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Electrochemical evaluation of the stability of ceramic nanostructured titanium oxide layers in Ringer solution

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The paper presents the results of the stability evaluation by electrochemical polarization of experimental samples in a synthetic biological electrolyte, the Ringer solution. The cyclic voltammetry and the transmission electronic microscopy investigations show that the anodically oxidized and thermally untreated samples posses a thin, nanostructured, stable oxidic layer, with an ohmic behavior in the case of TA6V4 alloy. Titanium shows a typical behavior of electrochemically passivating metal, by polarization being evidenced a critical passivation potential with a corresponding critical current and a passivity domain characterized by a reduced passivity current. The electrochemical reactivity of the samples is unfavorably raised by thermal processing at 350 and 600^{o}C in air, when the presence of detrimental anatase in the layers is evidenced by X-ray diffraction analysis. The same analysis shows that the favorable rutille appears in the the oxidic layer at 600^{o}C, but it predominates or even becomes exclusive after the thermal treatment in air at 770^{o}C. The thermochemical treatment at this temperature and the resulted crystalline nanostructures ensure an increase of the interface stability and an improvement of the ohmic behavior and biocompatibility characteristics for the oxidic layers achieved by following an anodic oxidation formula, both on titanium and its alloy.

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Keywords: Biomaterials, Titanium, Anodization, Cyclic voltammetry, Anatase, Rutile, X-Ray Diffractometry

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1. Introduction

Although titanium and its alloys are extensively used in medicine since 1960, due to a high strength-to-weight ratio and high corrosion resistance in the environment of the human body, the achievement of new titanium surgical implants and biomedical prosthetic devices and new better surface processing formulas is still topical [1-6]. The superior bioactivity of an interface, which constitutes a key characteristic for osseointegration, is accomplished by a reduced ionic transfer; it can be improved by special processing that stabilizes the interface of the implant/human body biological environment. Such coatings with nanostructured ceramic layers (composed of titanium oxides, anatase and rutille) can be achieved by anodic oxidations (in one or several stages, in aqueous, acidic or alkaline electrolytes) and subsequent thermal treatments. The paper contends the utility and sensitivity of these techniques in optimizing the technological parameters of anodic oxidation and thermochemical treatment of titanium and its alloys [7].

2. Experimental

Electrochemical investigations on oxidic layers were performed with a VOLTALAB 40 research equipment, by cyclic voltammetry (100mV/s) in a large range, from -1000 to +4000mVs.c.e., in three complete cycles, in Ringer solution, at 25^{o}C, in a three-electrode cell, the reference electrode is the saturated calomel electrode (s.c.e.). Each time the electrochemical polarization was applied to a circular surface with an area of only 0.2cm^2.

The titanium samples (grade 1: N=0,0069; C=0,040; Al<0,01; V<0,01; Fe=0,093; Si≅0,005; Ni<0,005; Cr<0,005; Co<0,005; Cu<0,001; Pb<0,005, weight percentages) and of TA6V4 alloy (N=0,0051; C=0,030; Al=5,53; V=3,90; Fe=0,13; Si=0,05-0,1; Ni=0,01-0,05; Cr=0,005-0,01; Co<0,005; Cu≅0,001; Pb<0,005, weight percentages), of 28x20x0,5mm, were prepared by successive polishing with abrazive paper 150 and 400 granulation respectively and degreasing in a solution of 50g/l NaOH at the lab temperature. After rinsing with warm water, the samples were subjected to an electrochemical polishing in an acidic solution containing H_2SO_4 95%, HF 6% and H_2O in 16:3:1 volume ratio and to an acid etching in an aqueous solution of 1% HF and 15% HNO_3 at 40^{0}C, for 10-60 s. These operations ensure the achievement of an interface relief which is favourable to medical applications, Fig. 1.

