Introduction

Titanium and many of its alloys have a high corrosion resistance in physiological salt solutions. Titanium has been included in previous studies of materials for biological implant use (1-5) and it compared favorably with stainless steels, vitallium and other materials considered. However, compared to these other materials, relatively little is known on the detailed corrosion reaction of titanium in physiological media. Hoar and Mears (1) conducted an extensive investigation of the electrochemical properties of surgical implant materials and some of their techniques have been employed in the present study. Most previous electrochemical measurements have been made in vitro in saline solutions or in some cases in vivo with animal tests. Titanium has shown good corrosion resistance in every case. Polarization measurements in Ringer's solution showed titanium to be passive (5). Experiments involving refinements in surface roughness and sterilization (3,4) showed that both processes affect and can improve the corrosion resistance of titanium. The mechanical, metallurgical and corrosion properties of titanium and some of its alloys have been reviewed and compared with the same properties of other alloys currently used as implant materials (6,7). It was concluded there that titanium could be used as an alternative to stainless steel or vitallium devices.

*McGill Univ., School of Medicine, Montreal, Canada

"CONTRIBUTION OF THE NATIONAL BUREAU OF STANDARDS, NOT SUBJECT TO COPYRIGHT"
The present paper reports on a study underway on titanium to observe initial surface microstructural changes and the electrochemical effects of exposure to physiological solutions containing uric and some some representative amino acids*. Specimens of pure titanium, Ti-6Al-4V and Ti-0.2 Pd alloys were studied (all compositions are given in weight percent). There was particular interest in correlating the electrochemical data with transmission electron microscopy results. The latter technique shows surface reactions on a fine scale and permits the identification of surface films and deposits.

Experimental Procedure

Electrical measurements were conducted on flat sheet specimens of commercially obtained Ti, Ti-6Al-4V and Ti-0.2 Pd alloys. Both mechanically polished and electropolished specimen surfaces were prepared. The specimens were then welded to thin titanium leads. The electrical connecting junction and lead were coated with epoxy cement to prevent a solution-air interface on the metal. These specimens were immersed in 100 ml. beakers containing Hanks' (8) solution with uric and amino acids added individually to separate beakers in the following amounts; 0.002M glycine, 0.001M cystine, 0.002M and 0.1M cysteine, 0.002M tryptophan, and 0.002M uric acid. No attempt was made to adjust the oxygen concentration in the solutions used for open circuit potential measurements. Solutions were refrigerated and kept at 4°C to inhibit microbial growth. The beakers were covered with plastic wrap. An electrometer was used to measure specimen potentials with respect to a saturated calomel electrode placed in the solution prior to measurement (the potentials were subsequently converted to the hydrogen scale). These voltages were read daily for the first three weeks and then weekly for three months, and finally on a monthly basis. There was little change in any of the curves after one month. Hanks' salt solution with a pH of 7.6 (buffered) was used as the basic solution throughout the tests. Unbuffered 0.17M NaCl solution and Ringer's** solution were used briefly only for comparison. Current-potential measurements were made using a potentiostat arrangement (9), allowing 24 hrs. for electrical equilibration. In several tests, oxygen gas was bubbled through the solution at a rate of 50 ml/min. to ensure oxygen saturation of the solution. In other tests, helium was bubbled through at the same rate to produce a low oxygen concentration in the solution.

*Glycine, the simplest amino acid has one amino group (NH₂); cysteine has a readily oxidizable SH group; cystine has the more stable S-S linkage; and tryptophan has an aromatic ring which also is subject to oxidation.
Transmission electron microscopy (TEM) and transmission electron diffraction techniques were used to study thin foils prepared by electropolishing from the flat sheet specimens (see (10) for details). These specimens were contained in a closed air-tight vessel during 80 hours exposure to Ringer's, Hanks' and other solutions at human body temperature (37°C) and at 100°C. Foils that were steam sterilized in an autoclave at 120°C and 15 p.s.i. (0.10 MN/m²) pressure also were examined using TEM techniques.

Results and Discussion

The formation of the surface oxide film on titanium and any film breakdown can be monitored conveniently by measuring the open circuit potential versus time. Figure 1 shows three types of potential-time curves from the work of Hoar and Mears (1). The curve of type a has been described as being the most desirable for implant materials to exhibit since there is no apparent interruption in the formation of the film as is indicated in curves b and c.

