

# Electrochemical characterization of titanium biomaterials using the Mini-cell System

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The aim of this work was the electrochemical characterization of modified Titanium surfaces for implants with help of the Mini-cell System (MCS). The materials tested were Cp titanium specimens, designed for animal experiments, with 8 mm length and 4 mm diameter, with different surface conditions: one had machined surface, the other was blasted with a bioceramic (GB14+AP40) and the third was blasted with aluminum oxide. Roughness measurements were also made on the materials. The results showed that MCS has sensitivity to detect differences in the electrochemical point of view due to surface modifications. The differences between the materials are small, but systematic. The aluminum oxide blasted material had the highest current density, however due to the roughness increase. The material with bioceramics blasting had the highest chemical activity. The higher activity of the bioceramics treated surface was explained as (i) an interaction between the modified surface and electrolyte; or (ii) the calcium phosphate dissolves in the electrolyte and leaves the surface of the metal, and then the free metal reacts immediately to form new titanium oxide. These results may help to explain the biological effects observed by modified surfaces, in particular with bioceramics. © 2006 Springer Science + Business Media, Inc.

## 1. Introduction

Titanium has been used since long time as an implant material, mainly because of its good biocompatibility with the bone, but also for its mechanical strength and high resistance to corrosion, being the last one a consequence of the presence of a thin surface layer of titanium oxide [1–5].

The biocompatibility of titanium has been associated with this oxide layer, but now it is known that not only the chemical properties of the implant surface affects the cell and tissues response, but that it also depends on the surface roughness [1, 6].

Corrosion behavior can be studied successfully using electrochemical techniques, as they are fast, convenient and sensitive even in measurements involving low corrosion rates [2]. Due to the common use of coatings in the increase of biological activity of titanium materials [1, 7–31], we wanted therefore to study the electrochemical properties of coated titanium materials using an electrochemical technique, with the setup Mini-cell System [32].

The Mini-cell System (MCS) is based on a transportable mini-cell and it performs non-destructive electrochemical measurements on solid samples, without additional preparation of the specimens, therefore it can analyze any metallic biomaterial as applied in the patients. The reference electrode is inside a tube which contains a saturated calomel electrode and the counter electrode (a platinum wire); the sample is the working electrode. The contact between electrolyte and material is made by a tip and therefore the measurement area is very small (0.008 cm<sup>2</sup>). The whole system is connected to a potentiostat and a computer [32, 33].

From the graphic results obtained and using the software *Corrview* for Windows, several electrochemical parameters are calculated:  $E_0$  is the *corrosion potential*, the potential where the total oxidation rate is equal to the total reduction rate, and by definition the current at this point is zero;  $i_0$  is called *exchange current density*, this value is determined by indirect methods, such as by the Tafel

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TABLE I Results obtained for the three titanium materials (Mean  $\pm$  SEM)

Material	Surface type	Ra ( $\mu\text{m}$ )	$C_{\text{rate}}$ (mmPY)	Rp ( $\Omega$ )	$i_0$ (A/cm <sup>2</sup> )	$E_0$ vs. NHE (V)
1	Machined surface	0.340 $\pm$ 0.090	0.062 $\pm$ 0.003	9.33E5 $\pm$ 4.10E4	3.55E-6 $\pm$ 1.77E-7	-0.678 $\pm$ 0.033
2	Blasted with bioceramics	0.420 $\pm$ 0.055	0.072 $\pm$ 0.006	8.28E5 $\pm$ 6.70E4	4.13E-6 $\pm$ 3.45E-7	-0.844 $\pm$ 0.036
3	Blasted with aluminum oxide	0.994 $\pm$ 0.056	0.098 $\pm$ 0.011	6.42E5 $\pm$ 8.22E4	5.62E-6 $\pm$ 6.39E-7	-0.606 $\pm$ 0.045

equation. Also can be calculated the *corrosion rate* ( $C_{\text{rate}}$ ) through Faraday's law and represents the loss of mass of material in function of time and per unit area. Moreover, by the Ohm's law is calculated the *polarization resistance*  $R_p$ , that is the total resistance in the corrosions circuit.