Subsequently, the anodic oxidation was performed in three different formulas, AF4, AF5 and TEG, in one of the electrolytes E3 (phosphoric acid 0,5N and sodium bicarbonate 10%, weight percentages) and E4 (phosphoric acid 1N and citric acid 20g/l in 1:1 ratio). After the anodic oxidation, some samples have been thermally treated in air, in an electric furnace SM-3B KANTHAL SUPER, at different temperatures: 350^{o}C, 600^{o}C and 770^{o}C. Samples codification and the applied parameters in each case are presented in the tables 1 and 2. The oxidic layers were also investigated by scanning electron microscopy (HITACHI S2600N microscope), high resolution transmission electron microscopy (PHILIPS CM120ST HRTEM) and X-Ray Diffractometry (SCHIMADZU XRD 6000 diffractometer).

Table 1 Samples with anodic layers achieved on Titanium

Samples code	Anodic oxidation				Thermal treatment	
	Electrolyte	$U_{max.}$ [V]	Time [min]	T [^{o}C]	Time [min]	T [^{o}C]
TAF4	E3	100	25	25	-	-
TAF43	E3	100	25	25	60	350
TAF46	E3	100	25	25	60	600
TAF47	E3	100	25	25	60	770
TAF5	E3	75	20	25	-	-
TAF53	E3	75	20	25	60	350
TAF56	E3	75	20	25	60	600
TAF57	E3	75	20	25	60	770
TTEG	E4	50	180	25	-	-
TTEG3	E4	50	180	25	60	350
TTEG6	E4	50	180	25	60	600
TTEG7	E4	50	180	25	60	770

Table 2. Samples with anodic layers achieved on the TA6V4 Titanium alloy

Samples code	Anodic oxidation				Thermal treatment	
	Electrolyte	$U_{max.}$ [V]	Time [min]	T [^{o}C]	Time [min]	T [^{o}C]
AF4	E3	100	25	25	-	-
AF43	E3	100	25	25	60	350
AF46	E3	100	25	25	60	600
AF47	E3	100	25	25	60	770
AF5	E3	75	20	25	-	-
AF53	E3	75	20	25	60	350
AF56	E3	75	20	25	60	600
AF57	E3	75	20	25	60	770
TEG	E4	50	180	25	-	-
TEG3	E4	50	180	25	60	350
TEG61 TEG62	E4	50	180	25	60	600
TEG7	E4	50	180	25	60	770

Structural investigations have evidenced two characteristical aspects, the presence of the pores in few cases, figure 2, and the nanostructural character of the experimental layers, figure 3.

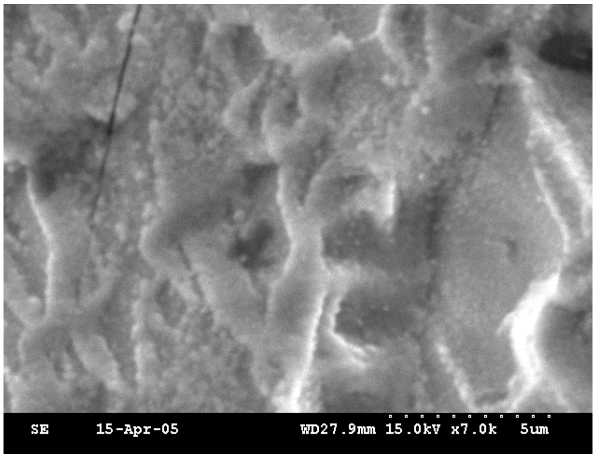

Fig.1 TEG6 sample, flakiness aspect of the surface (x7000)

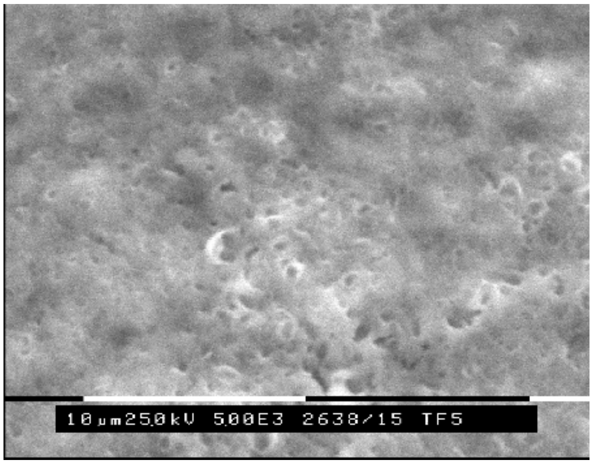

Fig. 2. TAF5 sample, oxidic layer with a medium pore density (x5000)

