TITANIUM AND TA6V4 TITANIUM ALLOY ANODIC OXIDATION AIMED TO IMPLANTOLOGY UTILITY

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ABSTRACT

The anodizing is the process that a coating layer is growth on a metal by an electrochemical way, by anodic oxidation. The paper describe the experiments regarding titanium and TA6V4 titanium alloy anodic oxidation aimed to their corrosion rate decrease as implants and to corrosion products liberation minimization in the human body. The samples surface needs, to get an adherent and uniform colored coating, of special preparation operations. Some phosphate ions content water electrolytes were used. The layers growth on titanium and TA6V4 titanium alloy contain titanium oxides and phosphorus compounds, they are adherents, homogeneous and elastic. The proposed surface treatment assures an excellent electrochemical stability at the interface implant/biological environment, minimizing the local and general toxic specific effects.

KEYWORDS: anodizing, titanium oxide, electrolyte, coating, phosphate ions, biocompatibility, implant.

1.INTRODUCTION

The paper presents the results of the laboratory experiments regarding implant materials, like titanium and TA6V4 alloy, oxidation, by electrochemical, controlled technology, using compatibles electrolytes with the structure and phisyco-chemical characteristics of the supports.

The titanium electrochemical oxidation, that is it anodization, represent a proceeding to artificial growth on the titanium surface of oxides layers, having, higher thickness than the natural, spontaneous one.

This proceeding has as purpose the increasing of the corrosion resistance in different environments and also to improve the plastic deformation conditions both titanium and titaniul alloys. This titanium and titanium alloys processing concern since long time the electrochemists [1÷10] but we estimate that the resources are not yet exhausted. In this process the titanium is the anode and the cathode consist of metals like lead, alluminium, stable metals in the used electrolytes. The anodic reaction is an oxidation process developed at the sample (titanium anode)/electrolyte interface:

$$Ti + 2H_2O \rightarrow TiO_2 + 4H + 4e^-$$

The cathodic reaction is a water reduction process:

$$4H_2O + 4e^- \rightarrow 2H_{2(g)} + 4OH^-$$

The hydrogen give off at the cathode as bubles during the anodizing process.

2.EXPERIMENTAL

Pure titanium and TA6V4 titanium alloy, having the table 1 chemical compositions were used.

Titanium and TA6V4 alloy anodic oxidation experiments were carry on figure one technological schedule.

The samples with the size of 28 x 20 x 0,5 mm were prepared according technological schedule. The samples were anodized in compatibles electrolytes (E0-E4), to realize on the titanium and titanium alloy surface of oxidic layers with phosphorus content (named here „phosphating"):

E0: NaOH 3,5% solution-initial electrolyte;

E1: Na_2HPO_4 , 3 ÷ 10% - phosphating electrolyte;

E2: Na_3PO_4, 1 ÷3% - phosphating electrolyte;

E3: H_3PO_4 0,5N + $NaHCO_3$10% - phosphating electrolyte;

E4: H_3PO_4 1N : citric acid 20g/l 1:1 - phosphating electrolyte.

Energy Dispersive X-ray Microanalisis indicate the presence of the phosphorus in the chemical composition of the oxidic experimental layers.

The experiments were accomplished with a d.c. power supply of max. 150 V /10 A, in a thermostable electrolytic A special unit cathodes – anode device was used, the cathodes plates being made of stainless steel or titanium, as indicate figure 2.

