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A STUDY OF PITTING CORROSION ON Al_2O_3-COATED STAINLESS STEEL USED IN BIOMATERIALS

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Abstract

Stainless steel has been commonly used as a biomaterial, particulary for orthopeadic applications. Recent developments have introduced not only other metallic alloys but also ceramic coated stainless steel to improve wear and corrosion resistance. In this work results are presented on the study of pitting corrosion of Al_2O_3-coated and uncoated stainless steel. A significant decrease in the passivation current was found for the coated samples.

Introduction

All materials used as substitutes of portions of bones and joints must satisfy a number of mechanical, chemical and biological requirements. A wide variety of metallic, polymeric and ceramic materials has been used in biomaterials, as attempts to satisfy all these requirements. It is however well known that most metals corrode when present in physiological environments, and those showing better corrosion resistance, like titanium, suffer from low wear resistance. On the other hand, most ceramics don't show enough toughness. An efficient way to conciliate so many different desired properties is by using ceramic coated metals (1,2).

Al_2O_3-coated AISI 316L stainless steel may be considered as an interesting candidate, as it associates a highly tenacious metallic core with a surface coated layer showing excellent corrosion and wear resistance. Also, Al_2O_3 is reputed as a highly biocompatible material (3), largely used in maxilo-facial surgery.

In this work an attempt was made to check whether the pitting corrosion behaviour of AISI 316 L stainless steel in a physiological environment was improved when plasma spray coated with Al_2O_3, as this is one of the types of corrosion stainless steel is susceptible to in such environments (4). Coated and uncoated stainless steel samples were tested.

Experimental Technique

AISI 316L steel samples had the following chemical composition, in weight percentage:

C=0.03%; Cr=18.00%; Ni=12.50%; Mn=1.60%; Si=1.20%.

The technology chosen for coating Al_2O_3 was Plasma Spraying. This allows for ceramic deposition with substrate keeping a low temperature, typicaly under 200 °C, which is a very important aspect, specially when stainless steel is used as a substrate, as it inhibits the $Cr_{23}C_6$ precipitation at grain boundaries leading to intergranular corrosion susceptibility phenomena, that generally occur when higher temperatures are reached (5).

Samples preparation and Al_2O_3 Plasma Spraying were performed following procedures previously described (5,6).

For the electrochemical tests all samples were mounted in epoxy resin moldings under vacuum, to minimize the tendency for crevice corrosion at the steel/resin interface.

The electrochemical behaviour studies consisted of open circuit corrosion potential measurements, E_{corr}, and anodic potential polarizations. Saturated Calomel Reference Electrodes were used. Potential scanning rate was $10^{-3}\ Vs^{-1}$. The solution used to simulate the physiological environment was Ionosteril, with the following composition in g/l :

$Na^+=3,151$; $K^+=0,156$; $Ca^{2+}=0,0066$; $Mg^{2+}=0,030$; $Cl^-=3,9$; $CH_3COO^-=2,173$

All tests were carried out at room temperature.

Results

When α-Al_2O_3 is Plasma Sprayed onto a metallic substrate, it partially converts into other less stable phases,. particularly γ-Al_2O_3 and η-Al_2O_3, which show a decreased corrosion resistance in physiological environment.

X-ray diffraction was therefore used to characterize both the Al_2O_3 powder and the Al_2O_3 plasma coated layers .

This study has shown that in the powder only α-Al_2O_3 was present, but in the coatings this form coexisted with either γ-Al_2O_3 or η-Al_2O_3. Due to the overlapping of positions corresponding to γ-Al_2O_3 and η-Al_2O_3 interplanary distances it has not been possible to determine conclusively which one of these two was present.

Fig. 1 and 2 present the X-ray diffraction patterns obtained.