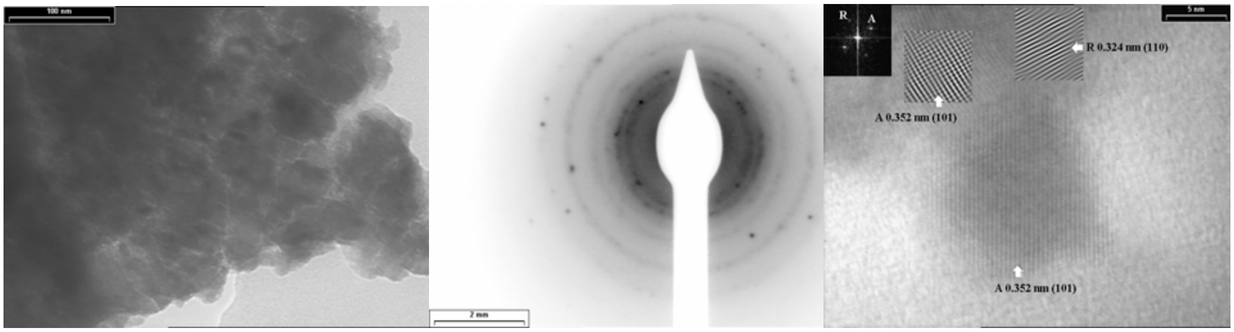

Fig.3 TTEG6 sample, a-transmission electron microscopy bright field image (TEMBF), b-electron diffraction image (SAED) associated to the a micro area and c-high resolution transmission electron microscopy (HRTEM) images with a Fast Fourier Transform and Inverse Fast Fourier Transform

3. Results and discussion

From electrochemical point of view, it is pursued the spontaneous passivation (alternatively, the critical passivation current minimization i_{cp}, at the electrochemical passivation critical potential E_{cp}) and ohmic behaviour improvement, the increase of the mixed corrosion potential E_{MC} and the minimising of the passivity current i_p in the environments of interest, against unprocessed titanium and its TA6V4 alloy. The electrochemical analysis is a qualitative one, focusing on the general behavior of the samples subjected to polarization, during polarization cycles 1 and 3.

The Figs. 4 and 5 present the comparative behavior of titanium and TA6V4 alloy, anodically oxidized in the formulas AF4 and TEG, thermally untreated, under electrochemical polarisation in the Ringer solution at 25°C. The thermally unprocessed oxidic layers show different electrochemical properties by polarisation. All titanium samples suffer electrochemical passivations in a single stage, at electrode potentials above -500mVs.c.e. and it is defined a passivity domain with a reduced passivity current, but the electrode process is amplified in the superior polarization cycles when, probably due to the presence of porosity; the TA6V4 alloy samples passivate spontaneously and the passivity state is more pronounced as a consequence of successive anodic polarizations; in these cases, the reduced hysteresis of the voltamograms and the almost linear potential – current dependence indicates a pronounced electrochemical inertness of the surface, a reduced electrical conductibility and an ohmic type behavior of the oxidic layers grown on TA6V4 alloy. All oxidative processes recorded in the -1000÷4000mVs.c.e. domain on the thermally untreated experimental samples are irreversible processes, since the cathodic branches of the voltamograms are not marked by maxima.

