THE CORROSION BEHAVIOR OF TITANIUM ALLOYS IN CHLORIDE SOLUTIONS: MATERIALS FOR SURGICAL IMPLANTS

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The corrosion behavior of titanium alloys 8Al-1Mo-1V in both the single and duplex annealed condition, and 6Al-6V-2Sn at yield strength levels of 140, 160 and 180 ksi were studied in 0.17M sodium chloride solution (the approximate NaCl concentration in blood, plasma, and lymph) and Hanks's physiological solution (a fairly close imitation from the chemical viewpoint, of the fluid in muscle and bone) at a temperature of 37°C by electrochemical means, i.e., potential-time, anodic polarization, current density-time for the anodes under potentiostatic control at the equilibrium potential. Electrochemical measurements were made with these alloys in both the unstressed and stressed conditions, and finally conditions of cyclic stress.
Introduction

Studies of the corrosion behavior of commercially available titanium alloys in chloride environments have specific applications in Army systems and will prove useful in the field of materials for surgical implants, metal components of which must be singularly resistant to all forms of corrosion in chloride environments.

In England, both unalloyed titanium and titanium alloy 6Al-4V are being used fairly extensively for surgical implant applications. In the United States, titanium has not gained widespread acceptance. However, unalloyed titanium is presently being used for several types of fixation and prosthetic devices, and the higher strength alloy 6Al-4V has recently been approved for surgical use. Additional applications for still higher strength titanium alloys would include pins, hip nails, plates and screws for fracture fixation, and prosthesis for the replacement of damaged bones and joints.

There are three primary problems involved in the selection of a metal for implants: (1) strength; (2) corrosion resistance; (3) toxic effects of the implant on the surrounding tissue and the body as a whole. We are concerned with the first two problems only.

The corrosion behavior of titanium alloys 8Al-1Mo-1V in both the single and duplex annealed condition, and 6Al-6V-2Sn at yield strength levels of 140, 160 and 180 ksi were studied in 0.17M sodium chloride solution (the approximate NaCl concentration in blood, plasma, and lymph) and Hanks's physiological solution (a fairly close imitation from the chemical viewpoint, of the fluid in muscle and bone) at a temperature of 37°C by electrochemical means, i.e., potential-time, anodic polarization, current density-time for the anodes under potentiostatic control at the equilibrium potential. Electrochemical measurements were made with these alloys in both the unstressed and stressed conditions, and finally under conditions of cyclic stress.

Materials

The chemical analysis of the titanium alloys examined is listed in Table I. Their heat treatments and mechanical properties are given in Table II.

Table I

Chemical Analysis of Titanium Alloys

<table>
<thead>
<tr>
<th>Nominal</th>
<th>Ti</th>
<th>C</th>
<th>Fe</th>
<th>N</th>
<th>Al</th>
<th>Mo</th>
<th>Va</th>
<th>H</th>
<th>Sn</th>
<th>Cu</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-6V-2Sn Bal</td>
<td>.022</td>
<td>.79</td>
<td>.014</td>
<td>5.6</td>
<td>5.7</td>
<td>.007</td>
<td>2.0</td>
<td>.74</td>
<td>.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-8Al-1Mo-1V Bal</td>
<td>.022</td>
<td>.06</td>
<td>.008</td>
<td>7.6</td>
<td>1.1</td>
<td>1.1</td>
<td>.005</td>
<td>.09</td>
<td></td>
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</tbody>
</table>
CORROSION BEHAVIOR OF TITANIUM ALLOYS IN CHLORIDE SOLUTIONS

Table II
Heat Treatment and Mechanical Properties of Ti-6Al-6V-2Sn and Ti-8Al-1Mo-1V

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Heat Treatment</th>
<th>Yield Strength (PSI)</th>
<th>UTS (PSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-6V-2Sn (TMCA Heat G-3213)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-received (MA)</td>
<td>Mill Anneal</td>
<td>142,900</td>
<td>147,800</td>
</tr>
<tr>
<td>STA (160 KSI YS)</td>
<td>1650°F (2hr), WQ +</td>
<td>160,350</td>
<td>163,400</td>
</tr>
<tr>
<td></td>
<td>1220°F (4hr), AC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>STA (180 KSI YS)</td>
<td>1650°F (2hr), WQ +</td>
<td>181,250</td>
<td>186,300</td>
</tr>
<tr>
<td></td>
<td>1130°F (4hr), AC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-8Al-1Mo-1V (TMCA Heat G-1406)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-received</td>
<td>Mill anneal</td>
<td>127,250</td>
<td>134,600</td>
</tr>
<tr>
<td>Duplex Anneal</td>
<td>1650°F (1hr), AC +</td>
<td>136,750</td>
<td>145,200</td>
</tr>
<tr>
<td></td>
<td>1100°F (8hr), AC</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bar stock was used for rotating bending fatigue specimens, and cylindrical specimens of 1 sq. cm. surface area for experiments involving the unstressed alloys. Wire specimens of 0.035 inch diameter were used in the SCC experiments, and corrosion fatigue crack propagation studies were conducted on specimens cut from 0.125 inch thick sheet and ground to a thickness of 0.100 inch.

