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Galvanic Corrosion Between Ti/Ti6Al4V and Various Dental Alloys

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Abstract

The corrosion tendencies of metals are related with their position in the electromotive series. These electrode potential degrees may change due to the composition of the alloys, the surrounding medium or due to the alterations in the composition because of the recurrent costing. The galvanic corrosion appears when different electrochemical potentials are bound to one another and the electrical conductibility is assured by the presence of an electrolyte. It is difficult to avoid coupling of different metals, a problem concerning the choice of the alloy used for the implant bone supra-structure. One has studied the galvanism of several couples formed between a dental implant and diverse dental alloys in Afnor saliva. The electrochemical behavior of 8 commercial dental alloy superstructures with titanium and titanium alloy (Ti6Al4V) implants was investigated by electrochemical techniques. Non-precious alloys were Ni-Cr based (Wiron NT and Verasoft), Co-Cr based (Vitallium alloy) and Cu based (Gaudent). Semi-precious alloys were Ag-Pd based (RX91 and Unique White). The precious alloys were Au-Pd based (Ceram) and Au-Ag based (Argenco). Some of the corroded and non-corroded surfaces were observed by optical microscopy. From linear polarization curves the corrosion potential and the current densities were evaluated. The results showed very low corrosion rates, ranking from 10^{-6} to 10^{-9} A/cm^2. All the results obtained indicate the fact that the corrosion process intensity corresponding to the coupling between titanium (respectively Ti6Al4V) and semi-precious alloys is reduced. The surface of precious and semi-precious alloys is not attacked, but the titanium (Ti6Al4V) surface is oxidized in time.

Introduction

Titanium and titanium alloys are used as biomaterials is due to advantages presented in comparison with other similar materials: chemical inertia [1], low densities [2], toxicity absence [3] and increased biocompatibility [4]. The passive state of titanium and it's alloys is determined by a film with reduced thickness, formed on metal surface and very adherent to it. This film functions as a barrier blocking the metal tendency to interact with the corrosion medium.

Galvanic corrosion may appear when metals having different electrochemical potentials are electrically connected and the electrical conductibility is assured by the presence of an electrolyte. This type of corrosion occurs due to differences that exist between corrosion potentials of the two metals immersed in the same corrosion environment.

The complexity of electrochemical processes that occur at the contact zone between a biomaterial and a dental superstructure covering this material is due to the coexistence both a galvanic couple and a pitting corrosion process.

In an earlier paper the galvanic corrosion between Ti6Al4V alloys and some noble and semi-noble dental alloys was studied in two artificial saliva types by electrochemical techniques and auger spectrometry [5].

Our study extends these researches considering other noble, semi-noble and especially non-noble commercial alloys in Afnor saliva.

Materials and Methods

The galvanic corrosion was investigated by electrochemical methods using 8 types of dental alloys available in Romanian market. The commercial name and composition of these alloys are presented in Table

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1 alongside of chemical composition of the Titanium implant and Ti6Al4V alloy.

The corrosive environment used was an Afnor saliva [5]: NaCl – 0.7 g/L, KCl – 1.2 g/L, Na_2HPO_4 – 0.26 g/L, $NaHCO_3$ – 1.5 g/L, KSCN – 0.33 g/L, urea – 1.35 g/L (pH = 8).

The values of Tafel slopes and the corrosion current densities in the range (E_{corr} = ±150 mV) were obtained using the electrochemical system VOLTALAB 32, which contains a potentiostat, electrochemical interface and a PC. Experimental data were acquired and processed with the VoltaMaster 2 program. The electrochemical system is equipped with a measurement cell containing three electrodes. The working electrode, made from alloy sample was processed into a cylindrical shape and mounted in a Teflon support, constructed in order to realize mechanical and electrical connection with apparatus rotative electrode. Before experimental determinations the sample was mechanically polished using abrasive SiC paper up to 2500 mesh. Then it was washed with water, degreased with ethyl alcohol and introduced in double-distilled water. The reference electrode was a saturated calomel electrode (SCE) and platinum as a counter electrode. In all cases the potential electrode scanning rate was dE/dt = 0.5 mV/s.