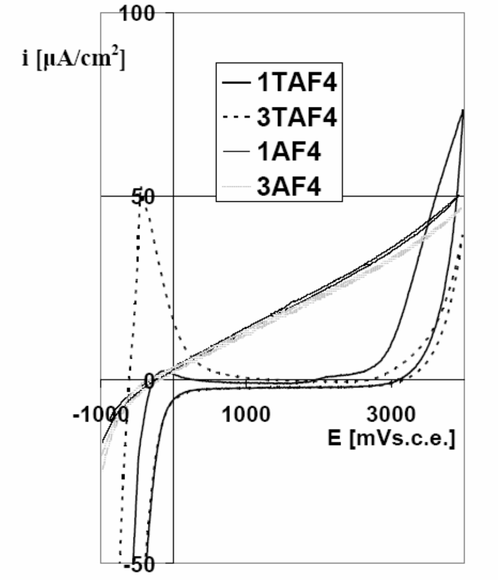

Fig. 4. Cyclic voltamograms obtained in Ringer solution, at 25°C, polarization rate 100 mV/s

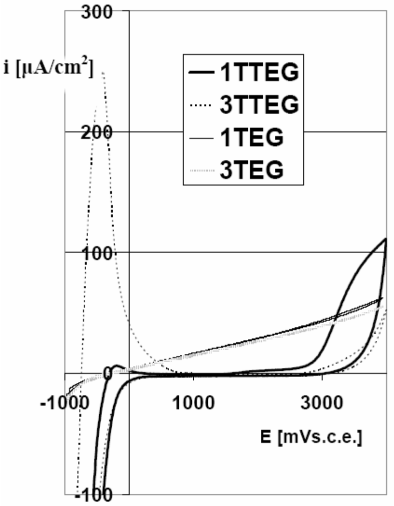

Fig. 5. Cyclic voltamograms obtained in Ringer solution, at 25°C, polarization rate 100 mV/s

The X – ray diffraction analyses performed on these samples have evidenced the presence of rutille on the TA6V4 alloy samples, oxidized in any of the formulas AF4, AF5 or TEG; on the Titanium samples, the same analysis has identified only hexagonal Mg type αTi, obviously from the metal base, the formed oxidic layers are probably very weakly crystallized or they are too thin, Fig.s 6 and 7.

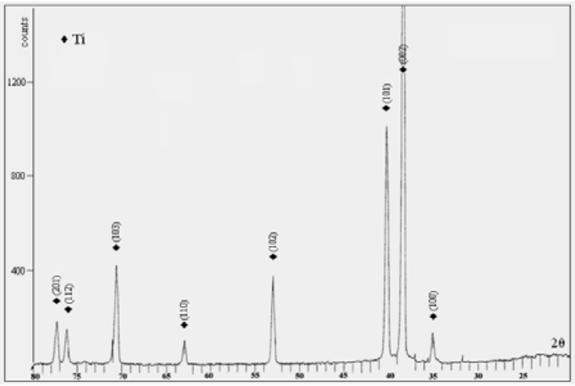

Fig. 6. T-TEG sample. X-ray diffractogram

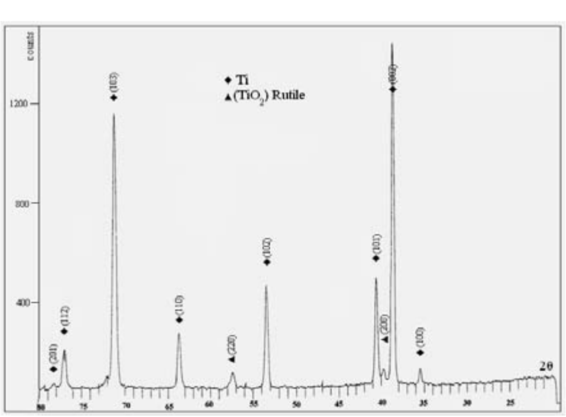

Fig.7 TEG sample. X-ray diffractogram.

The thermal treatment of the oxidic layers substantially changes their electrochemical behavior. In the figures 8÷11 there are presented a few voltamograms, cycle 1, that stand for this assessment and underline the differences in electrochemical behavior between the layers achieved on different supports or by different technological procedures.

