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STUDY ON CORROSION OF PRIMARY MANDIBULAR RECONSTRUCTION PLATES

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Titanium primary reconstruction plates are used for rapid rehabilitation after mandible resection. Titanium shows remarkable corrosion resistance in oxidizing acid environment. The purpose of our study was to investigate the corrosion behaviour of titanium primary plates. The corrosion behavior versus corrosion duration was examined by Scanning Electron Microscopy coupled with Energy Dispersive System and X-Ray Fluorescence. Our results show that titanium plates are not completely inert and can be susceptible to pitting and crevice attack, especially at long term exposure. Titanium is protected from corrosion by a thin film of oxygen on its surface. It reacts with titanium to form titanium dioxide, which acts as a barrier against corrosion. This barrier can only be broken if the titanium is placed in an environment that is very rich in chloride. However, mandibular reconstruction plates are not meant to be immersed in saliva, oral exposure of these plates being a complication that should be dealt with as soon as possible. Since we could not find a significant quantity of toxic products, our study validates the use of these plates, as long as the above mentioned complication does not occur. However, as soon as the plate is exposed to saliva, surgical retreatment in mandatory.

Keywords: corrosion, reconstruction plates, titanium

INTRODUCTION

Titanium reconstruction plates can be used for temporary, or sometimes even permanent, reconstruction after mandible resection. The purpose of our study was to investigate the corrosion behaviour of titanium primary plates used for mandible reconstruction. We emphasize two aspects of inserted material corrosion: 1.How susceptible is implant material to corrosion? 2.What is the effect of any corrosion (even very small amounts) on the body?

The interest in using titanium plates, is due to its excellent properties of biocompatibility, low density, low thermal conductibility, mechanical behavior and corrosion resistance [1–8].

Titanium shows remarkable corrosion resistance in oxidizing acid environments by virtue of a passive oxide film[1,6,9, 10,11]. Like stainless steels, it is dependent upon an oxide film for its corrosion resistance. The oxide film formed on titanium is more protective than that on stainless steel, and it often performs well in media that cause pitting and crevice corrosion in the latter (such as seawater, wet chlorine, organic chlorides[1,6]. In reducing environments in which the oxide film breaks down, titanium becomes the anode in a galvanic couple. In slightly reducing environments or in environments that form complexions with titanium, tendencies to corrode depend upon the presence of metal ion inhibitors, alloying elements, temperature, and other variables[12,13]. However, some scanning electron microscopic studies showed varied amount of titanium particles in the tissues surrounding the plate[11]. Even more, titanium and its alloys are often damaged during their use in some complicated environments, such as oral environment.

There also have been several studies describing patients who did not adapt to titanium [13-,19] or patients allergic to titanium [14],[17–20], which is an important issue to be considered [21,22]. To find out the real reason, one of the

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key issues at present is to learn the corrosion behavior and mechanism of titanium in human body.

MATERIAL AND METHODS

The corrosion behavior versus corrosion duration was examined by Scanning Electron Microscopy coupled with Energy Dispersive System and X-Ray Fluorescence. Commercially pure titanium, ASTM F67 grade 1, was used for our experiments. The Ti substrate was immersed in a synthetic solution of artificial saliva with the pH adjusted to 4.95 at 27ºC. As reference electrolyte used was Fusayama–Meyer artificial saliva.

KCl (0.4 g/l),
NaCl (0.4 g/l),
$CaCl_2.2H_2O$ (0.906 g/l),
$NaH_2PO_4.2H_2O$ (0.690 g/l),
$Na_2S.9H_2O$ (0.005 g/l),
urea (1 g/l).

Table 1. The composition of the artificial saliva, which closely resembles natural saliva

The corrosion, was measured as a function of time over a 21 days period in artificial saliva solution at 27ºC. The microstructure of commercially pure Ti plate was characterized by means of scanning electron microscopy (SEM) and semi-quantitative analyses by energy dispersive spectrometry (EDS). We measured pH and electrical conductivity over time, using the HACH sensION156 Portable pH/Conductivity Meter. We used the Hach double cell probe, with a range between 0.1 µS/cm and 1000mS/cm.