Tab.1 Samples chemical composition (base material)

Simbol	Chemical composition [% weight]													
	Ti	**O**	**H**	**N**	**C**	**Al**	**V**	**Fe**	**Si**	**Ni**	**Cr**	**Co**	**Cu**	**Pb**
Ti	rest	0.12	0,012	0,04	0,06			0,15						
TA6V4	rest			0,005	0,03	5,53	3,9	0,13	0,05-0,1	0,01-0,05	0,005-0,01	<0,005	0,001	<0,005

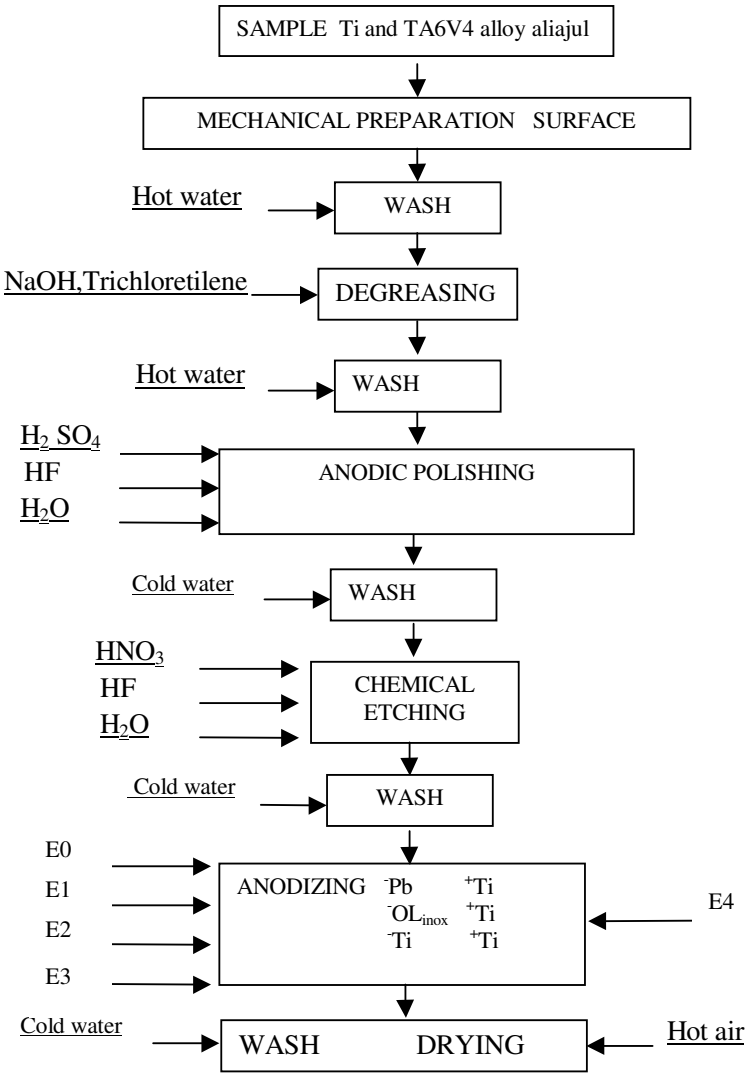


Fig.1 Titanium and titanium alloys anodic oxidation schedule

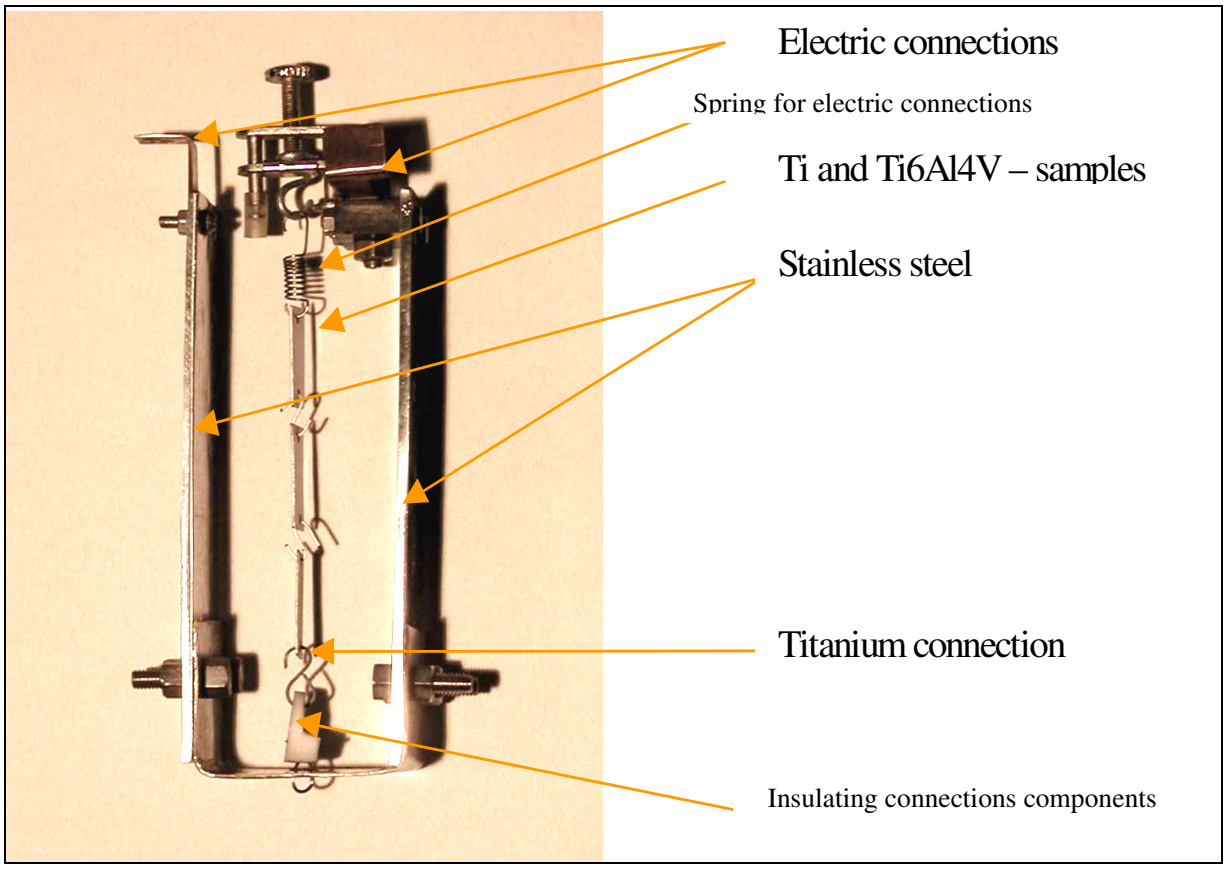


Fig.2 Experimental anode/cathode unit device

A several number of experiment were accomplished using a number of phosphorus containing electrolytes, both at elevated (80^0C) and laboratory ($25\text{-}30^0$C) temperature. A number of technological parameters were applied to surprise accuracy the titanium and titanium alloy behaviour during the whole anodizing process.
The anodizing experiments were both simple and multiple, accompanied sometimes by intermediary thermal traitments at temperatures till 350^oC, even 700^oC in a case.

3.RESULTS AND DISCUTIONS

The experimental conditions and some layers characteristics are presented in the tables 2÷5. Both titanium (index „T") and TA6V4 alloy (index „A") samples were used, the paper presenting the characteristic features of their anodic oxidation.
In the case of OT sample, for instance, table 2, an initial anodic oxidation in the EO electrolyte, at 80^oC, under a d.c. constant voltage of 5V was carry out for 10-15 min. In a second stage the E1 electrolyte was injected into the initial one. In this stage a constant current density of 20 mA/cm^2 was mentained by manual, gradually increasing of the voltage during an „attack" period of 60 minutes. After touch the maximum voltage of 110V, this is maintained for other 60 minutes, while the oxidic layer cotinue to growth. In this period the current sever decreases, finaly under1mA/cm^2.
The electrochemical cell voltage and current evolution for OT sample are presented in the figures 3 si 4 respectively.
An emphasised increase of the voltage can be observed in the figure 3 diagram, after 60 minutes the maximum value of 110V is tuched, superior to 100V, considered critical voltage for titanium anodic oxidation; no glow discharge at the electrodes in this case; both on anode and cathode a gaseous bubles strong give off, oxigen at the anode and hydrogen at the cathode, was observed.