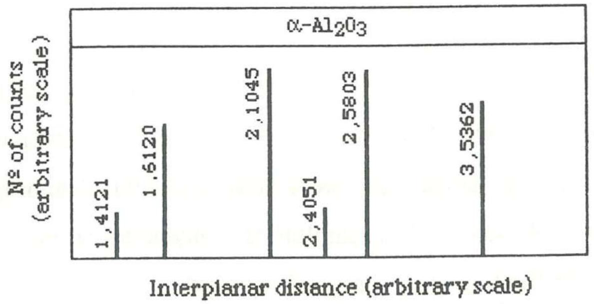

Fig. 1 - Al_2O_3 powder X-ray diffractogramme

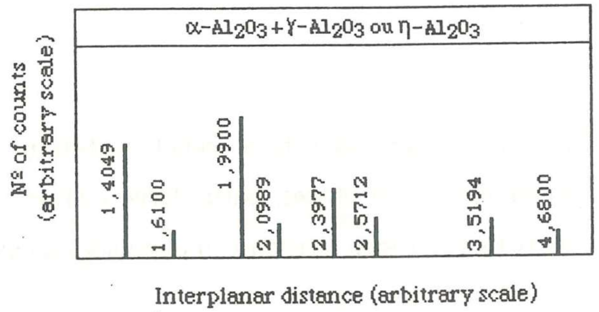

Fig. 2 - Al_2O_3 coating X-ray diffractogramme

Open-circuit corrosion potential values were obtained both for Al_2O_3 coated and uncoated AISI 316L stainless steel, showing the values of +55 mV and -130 mV, respectively.

Anodic polarization curves were then obtained, starting from these values, as it may be seen in Fig. 3.

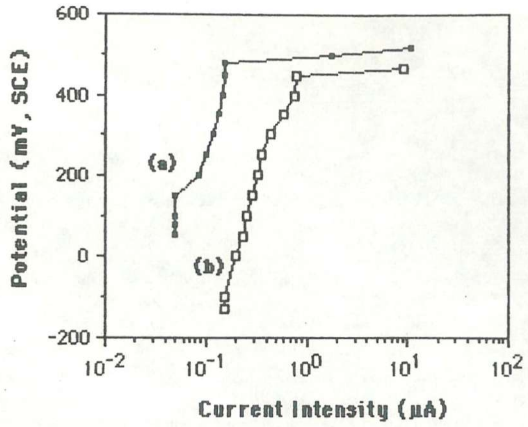

Fig. 3 - Anodic polarization curves for AISI 316L stainless steel in Ionosteril

for surfaces: Al_2O_3 coated (a)
uncoated (b)

The most relevant feature observed was the considerable decrease of the current intensity within the passive region of the anodic polarization curve of AISI 316L samples coated with Al_2O_3, with respect to those uncoated, showing approximately a one decade shift.

S.E.M. studies of the surface morphology revealed the occurence of corrosion pits in the uncoated samples, as expected. Due to the presence of the 300 ± 2µm thick Al_2O_3 coating, no pits were detected in the coated samples. Also there were no signs of morphological changes occuring as consequence of the previous anodic polarizations.

An extreme situation was then tried as an attempt to generate corrosion in the coated samples, by a three fold polarization up to +1200 mV. Subsequent S.E.M. observation revealed the presence of corrosion products inside Al_2O_3 pores, as it may be seen in Fig. 4.

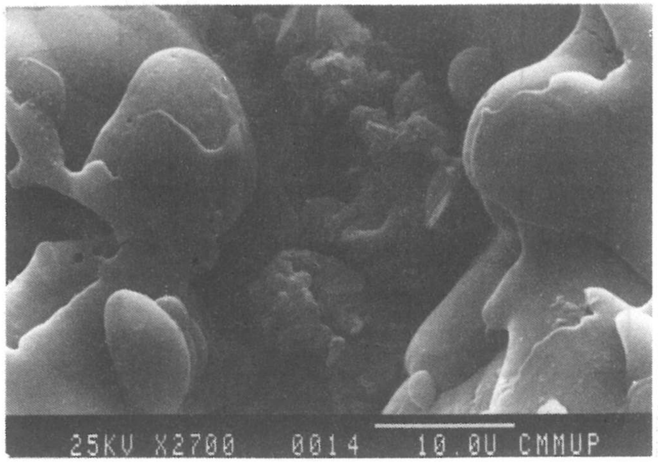

Fig. 4 - Corrosion products within the Al_2O_3 coating layer.

X-ray energy dispersive microanalysis has shown the presence of Fe, Cr and Ni in the corrosion products, as it may be seen in the Fig. 5.