The aim of this work was the determination of Mini-cell System amplitude in the detection of variations in the electrochemical properties caused by modification of surface roughness and composition.

## 2. Experimental

Cp titanium specimens, grad 2, (Semados), designed for animal experiments, with 8 mm length and 4 mm diameter, with different surface treatments were studied: material 1—machined surface, material 2—bioceramic blasted (GB14+AP 40) and material 3—aluminum oxide blasted [34].

The electrochemical measurements were performed using the MCS connected to a potentiostat (EI 1286, Schlumberger) and to a computer, using the program *Corrware* for Windows. The electrolyte was sodium chloride solution 1% with a constant pH = 6  $\pm$  1, the potential range applied was between -1,75 V and +1,45 V (vs.

NHE), and the scan rate was 10 mV/s; additionally measurements depending on the pH were performed in 1% NaCl between pH = 1 and pH = 12 with a step width of 1.

The study was complemented with roughness measurements, made using a profilometer (Perthen) with a needle with sharpness of 10  $\mu\text{m}$  and a resolution of 25 mm length per 750  $\mu\text{m}$  height.

## 3. Results and discussion

Figure 1 displays the selected anodic polarization curves in NaCl 1% of the three materials, from which were calculated the electrochemical parameters. The average of some of the parameters is presented in the Table I, as well as the average roughness (Ra).

It was possible to observe that the curves have a similar shape, the one of pure titanium, however differences exist: there is a direct relation between the roughness increase and the increase of current density, particularly visible in the curves at  $E = 0$  V (vs. NHE). Material 3 had the higher roughness and the higher exchange current density. Besides it is observable a change in the shape in the  $I$  vs.  $E$  curve and the distinct corrosion potential values of the three materials, which showed that the three materials

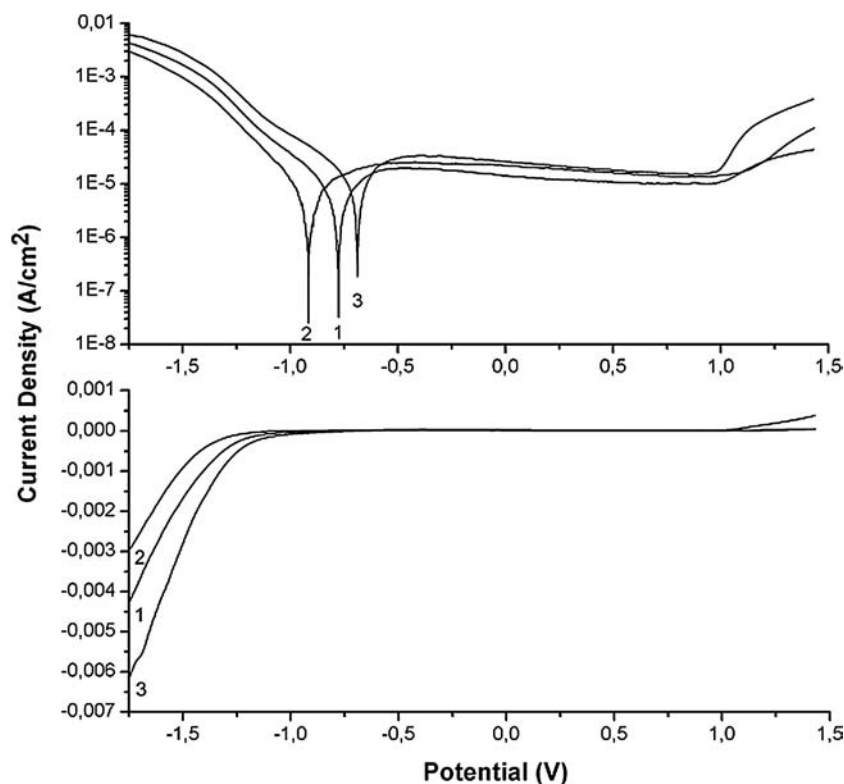


Figure 1 Selected  $i$  vs.  $E$  curves for the three materials in NaCl 1%.

have different surface composition. For example, material 2 had a more cathodic  $E_0$  due to the higher interaction of the metallic surface with the electrolyte caused possibly by the calcium and phosphate ions whereas material 3 had a more anodic potential due to the lower activity caused by the presence of aluminum oxide on the surface.