Tab.2 Single anodic layers samples on titanium

Sample Code	Anodic Oxidation				Thermal Traitment		Glow Discharge	Layer Characteristics	
	Electrolyte	$U_{max.}$ [V]	Time [min]	T [°C]	Time [min]	T [°C]	[$U_{min.}$ V]	Aspect	Color
OT	E0+E1	110	120	80	-	-	-	Homo geneous , mat. Gray spot	Dark gray
TF5	E0+E1	115	60	80	-	-	85		
TF7	Eo+E1	112-113	120	80	60	350	-	Gray	Green, dark zones
TF4	E3	120	20	25	90	350	-	Homogeneous, brillant	Dark gray with dark blue shade
TF1	E3	25	20	25	-	-	-	Homogeneous, brillant	Blue
TF3	E3	25	3	25	-	-	-	Homogeneous	Itense blue

Tab.3 Multiple anodic layers samples on titanium

Sample Code	Anodic Oxidation				Thermal Traitment		Glow Discharge	Layer Characteristics	
	Electrolyte	$U_{max.}$ [V]	Time [min]	T [°C]	Time [min]	T [°C]	[$U_{min.}$ V]	Aspect	Color
TO1 $TO2_{id}$	E0+E1 E0+E1	114 112	120 120	80 80	60 60	350 300	-	Homogeneous , mat uniform	Dark gray
TO3 TO4	E0+E1 E2	115 35	120 45	80 80	60 120	110 700	100-110 (all the anode surface)	Uniform Homogeneous Uniform, homogeneous	Dark gray, mat Light gray mat
TO5 $TO6_{id}$	E0+E1 E2	114 35	120 30	80 80	60 120	110 150	-	Homogeneous	Green
TF8	E0+E1 E3 E3	70 25 90	30 20 30	25 25 25	- 60 60	- 350 350	-	Uniform, homogeneous	Dark mauve
TFT2 TFT3	E3 E3	50 100	30 20	25 25	60 60	350 300	-	Homogeneous , uniform Homogeneous uniform	Dark green Light green

The attack current variation in time, for an active surface of 22,4 cm^2, two samples simultaneous processed, is presented in figure 4. The zero moment in the figure 4 is the moment when the 448mA current value is tuched for the first time. 5 minutes intervals were established to correct the cell voltage to rebring the 448mA current value. In the first 5 minutes a severe decreasing of the current take place, as a consequence of the oxidic layer growing at the interface, in the next intervals the current decreasing is smaller, 350mA current reached after 35 minutes. Generaly, in a high temperature electrolyte the ions difuzion through forming oxidic layer is more intense (higher current), in comparison with laboratory temperature anodization processes where a current severe decreasing take place in a short time. Figure 5 present the current variation at the 110V maximum cell voltage, during 75-80 minutes, for the same OT sample. We can observe that in the first 40 minutes the current decreasing is slowly, than the curve slope change suddenly indicating a severe current decreasing, as a consequence of the oxidic layer growing and transformation on the titanium substratum.

Tab.4 Single anodic layers samples on TA6V4 alloy

Sample Code	Anodic Oxidation				Thermal Traitment		Glow Discharge	Layer Characteristics	
	Electrolyte	$U_{max.}$ [V]	Time [min]	T [°C]	Time [min]	T [°C]	[$U_{min.}$ V]	Aspect	Color
AF8	E1	25	5	25	-	-	-	Uniform homogeneous, brillant	Dark blue
AF9	E1	90	5	60	-	-	-	Uniform, homogeneous	Blue, gray and blue shade
AF7	E1	115	15	25	60	350	-	Ununiform spots, mat	Green with dark spots
AF10	E1	60	60	80	30	350	60	Homogeneous, mat, dark blue with mauve	
AF1	E3	75	60	25	-	-	-	Billant	Green shade
AF4	E3	100	25	25	-	-	-	Brillant	Green and yellow shade
AF5	E3	75	20	25	60	350	-	Ununiform, brillant	Dark blue with blue shade
TEG	E4	50const	180	25	-	-	-	Homogeneous brillant	Gold yellow