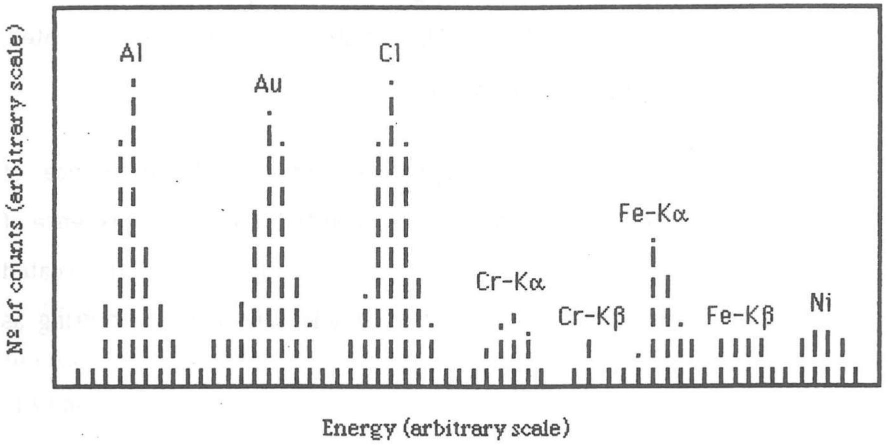

Fig 5 - X-ray energy dispersive microanalysis of the corrosion products.

The presence of Au in the X-ray spectra derives from the gold sputtering required prior to S.E.M. studies of Al_2O_3, to make it conductive at the surface, and thus avoid charging problems.

Discussion

Biomaterials are one of the areas of materials research and developments to which attention is being increasingly payed throughout Europe and in the United States. As people's life hope is expanding, medical care is finding increased need for protheses and implants capable of substituting portions of bones, organs and tissues with minimum damage to the pacients.

To be able to produce good results, biomaterials must fulfill several tasks which in many cases demand for very different and even opposite properties, such as high toughness of the core and high wear resistance at the surface.

In this work no other considerations besides corrosion behaviour were taken into account, but this is on its own right is a matter of great concern, as the eventual release of metal ions into the organic fluids may produce very serious damages.

The decision of studying Al_2O_3 coated stainless steel was based on the fact that, by coating, one could eventually reduce the corrosion of stainless steel, while providing a surface with well known corrosion and wear resistance, and presumably relatively inert to body reactions. Also the maintenance of a metallic core would grant enough toughness to be used as an implant.

From the X-ray diffraction results, it was possible to confirm what some authors had claimed **(7,8)** in terms of transformations occuring during plasma spraying, which partially converted α-Al_2O_3 into γ-Al_2O_3 or η-Al_2O_3. This may be considered as a drawback, as α-Al_2O_3 is considered as the most inert alotropic variety of Al_2O_3, whose biocompatibility is generally accepted.

Brown *et al* **(2)** have shown that plasma Al_2O_3 coatings could undergo degradation when present in Ringer solution, after 336 hours at 37 °C, with aluminium ions being detected in the solution.

J. L. Drummond *et al* **(8)** also have shown that by implanting Al_2O_3 coated stainless steel discs in rats an increase in aluminium was detected in their lungs and liver.

In this work prolonged immersion in ionosteril solution, for 430 hours at 37 ± 0.5 °C of Al_2O_3 plasma sprayed stainless steel samples has produced a concentration of aluminium of less than 1 p.p.m., that is below the detection limit of the atomic absortion spectrophotometer, thus not being totally conclusive.

On the other hand the pitting corrosion tests indicate that corrosion happened solely within the stainless steel substrate. Therefore, while for uncoated samples all the surface contacts with the aggressive environment, for Al_2O_3-coated ones, only at the bottom of the coating pores corrosion was allowed to occur significantly, thus reducing the area where stainless steel/solution contact was possible. This may be the cause for the one decade reduction in current intensity observed in the passive region of the

anodic polarization curves for the coated samples, with respect to the those uncoated. This indicates that Al_2O_3 coatings seem to act as relatively inert barrier layers, inhibiting the contact of the substrate with the environment.

Conclusions

1. During Al_2O_3 plasma spraying a portion of α-Al_2O_3 was converted into chemically less stable alotropic variety, γ-Al_2O_3 or η-Al_2O_3.

2. The Al_2O_3 coated layer didn't considerably change the anodic polarization characteristic curve profile of AISI 316L stainless steel, when present in a solution simulating the physiological environment, thus mantaining the safety interval for passivity within the same range of potentials.

3. There has been a shift of approximately one decade towards smaller values of current intensity, in the passive region of the potential polarization curves of Al_2O_3-coated stainless steel, when compared to uncoated samples, indicating that only areas within the coating pores were being affected by the polarization potential.

4. There weren't any clear indications of morphological changes occuring in the Al_2O_3 layers as a result of the contact with the simulated physiological environment.

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