The simulated body environments were 0.17M NaCl solution and Hanks's physiological solution. (Table III)

Table III
Composition of Hanks's Solution

<table>
<thead>
<tr>
<th>Material</th>
<th>g/l</th>
<th>Material</th>
<th>g/l</th>
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</thead>
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<tr>
<td>NaCl</td>
<td>8.00</td>
<td>MgCl₂·6H₂O</td>
<td>0.10</td>
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<tr>
<td>CaCl₂</td>
<td>0.14</td>
<td>Na₂HPO₄·2H₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>KCl</td>
<td>0.40</td>
<td>MgSO₄·7H₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.35</td>
<td>Na₂HPO₄</td>
<td>0.10</td>
</tr>
<tr>
<td>glucose</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Experimental Procedure

Polarization

Polarization measurements were made with the unstressed alloys using the potential sweep method of potentiostatic polarization. The electrode potential was continuously changed at a constant rate of 5000 mV/hr and current was simultaneously recorded. A Wenking potentiostat in conjunction with a motor potentiometer for automatic programming of the operating potential and X-Y recorder were employed to automatically record current versus voltage. The polarization cell and general procedure have been described previously (1).

Potential-Time and Current-Time

The polarization cell was used in both potential-time and current-time experiments. A high impedance General Radio Electrometer in conjunction with a strip chart recorder was used for potential-time measurements.

For current-time measurements at constant potential, the Wenking potentiostat was used to polarize the specimen and the current was estimated by the potential drop across a fixed resistance in series with the cell, measured on a Keithley nanovoltmeter and recorded on a strip-chart recorder.

Stress Corrosion

The polarization cell was modified to perform electrochemical measurements on the alloys under stress (2). Tensile stress was applied to the wire electrode after insertion in the cell by attaching suitable weights. Potential versus time measurements were made automatically and continuously by means of a Luggin probe and associated salt bridge and saturated calomel reference electrode in conjunction with an electrometer and recording potentiometer. As the wire specimen was stressed at 75% of its tensile strength in the environment, a temperature-controlled heating mantle was used to maintain the solution at constant temperature. The experiment was terminated at fracture, or in 6 days when the alloy was not susceptible to SCC.

Rotating Bending Corrosion Fatigue

Stress vs. cycles-to-failure studies of smooth fatigue specimens were carried out using a Krouse rotating bending fatigue machine. The fatigue apparatus was operated at 3000 RPM, which is equivalent to a cyclic stress reversal frequency of 50 hertz and a stress ratio $R=-1$. The standard Krouse fatigue machine was modified by the addition of a lucite environmental chamber for corrosion fatigue studies, as shown schematically in Fig. 1. A Schaar Sigmamotor tubing pump delivered the test fluid through Tygon tubing from a
Fig. 1. Schematic for corrosion fatigue apparatus.
two-liter reservoir at the rate of 15 liters per hour. The pulsations
of the pumping system were removed in a settling chamber, so that
a steady stream of fluid would flow over the test section of the
fatigue specimen. The fluid was then returned to the reservoir by
gravity flow.

Potential versus time measurements were made using a Luggin
probe connected to a saturated calomel electrode in conjunction with
an electrometer and recording potentiometer. To maintain a continuous
path of electrolyte, fluid flow to the specimen was supplied using
an annular tube surrounding the Luggin probe. At speeds up to 3000
RPM, the fluid maintained good contact with the rotating specimen
as it flowed over and around the test section.

Rotating bending fatigue specimens measured 1/2" diameter by
5" long, with a 2" radius reduced section giving a minimum cross
section of 1/4" diameter at the specimen center. Stressing of the
specimen was accomplished using a sliding weight to apply a bending
moment. A counter kept track of the number of stress cycles, and
a limit switch shut off the machine at specimen failure.