When two different corroding alloys are electrically coupled, in the same electrolyte, both are polarized and the corrosion rate will be different for each alloy. In practice, the application of the mixed potential theory, allows us to trace the Tafel lines for each alloy and to sum the measurements of the anode and cathode lines of the couple under investigation. In this way two new Tafel lines are obtained and their intersection provides the values of couple potential (E_{couple}) and couple current density (J_{couple}) [6].

The measurement of open circuit potential and the potential difference between the coupled electrodes was realized for a period of 24 hours using a multi-parameter system CONSORT 831 C, connected to a PC.

The titanium and Ti6Al4V alloy were connected at negative pole of the galvanic cell because the open circuit potential values are higher compared to the other alloys at initial moment of immersion.

The effects of galvanic corrosion are insignificant when the electrode potential difference is lower than 50 mV.

The evaluation of surface structure after coupling for a period of 24 hours was performed using an optical microscope MC 1 equipped with a digital camera which assures a magnifying power of 770 times.

Results

The couple potentials and current density values for titanium-dental alloy couples are presented in the Table 2.

At the initial immersion moment all values of couple potentials are negatives, the lower ones being those for semi-precious alloys. The current densities of the couple for semi-precious alloys show the highest values in comparison with the alloys containing Ni-Cr and Co-Mo.

Table 1

The chemical composition of alloys used

Alloy commercial name		Main composition (%)	Elements under 1%
Precious and semi-precious alloys	ARGENCO	51Au 8.07Pd 22Ag 10Cu 7In 1Zn	Ir
	CERAM	65Au 26Pd 8.65In 0.25Ga	Ru
	RX 91	53.5Pd 37.5Ag 8.5Sn	In, Ru
	UNIQUE WHITE	22 Pd 66Ag 10Cu	In, Ru
Non-precious alloys	WIRON NT	61.4Ni 22.9Cr 8.8Mo 2,5Fe 3.9Nb	Mn, Ti
	VERASOFT	53.6Ni 19,5Mn 14.5Cr 9.5Cu 1.6Al 1.5Si	
	VITALLIUM	63.8Co 28.5Cr 6Mo	C, Si, Mn
	GAUDENT	82.4Cu 9.95Al 4.15 Ni 2.13Fe 1.35Mn	
Titanium		99.9Ti	
Ti6Al4V		6Al, 4V, 90Ti	

Table 2

E_{couple} and J_{couple} for titanium-dental alloy couples

Alloy	t = 0 hours		t = 24 hours	
	E_{couple} (mV)	J_{couple} (nA/cm^2)	E_{couple} (mV)	J_{couple} (nA/cm^2)
ARGENCO	-52	2754	104	2818
CERAM	-41	1380	-89	6166
UNIQUE WHITE	-51	1175	-1	501
RX 91	-36	1585	-88	4677
VITALLIUM	-337	74	-164	56
VERASOFT	-360	251	-187	93
WIRON NT	-343	102	-148	60
GAUDENT	-300	4571	-150	112

In case of GAUDENT alloy couple current density value decreased from 4571 to 112 nA/cm^2, after 24 hours in Afnor saliva. The semi-precious and precious alloys show an increase of couple current densities values in time, excepting UNIQUE WHITE alloy. The reduction of couple current densities values is determined by titanium and alloys surface passivation.

The values of couple potentials and current densities for Ti6Al4V-dental alloys couples introduced in Afnor saliva are presented in the Table 3.

In comparison with the couple current densities values recorded in case of couplings titanium-dental alloys there is an increase for couplings Ti6Al4V-dental alloys of approximately 400-600 nA/cm^2, but the couple current densities still have lower values.

Figure 1 shows the variation of galvanic potential corresponding to couplings formed by titanium and a series of semi-precious alloys after 24 hours in Afnor saliva medium.

In Table 4 there are presented the values of potential difference for titanium and dental alloys couples at the initial moment and after 24 hours of immersion in Afnor saliva.

