of the electrodes in saliva containing 0.005M NaF causing growth of the air-formed oxide film on these materials and increases its protectiveness.

*In the same solution, CoCrW alloy is more resistant to corrosion than pure Ti and its TAV alloy according the order CoCrW > Ti > TAV.

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