Corrosion Fatigue Crack Propagation

Fatigue crack propagation rates in air and aqueous salt solutions
were measured using an MTS closed-loop servo controlled hydraulic
test machine with a 50 kip load cell. For all crack propagation
tests, cyclic frequency was maintained at 10 hertz, using a stress
ratio R=0.1 and a haversine wave form. The specimens were short
(L/W = 0.92), clamped single-edge-notched sheet specimens, for which
an experimentally determined stress intensity calibration is given
in (3). Crack lengths were measured using a Gaertner traveling
microscope capable of measurements to .0001" accuracy.

The equipment for tests in liquid environments was similar to
that previously described for rotating bending tests, except that
no potential-versus-time measurements were made. A tubing pump
continuously supplied fluid to a lucite chamber attached to the
specimen, with gravity return flow to a four-liter reservoir.

Results and Discussion

Polarization and Potential-Time

Two parameters are important for a quantitative classification
of the corrosion behavior of active-passive alloys, (1) the break­
down potential above which the markedly increased titanium alloy
anode current indicates the breakdown of passivity and the onset of
pitting, and (2) the passive current or anode current generated in
the potential range where the alloy is passive, with a smaller
current indicating more nearly perfect passivity. Passivity is usually
associated with currents less than 100 \( \mu \text{a/cm}^2 \). Both of these parameters obtained from anodic polarization measurements in 0.17M NaCl and Hanks's solutions at body temperature (37°C) are summarized in Table IV along with long term isolated potentials taken from potential-time measurements at the end of 7 days. All of the alloys studied show very high breakdown potentials (above +1.35V) and were higher in Hanks's solution than in the 0.17M NaCl solution. The potentials of isolated titanium alloys ranged between +0.053 and +0.208V in 0.17M NaCl solution and between -0.195 and +0.218V in Hanks's solution. These data show that breakdown potentials for all alloys were considerably higher (more positive) than the highest potentials observed during long-term isolated exposure. Therefore, breakdown of isolated specimens, even after very long exposure, is quite unlikely.

Potential-time curves for isolated specimens (not shown) of all alloys exhibited similar behavior, i.e., the rising and steady potential that typifies the behavior of an alloy having a film that becomes repaired, thickens somewhat and remains intact. Alloys giving this type of curve can be considered for applications where long-term inertness is essential.

<table>
<thead>
<tr>
<th>METAL</th>
<th>Passive Current ( \mu \text{a/cm}^2 )</th>
<th>Potential (V vs. S.C.E.) (Breakdown)</th>
<th>Potential (V vs. S.C.E.) (Long-Term)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unalloyed Ti</td>
<td>9 ( \approx 0 )</td>
<td>2.05</td>
<td>1.75* (+.208)</td>
</tr>
<tr>
<td>8A-1Mo-1V</td>
<td>5</td>
<td>1.40</td>
<td>1.45 (+.168)</td>
</tr>
<tr>
<td>6A-4V</td>
<td>6</td>
<td>1.55</td>
<td>1.9 (+.183)</td>
</tr>
<tr>
<td>6A-6V-2Sn (YS 140 ksi)</td>
<td>5 ( \approx 0 )</td>
<td>1.45</td>
<td>1.73 (+.198)</td>
</tr>
<tr>
<td>6A-6V-2Sn (YS 180 ksi)</td>
<td>6</td>
<td>1.40</td>
<td>0.173 (+.053)</td>
</tr>
</tbody>
</table>

A=0.17M NaCl
B=Hanks Solution
* A maximum current of 125\( \mu \text{a} \) was recorded.
The passive current densities for Ti-8Al-1Mo-1V and Ti-6Al-6V-2Sn even at yield strength levels of 160 and 180 KSI were very low and compared favorably with unalloyed titanium and Ti-6Al-4V already in use for surgical implant applications. The stability of the passivity of titanium alloys 8Al-1Mo-1V and 6Al-6V-2Sn to very high potentials precludes breakdown of passivity by Cl; any alloy showing a breakdown potential above the reversible oxygen potential cannot suffer breakdown through the action of an oxygen-reduction cathode. These data are in good agreement with the work of Hoar and Mears (4) who obtained similar results for other titanium alloys.