RESULTS AND DISCUSSIONS

Titanium alloys, like other metals, are subject to corrosion in certain environments. The primary forms of corrosion that have been observed on these alloys include general corrosion, crevice corrosion, anodic pitting, hydrogen damage, and stress corrosion cracking. In any investigated application of titanium, its susceptibility to degradation by any of these forms of corrosion should be considered.

Electrical conductibility of the corrosion solution

Conductivity of an electrolyte solution is a measure of its ability to conduct electricity. Positive and negative ions migrate towards the contrary electrodes, when a voltage is applied. The dispersion is influenced by the electric current and by solvent's properties (concentration, viscosity), as well as by their properties (ion size, concentration, electric charge, and so on). Rising the temperature leads to higher ion migrating velocity as well as a higher conductivity.

To measure conductivity, a 1 cm^2 cell is used. The cell contains two electrodes, set 1 cm apart.

Knowing that:

$K = L/A$

where:

L- cell length

A - transversal section area

For the standard cell, K = 1.0 cm^{-1}

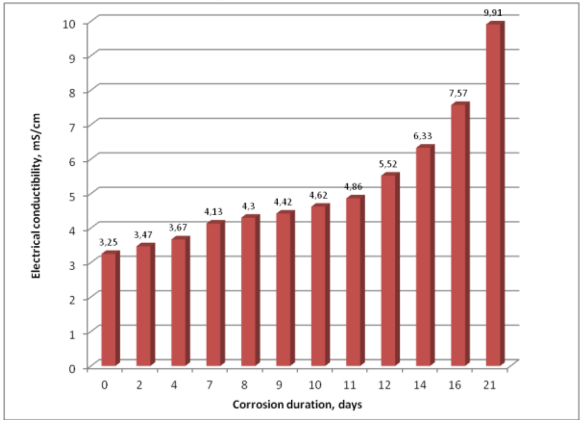


Figure 1. Evolution of the corrosion solution electrical conductibility versus corrosion duration

The evolution of the corrosion solution electrical conductibility versus corrosion duration is given in Figure. 1. The electrical conductibility of the reference artificial saliva was 3.25 ms/cm at 27^{o}C. Increasing the corrosion duration up to 21 days, it should be noticed a slight increase up to 4.13 ms/cm of the conductivity during the first 7 days, followed by a continuous growing up to 21 days of corrosion in 4.3 -9,91 mS/cm range.

Evolution of the corrosion solution pH

The evolution of the corrosion solution pH versus corrosion duration is shown in Fig.2. The pH of the reference artificial saliva was 4.95 at 27^{o}C. After two days of corrosion a decrease of pH to 4.83 was registered, followed by an obvious increase after 8 days. After 9 days a slight decrease with ~ 10% should be noticed. After 9, 10, 11, 12, 14, 16 and 21 days of corrosion the fluctuation of pH was not very significant.

The hydrolysis of the protective oxide layer in solution containing chloride ions (confirmed by EDS analysis) can explain the decrease of pH to a certain extent, that is the corrosion of titanium in artificial saliva solution will cause the pH decrease, as can be seen from the pH variation in the corrosion process of titanium (Figure 2).