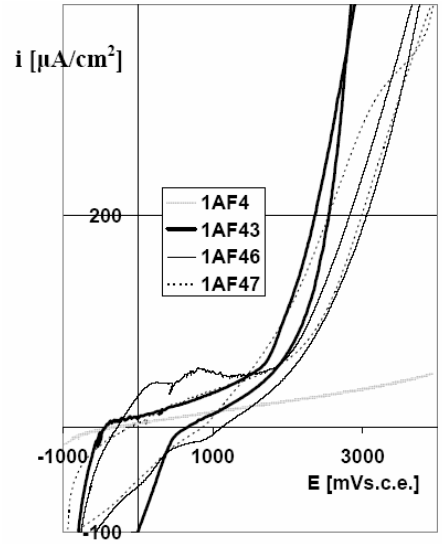

Fig. 8. Cyclic voltamograms obtained in Ringer solution, at 25°C, polarization rate 100 mV/s.

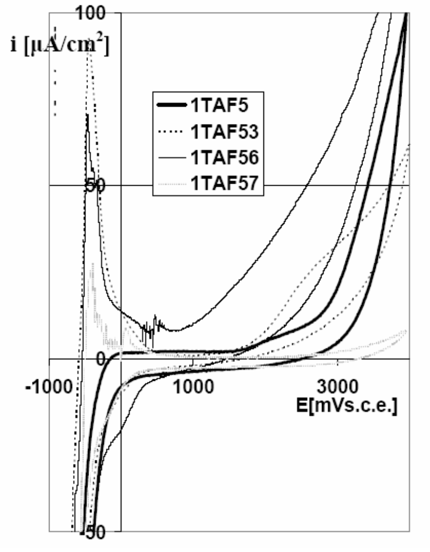

Fig. 9. Cyclic voltamograms obtained in Ringer solution, at 25°C, polarization rate 100 mV/s.

Generally, the thermal processing of the samples at 350 and 600°C is detrimental for the electrochemical properties of the oxidized samples. The negative aspects recorded in the case of titanium samples are the increase of the critical passivation current, of the passivity current and the appearance of an oxidative process (that differs from water oxidation) at more noble potentials than 2500mVs.c.e. In the case of the TTEG3 sample, the electrochemical passivation process takes place in two stages, at approx. –550 and –450mVs.c.e., respectively, while the oxidative process from transpassivity (different from the water oxidation) has a reversible character, figure 11. In the case of the TA6V4 alloy samples, the results are different. If the thermal processing at 350°C intensifies and diversifies the oxidative processes at the interface, especially in the transpassive domain, the thermally treated samples at 600°C suffer a two-stage electrochemical passivation, at least one of these two possessing a reversible character. The passivity currents specific to the samples thermally treated at 350 and 600°C are higher than those ecorded for the untreated samples, for which there were lso obtained values bellow 2,5μA/cm^2.

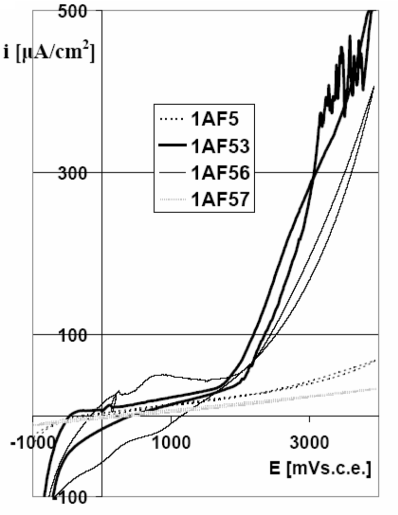

Fig. 10. Cyclic voltamograms obtained in Ringer solution, at 25°C, polarization rate 100 mV/s