![potential-time curves](image)

Fig. 1. Schematic potential-time curves: (a) film remains intact; (b) pitting corrosion; (c) general corrosion (after Hoar and Mears). Positive potentials indicate noble direction.

The small changes in the open circuit potential-time curves which are associated with typical tests of this study are shown in Figures 2 through 6. The potential represented in these curves cannot be related quantitatively to the corrosion rate. However, the shape of the curve indicates the manner in which the surface oxide film is forming.

**Ringer's solution contains 8.6g NaCl, 0.3g KCl, 0.32g CaCl₂ in 1L solution.**
Hoar and Mears (1) found that unbuffered 0.17M NaCl made titanium electrode potentials more positive than the same solution buffered. They found that electrode potentials measured in buffered 0.17 NaCl solution were almost the same as those made in Hanks' solution. Figure 2 shows potential-time curves measured here on Ti-6Al-4V at room temperature (24°C). The curve for unbuffered 0.17M NaCl is more electropositive than that obtained from measurements in Hanks' buffered solution. Ringer's unbuffered solution with a pH of 6 gives similar results in our tests to those obtained with the unbuffered 0.17M NaCl solution which has a pH of 6.7. It has been shown (10) that lowering solution pH produces increased surface oxide film growth within a given time and that the oxide crystallite size decreases with decreasing solution pH. In alkaline solutions the titanium oxide film is more soluble and the composition of the surface oxide film varies depending on ions present in the corroding solution. For this reason, and the buffering characteristics of the human body system, it is important that solutions buffered near a pH of 7 be used for in vitro corrosion studies of titanium implant materials.

Figure 3 shows the open circuit potential-time curves for the three alloys in Hanks' solution at 4°C for a period of six months. A single electrode potential value is approached with corrosion time for all three alloys but initially, the Ti-0.2 Pd alloy has a higher potential. This difference was not present when measurements were taken on the Ti-0.2 Pd alloy with a mechanically polished surface. The effects of mechanical polishing as compared with electropolishing on the subsequent electrochemical behavior at 24°C are shown in Figure 4. Electropolished specimens have a more positive electrode potential than do specimens mechanically polished in sequence through 600 grit emery paper. Finer polished surfaces using 0.05µm alumina produced results close to those of the electropolished specimens. Changes in corrosion rates due to surface preparation treatments have been discussed previously (4) and smoother surfaces were recommended for implant use. Our results show that a finer initial finish may shorten the time necessary for the specimen to reach a steady potential. Figure 4a shows that varying surface treatments used here cause very little change in the electrode potential of commercially pure titanium. There is a small change in the electrode potential of the Ti-6Al-4V alloy, Figure 4b, and a larger potential change for the Ti-0.2 Pd as shown in Figure 4c.

The effects on the open circuit potential at 4°C of the presence of uric and amino acids and of sterilization are shown in Figures 5 and 6 for periods up to 150 days. The commercially pure titanium specimens were least affected by our surface preparation and sterilization. The Ti-6Al-4V alloy progressively becomes more electropositive when the potential is measured with the material in the mechanically polished, electropolished and sterilized conditions, respectively. Changes resulting from amino and uric acid additions
Fig. 2. Ti-6Al-4V open circuit potential at 24°C in: (a) 0.17 M NaCl; (b) Hanks' solution.

Fig. 3. Open circuit potentials in Hanks' solution at 4°C for electro-polished (a) Ti; (b) Ti-6Al-4V; (c) Ti-0.2 Pd.
Fig. 4. Open circuit potential for mechanical (——) and electropolished (---) surfaces in Hanks' solution at 24°C for (a) Ti; (b) Ti-6Al-4V; (c) Ti-0.2 Pd.

Fig. 5. Open circuit potentials in Hanks' solution (——) and various organic acids (observed range is hatched) at 4°C for electropolished (a) Ti; (b) Ti-6Al-4V; (c) Ti-0.2 Pd.
Corrosion of Titanium Alloys in Physiological Solutions

(Figure 5) were not great, although in the electropolished condition, potential values were slightly above those measured in Hanks' solution only. Most of the amino acid additions altered the solution pH only slightly but a 0.1M cysteine addition lowered the solution pH to 1.9. Electrochemical measurements in the cysteine solutions were difficult because there was always a drift in the potential in the positive direction. These measurements also were sensitive to solution agitation. The Ti-0.2 Pd alloy again was the most subject to these variations in cysteine solutions.