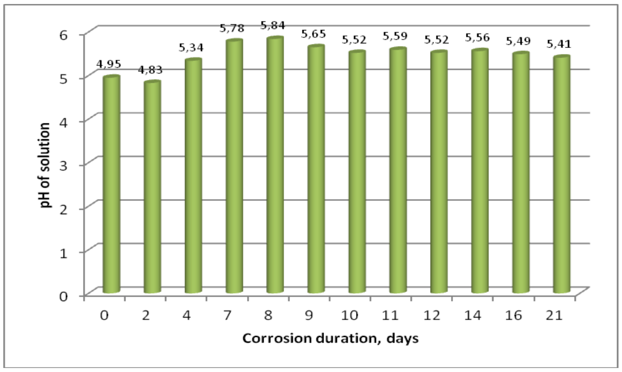
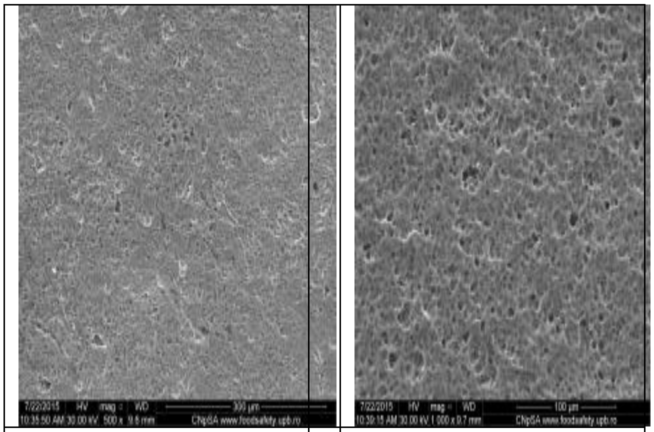


Figure. 2 Evolution of the corrosion solution pH versus corrosion duration

Scanning Electron Microscopy Analysis on Ti plate surface

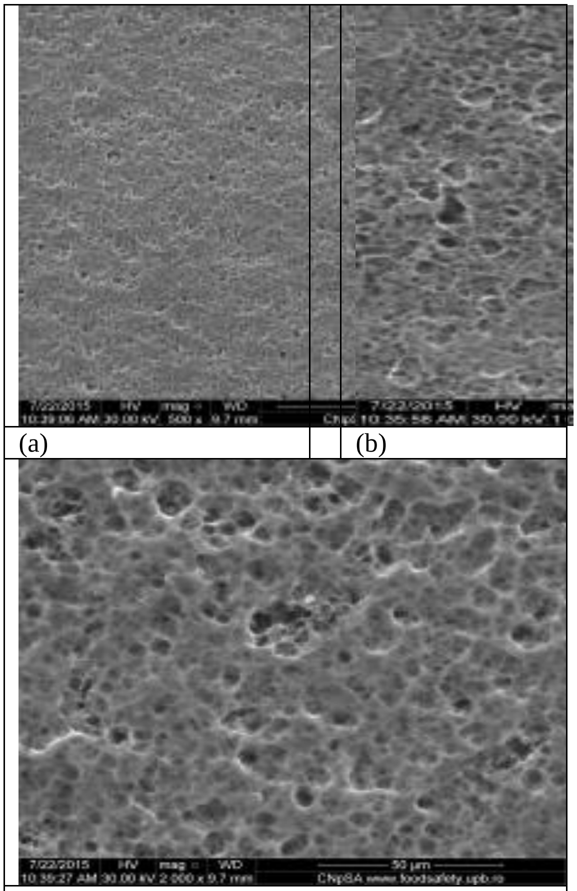
In order to further study the surface morphology of titanium before and after immersion, scanning electron microscopy is used to characterize the corrosion surface. Figure.3 (a,b) show the surface morphologies of titanium plate before the immersion in artificial saliva.



(a) (b)

Figure 3. Surface morphologies of titanium plate before immersion in artificial saliva:
(**a**) general view (**b**) detail of (a)

As can be seen from these figures, the surface looks rather smoother, is more uniform in character, and there is little tendency towards local enrichment of products on the surface. In addition, parallel features, which can be associated with abrading scratches, are also observed in Figure. 3 a and b. Figure.3a shows that the Ti plate had a typical cast microstructure, with non-homogeneous size distribution of phase grains.