Tab.5 Duplex anodic layers samples on TA6V4 alloy

Sample Code	Anodic Oxidation				Thermal Traitment		Glow Discharge	Layer Characteristics	
	Electrolyte	$U_{max.}$ [V]	Time [min]	T [°C]	Time [min]	T [°C]	[$U_{min.}$ V]	Aspect	Color
AF6	E1 E1 E2	70 26 1	90 60 60	80 80 80	30 30 60	350 350 700	-	Uniform, homogeneous, mat	Dark gray
AF3	E3 E3	100 25	25 20	25 25	30 30	350 350	-	Uniform, homogeneous, brillant	Light green

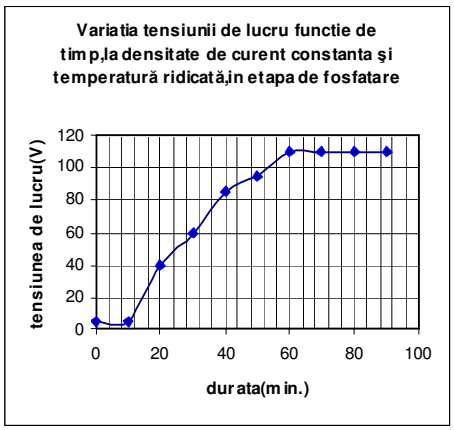


Fig.3 Cell voltage diagram

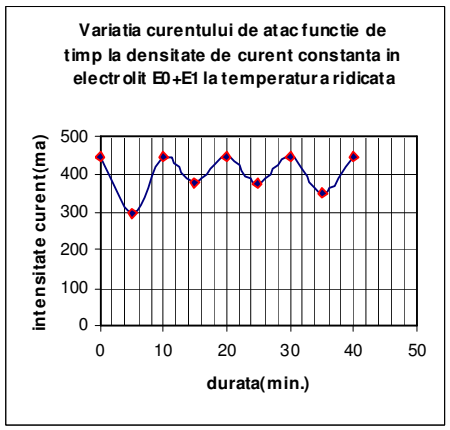


Fig..4 Cell current diagram

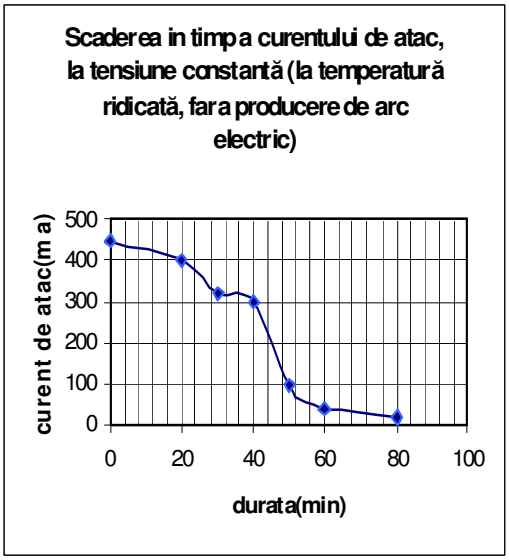


Fig.5 OT sample. Current/time diagram

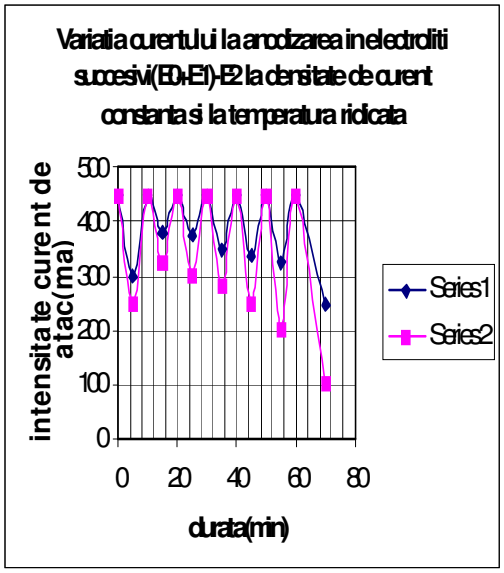


Fig.6 TO5 sample. Current in two successive attack period: series 1- E0+E1 electrolyte, series 2- E2 electrolyte