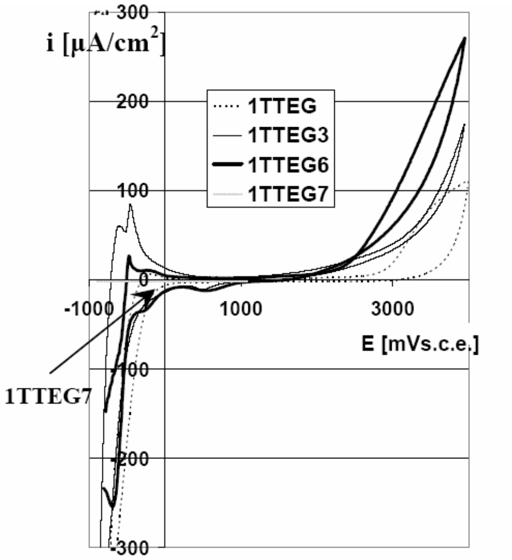

Fig. 10. Cyclic voltamograms obtained in Ringer solution, at 25°C, polarization rate 100 mV/s

The electrochemical analysis matches well with the X-ray diffraction analysis. So, the high electrochemical reactivity of the samples thermally treated at 350°C is always correlated to the presence of anatase in the layer (TAF43, TAF53 and TTEG3 samples), figure 12, or to the presence of the anatase accompanied by a variable, relatively small quantity of rutille (the titanium alloy samples AF43 and AF53), figure 13; the TEG3 sample, also thermally treated at 350°C, still contains only rutille, as in the thermally untreated case. The presence of anatase (and rutille) is generalized in the experimental oxidic layers obtained after the thermal treatment at 600°C and its presence has the tendency to increase, even on the extent of the rutille content diminishing, in the case of the AF46 and TEG6 samples, figures 14 and 15, along with the manifestation of the two-stage electrochemical passivation.