All four precious and semi-precious alloys coupled with titanium show potential difference values over 500 mV at the initial moment. The potential difference value decreases continually in time, being approximate constant after 20 hours. These values remain positives after 24 hours. The lowest potential

Table 3

E_{couple} and J_{couple} for Ti6Al4V-dental alloy couples

Alloy	t = 0 hours		t = 24 hours	
	E_{couple} (mV)	J_{couple} (nA/cm^2)	E_{couple} (mV)	J_{couple} (nA/cm^2)
ARGENCO	-276	3548	40	3236
CERAM	-321	2138	-89	6761
UNIQUE WHITE	-345	1950	-98	1047
RX 91	-305	2344	-90	5012
VITALLIUM	-440	831	-160	603
VERASOFT	-327	2512	-162	631
WIRON NT	-439	851	-158	603
GAUDENT	-336	5248	-158	646

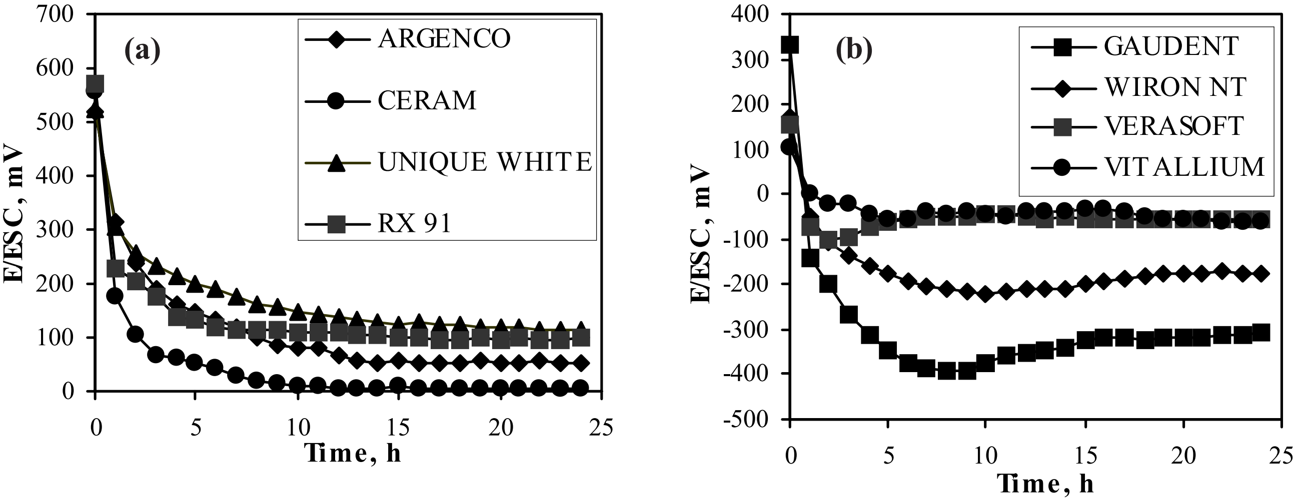

Fig. 1. Variation of the potential difference for couples: (a) titanium/precious alloys and titanium/semi-precious alloys and (b) titanium/non-precious alloys.

Table 4
The values of potential difference for titanium and dental alloys couples at the initial moment and after 24 hours of immersion in Afnor saliva

Alloy	Potential difference, E (mV)	
	Initial	After 24 hours
ARGENCO	517	54
CERAM	559	7
UNIQUE WHITE	524	115
RX 91	572	98
WIRON NT	175	-175
VERASOFT	157	-56
VITALLIUM	104	-60
GAUDENT	332	-308

difference value was recorded for CERAM alloy. The alloys containing a higher quantity of silver show potential difference values around 100 mV. After titanium is coupled with the four alloys, these will be cathodic protected.

At the initial moment the potential difference values corresponding to non-precious alloys are positives. These values decrease continually in time being approximate constant after 20 hours of immersion in artificial saliva. Finally, all couplings show negatives values of potential difference. Figure 2 indicates the variation of the potential difference for couples: Ti6Al4V/precious alloys, Ti6Al4V/semi-precious alloys and Ti6Al4V/non-precious alloys and Table 5 shows the values of potential difference for titanium and dental alloys couples at the initial moment and after 24 hours of immersion in Afnor saliva. The variation of open circuit potential demonstrates that titanium become more precious than the alloys containing nickel and cobalt. The study results in that the highest value of galvanic potential corresponds to the copper containing alloy (GAUDENT) and lower values of galvanic potential occurs when titanium is coupled with alloys Ni-Mo and Co-Cr (VERASOFT, VITALLIUM) based. The potential difference between titanium and GAUDENT alloy achieves the value of 300 mV, proving the fact that GAUDENT alloy is the poorest biomaterial as compared to the others alloys.