In the case of titanium samples oxidation in succesive electrolytes a down translation of the current curve can be observed, as a result of titanium oxide layer formation and difusion decreasing at the interface, figure 6. In the figure 7

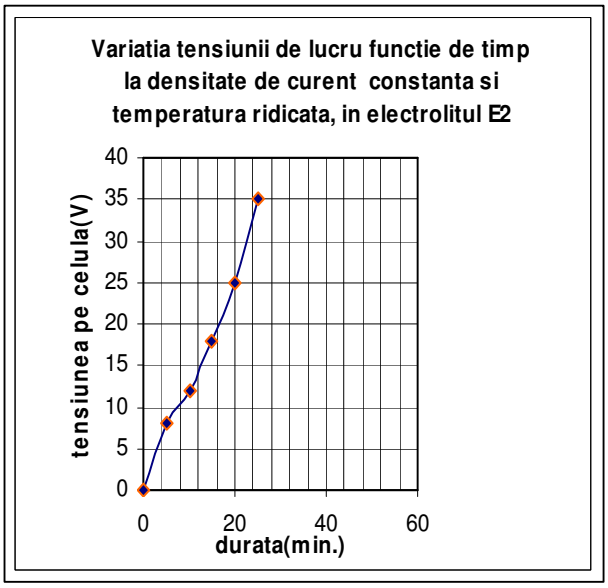


Fig.7 TO5 sample. Attack voltage/time diagram

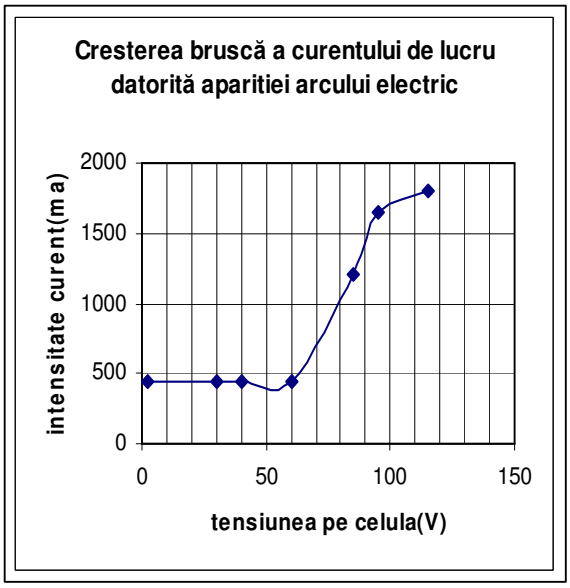
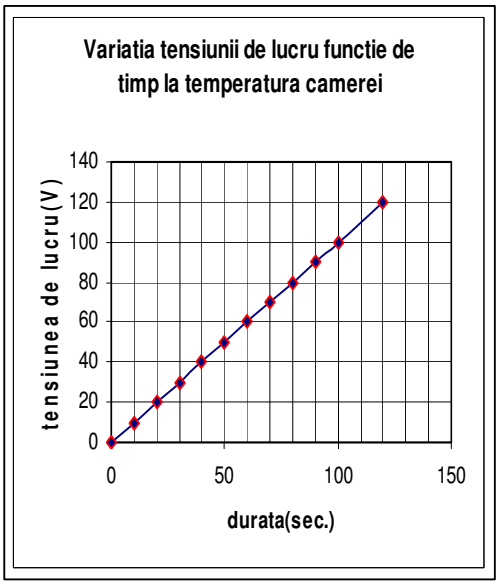


Fig.8 TO3 sample. Cell voltage during glow discharge

Is presented the cell voltage variation during attack period into E2 electrolyte, in the case of TO5 sample. The increase of the cell voltage in the anodic oxidation stage 2 is faster than in the stage 1 because of the ions difuzion decreasing through the more compact oxid layer containing phosphorus compounds.