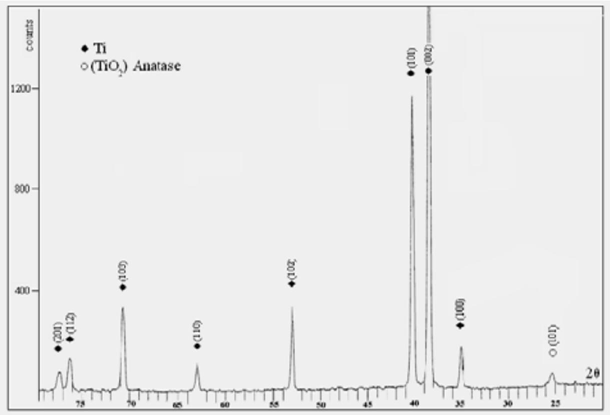

Fig.12. TTEG3 sample. X-ray diffractogram

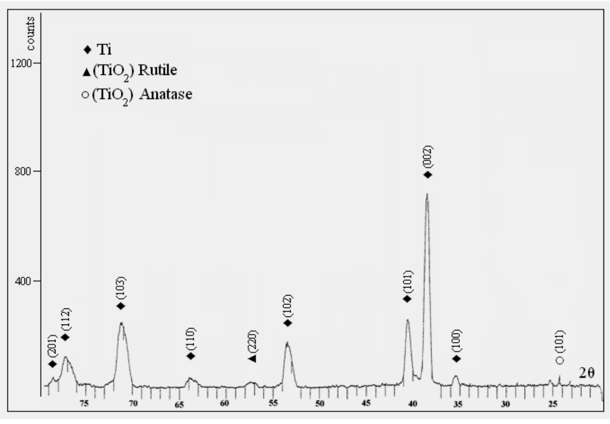

Fig.13 AF53 sample. X-ray diffractogram

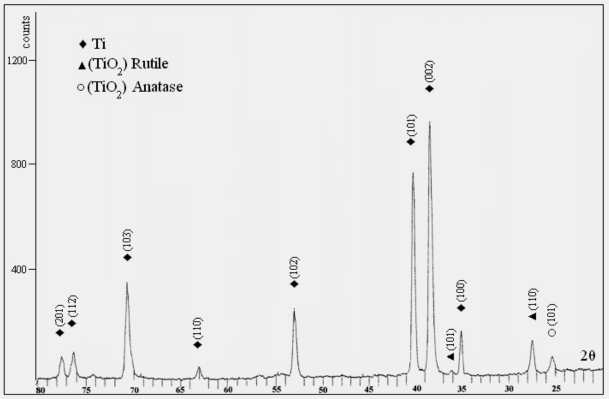

Fig.14 TTEG6 sample. X-ray diffractogram

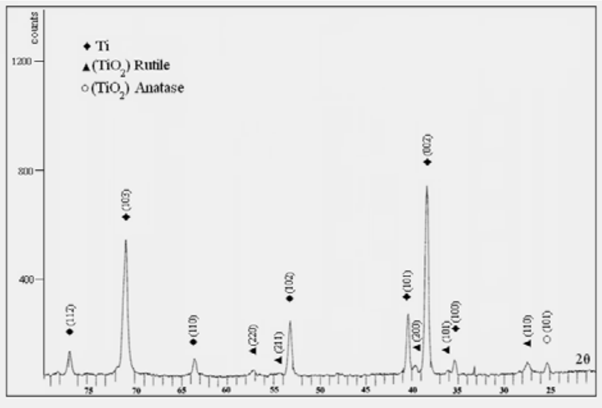

Fig.15 TEG6 sample. X-ray diffractogram

The samples thermally treated at 770°C show superior electrochemical characteristics. The passivation critical currents recorded for the TAF47 and TAF57 titanium samples have minimum values, the passivity currents also, figure 10, while for the electrochemical polarization of TTEG7 sample, no interface oxidation process in the domain -1000÷4000mVs.c.e. wasn't identified, figure 11, situation which also reproduces in the third polarization cycle, figure 16, this aspect emphasizing the dielectrical and compact character of the oxidic layer. For all alloy samples, all aspects that describe the ohmic, favorable behavior mentioned above are emphasized by thermal treatment at 770°C, especially in the case of TEG7 samples, figure 17, and AF57, figure 10. The TEG anodic oxidation formula in the E4 electrolyte confers the best electrochemical properties, both on titanium and on the TA6V4 alloy.

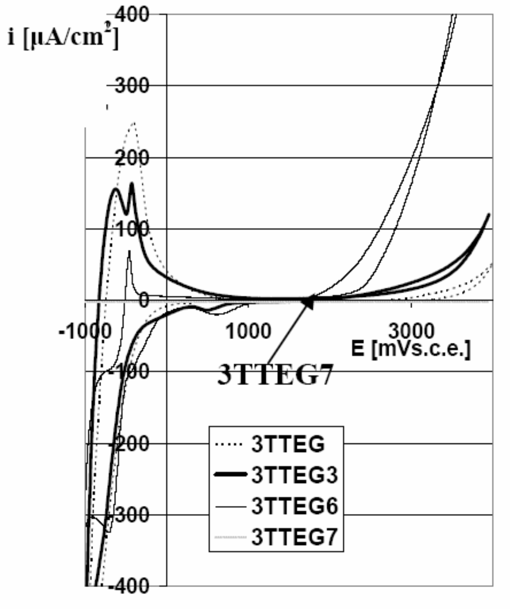

Fig. 16. Cyclic voltamograms obtained in Ringer solution, at 25°C, polarization rate 100 mV/s

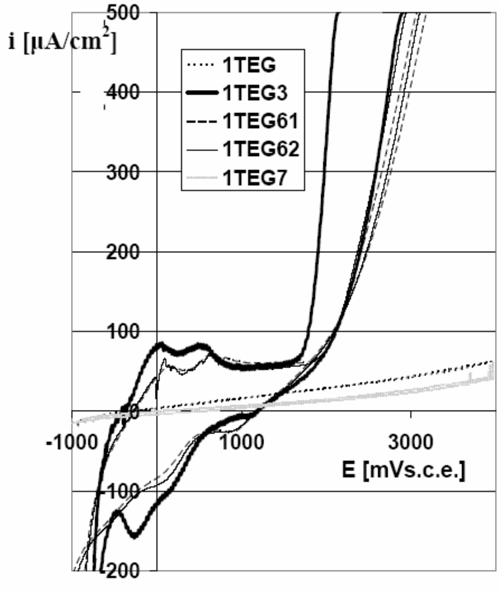

Fig. 17. Cyclic voltamograms obtained in Ringer solution, at 25°C, polarization rate 100 mV/s