Current-Time

Figure 2 contains current-time curves for the alloys polarized at their respective long-term potentials in Hanks's solution. The current density for each alloy decreased to the end of the experiment. Similar behavior was observed in 0.17M NaCl solution. This behavior is highly desirable for implants where the alloy remains in situ for long periods of time. Since current densities measured in the passive region represent the rates of conversion of metal into oxides having low solubilities and rates of dissolution in simulated body fluids, and the data show decreasing passive current densities, then, according to Hoar and Mears (4), even lower rates of oxide formation can be expected after still longer exposure. Also, the passive film still thickens and becomes a better barrier rather than dissolving at its outer surface.

Stress Corrosion Cracking

Figure 3 shows potential-time curves for Ti-8Al-1Mo-1V and Ti-6Al-6V-2Sn stressed at 75% of their tensile strength in Hanks's solution. The alloys are not susceptible to SCC in Hanks's solution. Similar results were obtained in 0.17M NaCl solution. For comparison, a potential-time curve for Ti-8Al-1Mo-1V similarly stressed in a methanol-HCl solution is included. In this environment the alloy fails in 45 minutes.

In Hanks's solution, in which the alloys did not fail, similar potential-time curves were observed. The potentials became more electropositive with time as was the case with the unstressed alloys. This represents film repair, the film becoming somewhat thicker with time and remaining intact. Where failure occurred in the methanol-HCl solution, the initial segment of the curve was characterized by a marked change of potential in the more negative direction followed by a more gradual negative shift. This induction or incubation period, during which corrosion is proceeding, is immediately followed by a marked shift in potential in the more active (negative) direction just prior to failure. The induction period is the major part of the life of the specimen.
Fig. 2. Current-time curves for alloys at controlled potential.
Rotating Bending Fatigue

Stress vs. cycles-to-failure (S-N) curves were determined in air and simulated body environments for smooth, unnotched specimens of Ti-6Al-6V-2Sn (Fig. 4) and Ti-8Al-1Mo-1V (Fig. 5). Air fatigue tests revealed that heat treatment had no apparent effect on the fatigue limit for either of the alloys. Ti-6-6-2 tested in three different heat treatment conditions exhibited a fatigue limit at 10 cycles of about 95 ksi; Ti-8-1-1 tested in two conditions showed a fatigue limit of about 85 ksi.

It can also be seen from Figs. 4 and 5 that testing in 0.17M NaCl solution and Hanks's solution had no significant effect on either the shape of the S-N curve or the fatigue limit for either alloy. The lack of environmental effect on the fatigue limit is not entirely unexpected. As corroborated in our study titanium and its alloys are known to be resistant to pitting and generalized corrosion in most aqueous chloride solutions at room temperature (5), including simulated body environments (4). It has also been shown in this study that smooth specimens of titanium are immune to stress corrosion cracking in 0.17M NaCl and Hanks's solution. The fatigue limit in an S-N plot is influenced primarily by those factors which have an effect on the crack initiation phase of the fatigue process, since the cyclic life \(10^7\) cycles is presumably long enough that a crack, once initiated, would have sufficient time to propagate to failure. The lack of pitting attack or severe generalized corrosion in simulated body environments appears to correlate with the absence of environmental effect on the initiation of either corrosion fatigue or stress corrosion cracks.

The lack of effect of environment on the life of specimens in the high stress/short life region of the S-N curve was more surprising. In this region, the crack propagation phase of the fatigue process constitutes an ever-increasing portion of the total cycles-to-failure as the alternating stress is increased. Since it is known that aqueous chloride environments cause an increase in the fatigue crack propagation rate in many titanium alloys (6), it was expected that the S-N curves in 0.17M NaCl and Hanks's solution would be shifted toward shorter cyclic lifetimes. It is evident from Figs. 4 and 5 that this did not happen: comparison of the data for these environments with the air fatigue data shows no significant difference. This may be partly due to normal scatter found in generating any S-N fatigue curve, and partly due to the fact that the crack initiation phase still occupies a considerable portion of the total cyclic life even at high stresses (see following section on the potential vs. time measurements).

In any case, the most important points which should be made are the lack of effect of the simulated body environments and heat treatment on the fatigue limit, since it is this part of the S-N curve which is most useful to the design engineer.
Fig. 3. Potential-time curves for alloys stressed in 0.17M NaCl solution and Hank's solution.