In the case of all couplings realized the potential differences decrease in time due to the passivation process suffered by titanium alloy. For the couplings between Ti6Al4V and precious and semi-precious alloys one finds that after 24 hours the potential differences have values under 50 mV, except UNIQUE WHITE alloy. The highest decrease was recorded in case of CERAM alloy. In this solution Ti6Al4V become anodic, potential differences being positives after 24 hours, except CERAM alloy.

The potential difference between Ti6Al4V alloy and non-precious alloys decreases continually from positives values to negatives ones and after 24 hours it was found that Ti6Al4V becomes cathodic protected. The corrosion process will be more intense as surface of precious alloys will be lower, as a consequence of the cathodic protection, which occurs in the system.

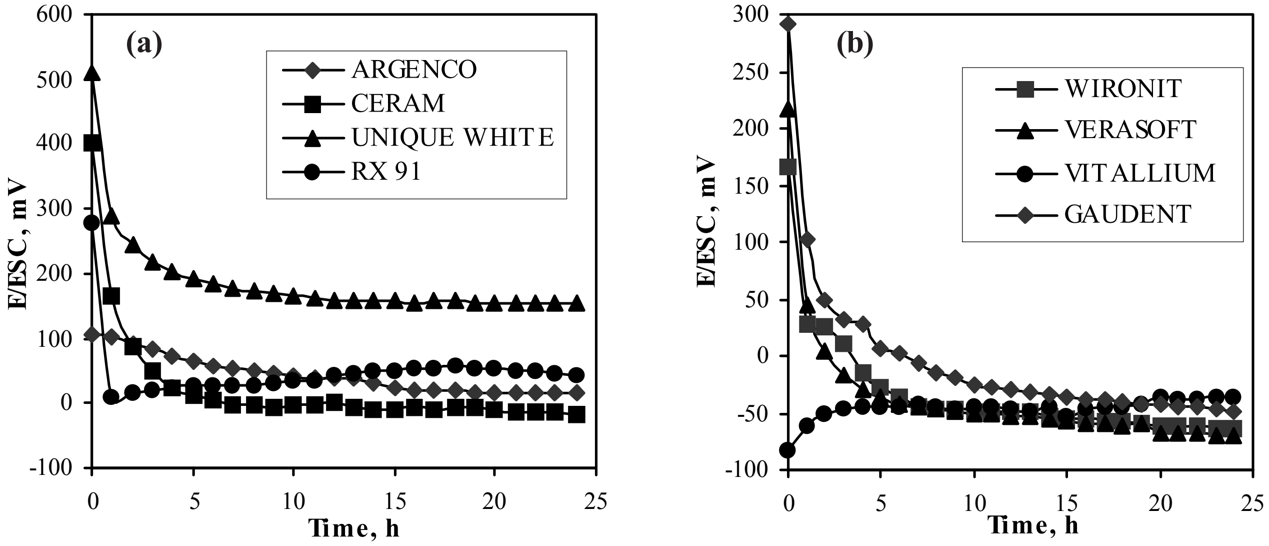

Fig. 2. Variation of the potential difference for couples: (a) Ti6Al4V/precious alloys and Ti6Al4V/semi-precious alloys and (b) Ti6Al4V/non-precious alloys.

Table 5

The values of potential difference for titanium and dental alloys couples at the initial moment and after 24 hours of immersion in Afnor saliva

Alloy	Potential difference, E (mV)	
	Initial	After 24 hours
ARGENCO	105	16
CERAM	401	-17
UNIQUE WHITE	509	154
RX 91	278	41
WIRON NT	165	-63
VERASOFT	218	-70
VITALLIUM	82	-36
GAUDENT	291	-48

The alloy surface was microscopically analyzed before and after galvanic corrosion test. In Figure 3 shows the titanium surface after 24 hours of coupling with CERAM alloy and in Figs. 4 and 5 there are presented the surfaces of GAUDENT and VERASOFT alloys after 24 hours of coupling with Ti6Al4V and titanium. The examination of the surfaces of semi-precious and precious alloys revealed no damage due to the corrosion process but it produced the evidence of titanium and Ti6Al4V alloys oxidation.