The superior electrochemical stability properties recorded for the samples thermally treated at 770°C are accompanied by a radical increase of the rutille proportion in the layer, while the anatase quantity is a lot diminished; only in a single case, at the TTEG7 sample, the anatase is entirely absent, figures 18 and 19. This sample shows the most performing electrochemical behavior in the working conditions, the passivity current being practically zero, as already shown.

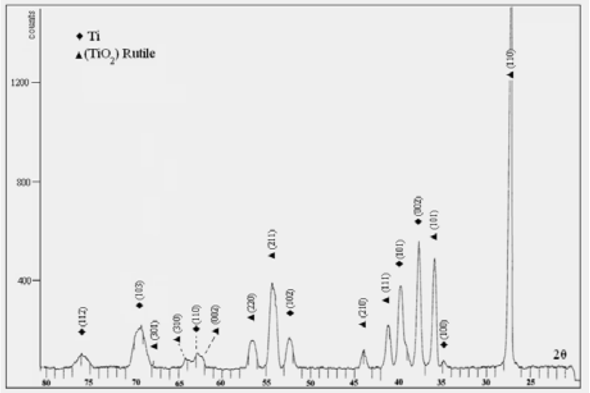

Fig.18 TTEG7 sample. X-ray diffractogram

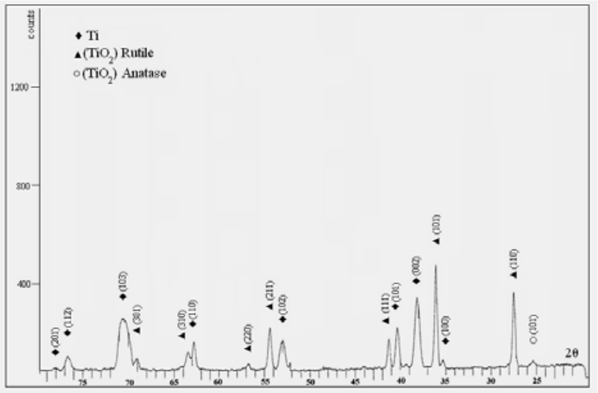

Fig.19 TEG7 sample. X-ray diffractogram

4. Conclusions

The cyclic voltammetry and the physical investigations show that the anodically oxidized samples by following one of the AF4, AF5 or TEG formulas and thermally untreated TA6V4 alloy samples present a thin, nanostructured, stable oxidic layer, with a low rutille content and an ohmic behavior; in the same conditions, titanium shows a typical behavior of electrochemically passivable metal, since by polarization there are evidenced a critical passivation potential and a corresponding critical current, a passivity domain characterized by a reduced passivity current, while the X-ray diffraction analysis does not evidence the presence of rutille.

The electrochemical reactivity of the samples is unfavorably increased (the appearance or intensifying of an electrochemical passivation process) by thermal processing at 350 and 600°C in air, when in the layers it is evidenced the presence of detrimental anatase; in the case of the TA6V4 alloy and of the oxidation formulas AF4 and TEG, the anatase growth at 600°C takes place along with the decrease of the rutille content in the layer. The X-ray diffraction analysis shows that the favorable rutille also appears in the oxidic layer of titanium at 600°C, but it becomes predominant or even exclusive on both supports after the thermal treatment in air, at 770°C. The thermochemical treatment of the samples anodically oxidized at this temperature by following the TEG process and the achieved crystalline nanostructures ensure a maximization of the electrochemical stability of the interface and of its biocompatibility by an increase of the ohmic type behavior of the oxidic layers achieved both on titanium and its alloys.

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