In the numeric values it is also possible to observe clear differences between the materials: material 1 had the lowest corrosion rate, the highest polarization resistance and the lowest exchange current density, which means that in the electrochemical point of view, is the most stable material. Material 2 had the more negative corrosion potential, which can be associated with a higher chemical activity. Material 3 had the less negative potential, but higher corrosion rate and exchange current density.

Figure 2 shows that the increase  $i_0$  values for material 3 is a consequence of the higher roughness because using a line to connect the roughness of materials 1 and 3 and putting the line with the same slope in the upper part of the graphic, it is possible to see that the increase of current density of material 3 follows exactly the increase of roughness in relation to the first material. Moreover, this increase cannot be from increase of chemical activity because, as was said before, the shift of corrosion potential in the anodic direction means that the material has a lower activity.

Observing the Fig. 3 where is plotted the current density in relation to the average roughness, it is to see that material 2 has a much higher current density than the one attributed only to the increase of roughness, as in this case

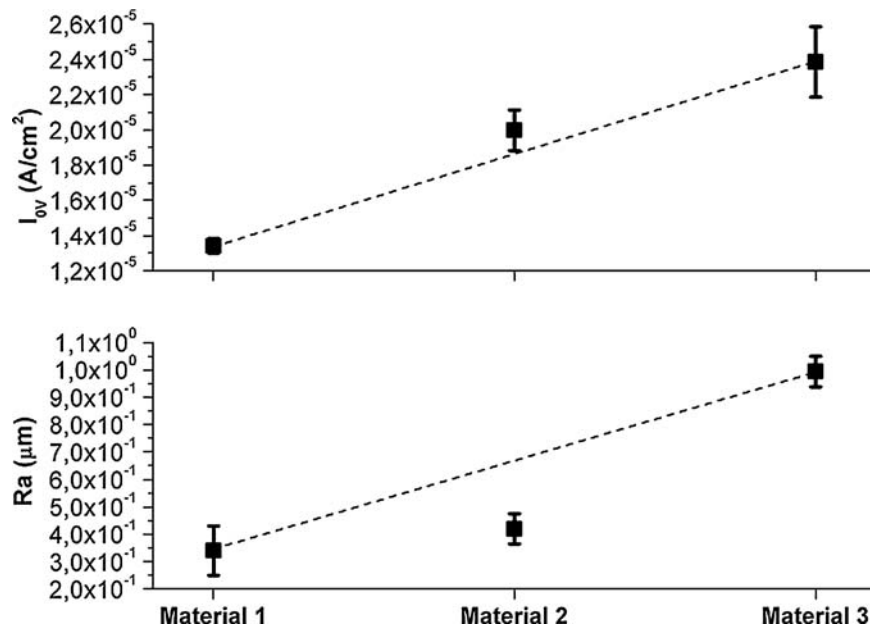


Figure 2 Comparison between the materials in terms of exchange current density and average roughness.

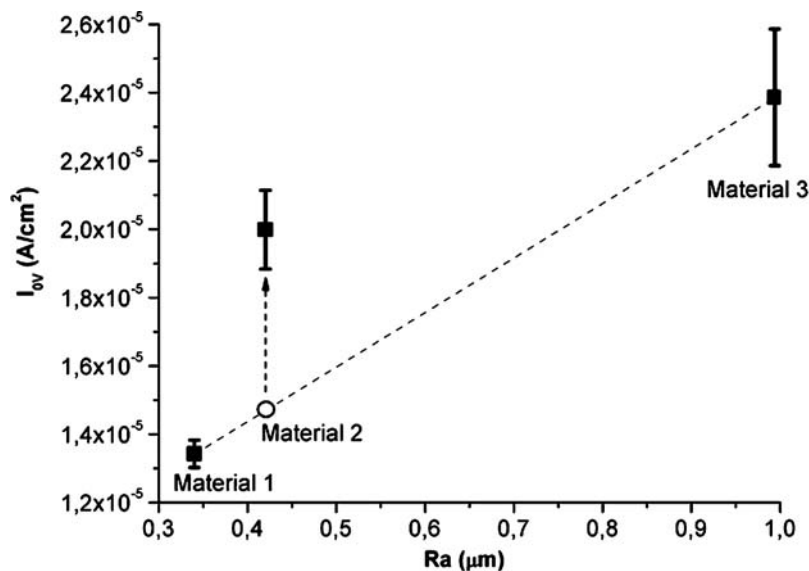


Figure 3 Exchange current density as function of average roughness for the studied materials.