Analyzing the surface of non-precious alloys it was found that after 24 hours of coupling with tita-

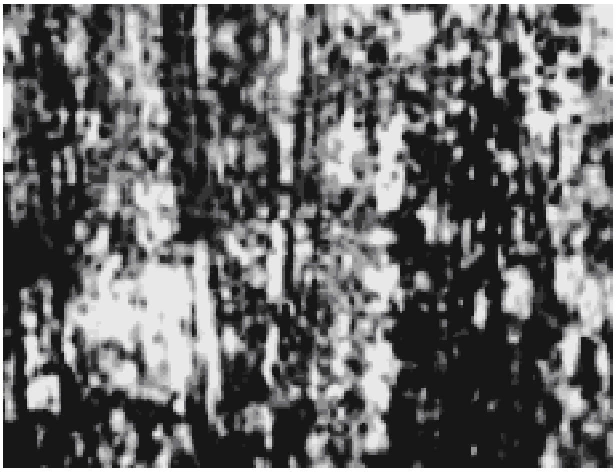

Fig. 3.Titanium surface after 24 hours of coupling with CERAM alloy (precious alloy).

Fig. 4. The surface of GAUDENT alloy after 24 hours of coupling with Ti6Al4V alloy.

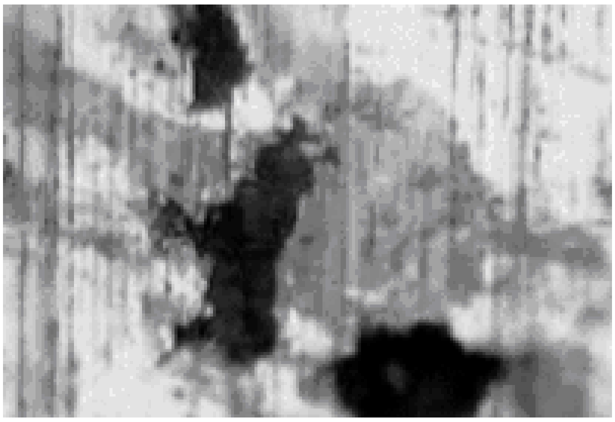

Fig. 5. The surface of VERASOFT alloy after 24 hours of coupling with titanium alloy.

nium/Ti6Al4V, an oxidation of their surface was evidenced. The surface of GAUDENT, VITTALIUM and WIRON NT was uniformly attacked and in case of VERASOFT alloy a pitting corrosion it was found.

Conclusions

The current densities of the Ti6Al4V/non-precious alloys in Afnor saliva, have lower values, of an magnitude order of 10^{-9} A, both at the initial moment and after 24 hours from coupling.

The coupling currents recorded in the case of pure titanium with the rest of alloys coupling have lower values than the ones corresponding to the coupling between Ti6Al4V and those alloys.

The couple current densities decrease in time for the non-precious alloys because the passivation processes take place on their surface.

All obtained results indicate the fact that the corrosion process intensity corresponding to the coupling between titanium (respectively Ti6Al4V) and semi-precious alloys is reduced. The surface of precious and semi-precious alloys is not attacked, but the titanium (Ti6Al4V) surface is oxidized in time.

The microscopic analysis indicates the apparition of a localized corrosion in case of VERASOFT alloy, the rest of non-precious alloys presenting a generalized attack.

References

1. Schutz, R.W., Thomas, D.E., Corrosion of titanium and titanium alloys. Metals Handbook, Metals Park, Ohio, USA, 1978, p. 669.
2. Hille, GH., J. Mat. 1:373 (1966).
3. Wälivaara, B., Aronsson, B.O., Rodahl, M., Lausmaa, J., and Tengavall, P., Biomaterials 15:827 (1994).
4. Ho, W.F., Ju, C.P., and Chern Lin, J.H., Biomaterials 20:2115 (1999).
5. Grosgogeat, B., Reclaru, L., Lissac, M., and Dalard, F., Biomaterials 20:933 (1999).
6. Dalard,F., Montella, C., and Sohm, J.C., Surf. Techn. 4:367 (1976).
7. Dabosi F, Beranger G, Baroux B, Corrosion localisée, Editeurs scientifiques, Paris, France, 1994, p. 389.

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