The cell voltage transformation during glow discharge on TO3 titanium sample is notted in the figure 8. In this case the glow discharge appeared at 60V, much under the critical titanium anodic oxidation voltage; an important current increasing appeare too, as a consequence of a local oxidic layer destruction.

In the figure 9 the cell voltage variation in the first 150 seconds of titanium, sample TF1, anodic oxidation at the laboratory temperature, is presented; at 25V an important electrode processes take place, with a great emission of gaseous, after a minute the current drastic decrease indicating the oxidic layer growth at the interface.



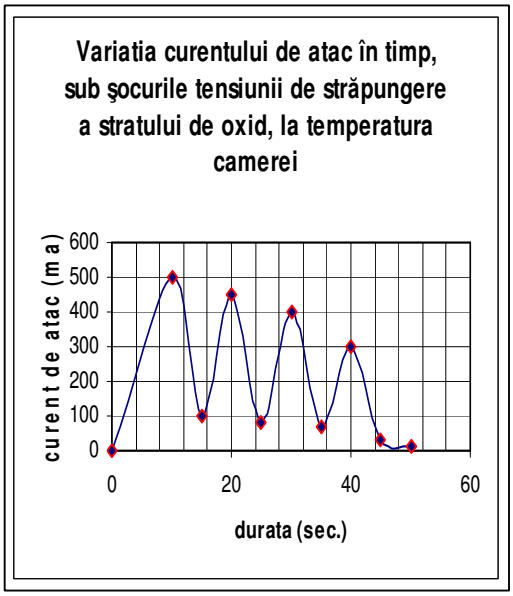


Fig.9 TF1 sample. The cell voltage during anodic oxidation beginning, 25°C

Fig.10 The cell attack current evolution, 25°C

Into an another case, figure 10, an anodic oxidation at the laboratory temperature of 25°C was conducted by maintan a constant cell current of 500 mA. Initialy, a severe current increasing can be observed durind cell voltage increasing. The current can not be mentained constant, this decrease in several seconds. By an another more increased voltage the current can not touch the previous maxim value, the maximum attack current values are situated on a descendent curve, after 50 sec. tending to 0. The processed samples were characterized electrochemicaly by cyclic voltametry in Ringer solution and microstructuraly by scanning electron microscopy, transmision electron microscopy (TEM) and dispersive energy X-ray microanalisis (EDAX).

Especialy the cyclic voltametry in the range of -1000÷4000mVs.c.e. revealed the benefic influence of the oxidic layers on the electrochemical stability of the interface titanium, TA6V4 alloy – Ringer solution. Biger passivity currents were measured in the case of the samples oxidized in hot electrolytes or in two or more succesive stages. The simple, at 25°C, anodic oxidation has generated compact, uniform and adherent layers. Some of these samples, AF4, AF5 and TEG, present, under polarisation in Ringer solution, in the range of -1000÷4000mVs.c.e., and

37°C, an extreme electrochemical inertia, argues by a typical ohmic behaviour.

4. CONCLUSIONS

During the experiments titanium oxides layers having the role of diffusion barrier and anticorosive protection, containing bioactive, phosphorus compounds that can increase the implants biocompatibility in the human body and the nucleation and grows of bone tissue has been obtained.

Generaly, high temperature oxidized samples has a less performant behaviour under electrochemical polarisation, as a result of the high porosity of the oxidic layers. Not even the succesive anodic oxidations and intermediary thermal traitments has not increased the anticorrosive behaviour of these samples. Contrary, the simple anodic oxidation at 25°C generated compact, uniform and adherent oxidic layers with excelent anticorrosive performance in Ringer solution, under electrochemical polarisation. The samples AF4, AF5 and TEG are characterised by an ohmic behaviour, under polarisation the relation current / potential being linear. The layers morpholoy is too favourable to growth and anchoring the human tisue on the implant.

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