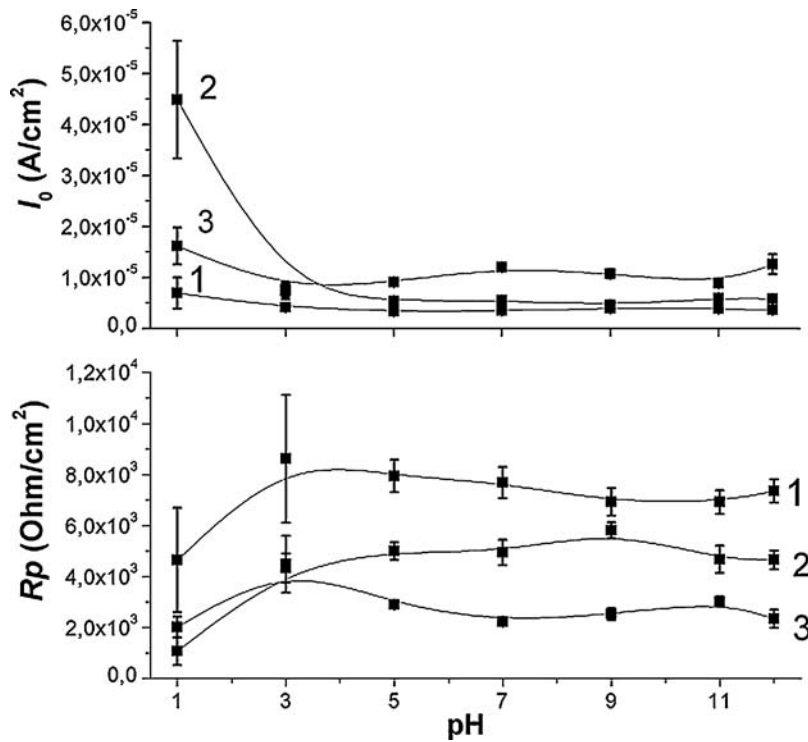


Figure 4 Comparison of corrosion potential and  $R_p$  between the materials at different pH values.

the current density of this material would be near the line. This means, together with the more cathodic potential, that the bioceramics blasting causes an increase of the materials activity.

Figure 4 shows the variation of polarization resistance and corrosion potential with the pH, for the three materials. It could be observed that the highest variation of activity occurred between pH 1 and 3, being this effect stronger to the material 2. However, in the intermediate pH values, this material seemed to be less affected by the pH changes than material 3. Material 1 was the less affected material by the pH, which shows that without modifications, the surface is more electrochemically stable or inactive.

#### 4. Conclusions

The results showed that MCS has sensitivity to detect differences in the electrochemical point of view due to surface modifications. The differences between the materials are small, but systematic. This method allows not only comparing between materials, but also allows the characterization of the material itself.

The key element of this experimental setup is clearly its sensitivity as it uses a small measurement area ( $0.0083 \text{ cm}^2$ ), and therefore it can give a concrete idea of the real electrochemical behavior of materials, even those with complex surface shape.

Titanium modified with bioceramics is chemically more active than pure titanium, whereas the material modified with aluminum oxide is less active, this because the aluminum oxide particles that adhere on the surface during

the blasting procedure are more stable than the calcium phosphate.

The higher activity of the bioceramics treated surface can be explained by: (i) there is an interaction between the modified surface and electrolyte; or (ii) the calcium phosphate dissolves in the electrolyte and leaves the surface of the metal, and then the free metal reacts immediately to form new titanium oxide.

These results can help to understand the effect of modified titanium materials when applied in the body, however, more studies involving surface modifications are essential, especially to explain the bioceramics modified behavior and the consequences to the stability of this type of implant materials.

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