Current-potential measurements were made under potentiostatic control on electropolished specimens of Ti-6Al-4V and Ti-0.2 Pd in 0.17M NaCl and in Hanks' solution. Figure 7 shows the polarization current vs. electrode potential for the voltage range 0.2 to 1.2 volts. The current is higher in the unbuffered solution for the Ti-6Al-4V alloy (compare curve a to curves b and c). Curve d in this Figure refers to the Ti-0.2 Pd alloy in oxygen saturated Hanks' solution. Comparing curves c and d shows the polarization current of the Ti-6Al-4V alloy to be greater than that for the Ti-0.2 Pd alloy at potentials less than 1.2 volts. At greater potentials the reverse is observed. The polarization current for the Ti-6Al-4V alloy is little affected by the oxygen concentration in the solution for voltages below 1.4 volts, as shown by curves b and c.

Effects of sterilization on stainless steel (types 304 and 316), titanium and vitallium have been studied (2) and found in some cases to be beneficial. It is understandable that oxide films formed during high temperature steam sterilization will provide more initial protection for metals such as titanium. Figures 8 and 9 show thin foil transmission electron micrographs of a Ti-0.2 Pd alloy foil which had been steam sterilized at 120°C under 15 psi for 15 minutes. Although a thin oxide (TiO) is present on the surface of Figure 8 (detected by electron diffraction), it is not visible in the photograph and the surface appears clear and smooth. However, Figure 9 shows a region having a small patch of TiO₂ (anatase) crystallites on the surface. This oxide has not been found on electropolished, unsterilized foils of this alloy, and hence is apparently a result of steam sterilization. Although the oxide provides good protection against corrosion, the crystallites cause a certain amount of surface roughening (3). The inset in Figure 9 is a selected area diffraction pattern from the TiO₂ (anatase). Thus, although sterilization may improve the corrosion resistance of titanium, it can produce surface variations especially if steam is present. Previous studies on initial stages of titanium corrosion in hot salt water have detected the progressive nature of oxide film formation (Ti...TiO...TiO₂) on titanium surfaces, using transmission electron microscopy and electron diffraction methods (11). Oxide films forming on titanium surfaces at body temperature and in body solutions probably will be of the lower oxide type.
Fig. 6. Open circuit potentials in Hanks' solution at 4°C for electropolished and sterilized (a) Ti; (b) Ti-6Al-4V; (c) Ti-0.2 Pd.

Fig. 7. Current-potential relations for Ti-6Al-4V in (a) 0.17 M NaCl; (b) Hanks', low oxygen; (c) Hanks', high oxygen; and (d) Ti-0.2 Pd in Hanks' solution, high oxygen.
Fig. 8. Ti-0.2 Pd alloy after electropolishing and sterilization at 120°C and 15 psi. No oxide film is visible but electron diffraction patterns show TiO present.

Fig. 9. Ti-0.2 Pd alloy after electropolishing and sterilization at 120°C and 15 psi. TiO₂ (anatase) crystallites are scattered on foil surface.
unless a prior TiO₂ film has been produced on the surface of the implant. Titanium surfaces can be prepared which are covered with a smooth protective oxide (lower oxide) or with a rough protective oxide coating (TiO₂). The latter type, TiO₂ (anatase), can be varied in surface roughness, and crystallite size simply by altering conditions of the exposing solution.

Conclusions

This study indicates a high degree of inertness of titanium to certain physiological saline solutions and selected organic acids. All corrosion effects were relatively minor. Titanium appears less affected by certain surface and sterilization treatments than are the alloys Ti-6Al-4V and Ti-0.2 Pd. The alloy, Ti-0.2 Pd appears more susceptible to surface treatment changes and solution variables than is Ti-6Al-4V. Buffered solutions are shown to be important for use in appropriate corrosion testing of titanium implant materials. Steam sterilization may produce a non-uniform oxide surface on titanium materials and should be carefully controlled.

References