(a) (b)

(c)

Figure 4. Surface morphologies of titanium plate after immersion in artificial saliva for 7 days:
(**a**) general view (**b**) detail of (a) and (**c**) detail of (b)

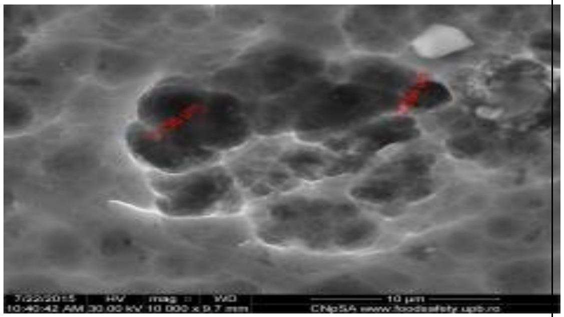
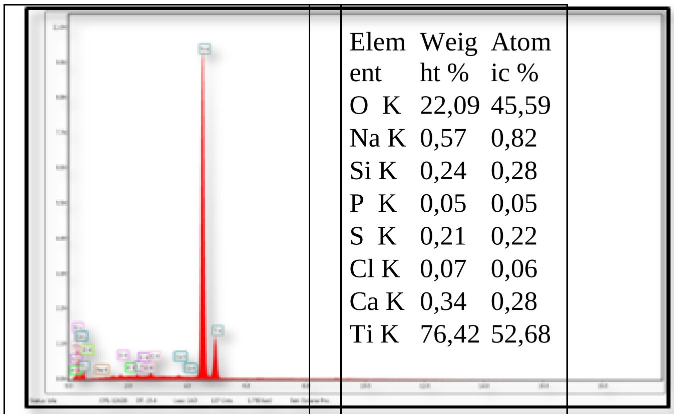


Figure 5 Detail of figure 4b



Element	Weight %	Atomic %
O K	22,09	45,59
Na K	0,57	0,82
Si K	0,24	0,28
P K	0,05	0,05
S K	0,21	0,22
Cl K	0,07	0,06
Ca K	0,34	0,28
Ti K	76,42	52,68

Figure 6. ESD analysis on titanium plate surface after immersion in artificial saliva for 7 days

However, in the presence of artificial saliva, pitting corrosion can be distinctly observed; by comparison, the pits in Figure. 4 are obviously larger and deeper than those in Figure.3. Therefore, the acid environment of artificial saliva can significantly affect the formation of pitting. Consequently, at the microscopic level, the effect of acid environment on generating pitting cannot be ignored. Our findings concure with the data from the literature [1,3,5-11]. Additionally, the adsorption of acid in the micro-point of pitting corrosion can hinder titanium passivation, providing a necessary premise and driving force for generating macro-pitting corrosion.

Figure. 4 shows SEM photomicrographs of the surface of Ti after the corrosion test in artificial saliva solution for 7 days. Figure.4 b, c show localized attack (pitting) could be seen on the surface Ti specimens after the corrosion test in artificial saliva solution.

Figure. 6 shows the EDS analysis of the chemical composition of the precipitate layer of Ti after the corrosion test indicates that the precipitates consist mainly of titanium oxide. Thus, although the coating of the oxide is not an effective anticorrosion layer, it hinders to some extent the electrochemical processes occurring at the metal substrate interface, hence contributing to a decrease in the metal ion release from the system.

A tiny bit of the dissolved TiO_2 causes the deficiency of the protective film, and small molecules, such as H_2O, O_2 and H^+, can spread to the substrate by defects, leading to the tendency toward pitting corrosion as seen in Figure.4.

CONCLUSIONS

The results show that, while titanium is resistant to most normal environmental situations, it is not completely inert and can be susceptible to pitting and crevice attack, especially at long term exposure. Titanium is protected from corrosion by a thin film of oxygen on its surface. It reacts with titanium to form titanium dioxide, which acts as a barrier against corrosion. This barrier can only be broken if the titanium is placed in an environment that is very rich in chloride. However, mandibular reconstruction plates are not meant to be immersed in saliva, oral exposure of these plates being a complication that should be dealt with as soon as possible. Since we could not find a significant quantity of toxic products, our study validates the use of these plates, as long as the above mentioned complication doesn't occur. However, as soon as the plate is exposed to saliva, surgical retreatment in mandatory.

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