Fig. 4. Effect of environment on fatigue life of Ti-6Al-6V-2Sn.
Fatigue Crack Propagation

In order to clarify the effect of body environment on crack propagation, fatigue crack growth rates were measured in air, 0.17 M NaCl, and Hanks's solution, using single-edge-notch sheet specimens of annealed Ti-6Al-6V-2Sn. Fig. 6 shows that for stress intensity ranges (ΔK) up to about 30 ksi√inch, cyclic crack growth rates in simulated body environments are 3 to 4 times higher than in air. The data for 0.17M NaCl and Hanks's solution is nearly the same, and is also virtually identical with data for 3.5% (0.6M) NaCl obtained in another study using the same material (7).

The data shown in Fig. 6 indicate a moderate environmental effect on fatigue crack growth rates for Ti-6-6-2 in simulated body environments. Similar behavior has been observed in another implant material, type 316 stainless steel, when tested in Ringer's solution (8). Such behavior is not necessarily a major handicap in implant applications: stainless steel has been used for over thirty years with generally satisfactory results. However, it is desirable that design engineers be aware of the effects of environment on fatigue crack propagation as well as fatigue life.

Potential-vs-Time Measurements (In Fatigue)

In some of the rotating bending corrosion fatigue tests, open circuit potential was measured as a function of time. Two typical plots are shown in Fig. 7, with major features numbered. In all tests, prior to starting the fatigue machine, the potential was

![Graph showing potential-vs-time measurements](image)

Fig. 5. Effect of environment on fatigue life of Ti-6Al-6V.
steady or slightly increasing (Region 1). Upon starting the test there was an initial transient drop in potential, followed by an increase as the passive film reformed (Region 2). If the test was long enough, the potential would again become steady or increase gradually due to film formation (Region 3). However, the potential was always lower (more anodic) than Region 1, indicating a quasi-equilibrium between film rupture due to fatigue cycling and film repair. Prior to failure, there was another, more pronounced negative shift in potential. The first detectable shift in potential (Region 4) was assumed to correspond to fatigue crack initiation.
In the high stress/short life tests, the crack initiation point could not be accurately determined, since steady Region 3 behavior was not achieved by the time the crack had initiated. After crack growth started, the potential shifted steadily toward the anodic direction, culminating in specimen fracture (Region 5). Following this, the fractured surface gradually built up a passive film, and the potential shifted in the positive direction.

As estimated by the potential-versus-time plots, the crack propagation phase of the fatigue life occupied anywhere from about 8,000 to 25,000 cycles for Ti-8-1-1, depending on stress level. For Ti-6-6-2, where stress levels were higher, propagation took from about 5,000 to 10,000 cycles. Since no measurements were made for the two alloys at the same stress level, the effect of composition on crack growth behavior could not be determined. The magnitude of the anodic potential shift from Region 3 to fracture was generally about 1.0 ± 0.05 volt for Ti-6-6-2, and about 0.85 ± 0.1 volt for Ti-8-1-1. There was no consistent pattern to the quasi-steady state potentials in Regions 1 and 3. For Ti-6-6-2 they ranged from +0.04 to -0.145 volts vs. SCE; for Ti-8-1-1 they ranged from +0.02 to -0.30 volts vs. SCE.

**Conclusions**

1. The alloys studied exhibited optimum characteristics of corrosion resistance in both 0.17M NaCl and Hanks's physiological solution, i.e., a high breakdown potential, and a low passive current.
The stability of their passivity to very high positive potentials precludes breakdown of passivity by Cl; any alloy showing a breakdown potential above the reversible oxygen potential cannot suffer breakdown through the action of an oxygen-reduction cathode.

2. The potential-time and current-time behavior exhibited by the alloys are highly desirable for implants where long-term inertness is essential.

3. Stress corrosion experiments with smooth specimens demonstrated that the alloys were not susceptible to SCC in either environment.

4. Simulated body environments have no apparent effect on fatigue crack initiation for Ti-6-6-2 and Ti-8-1-1, as reflected in their lack of effect on the fatigue limit in rotating bending fatigue of smooth specimens.

5. For Ti-6-6-2, fatigue crack propagation rates in simulated body environments are higher than rates in air by a factor of between 3 and 4 at stress intensity ranges up to about 30 ksi \( \sqrt{\text{in}} \).

6. Fatigue crack propagation in simulated body environments is marked by a substantial shift (up to 1 volt) of open-circuit potential towards the anodic direction.

Based on this data, both Ti-8Al-1Mo-1V and Ti-6Al-6V-2Sn appear very promising as alloys for surgical implant applications. Ti-6-6-2 offers the additional benefit of being heat treatable to higher strength levels than the Ti-6Al-4V alloy currently in use. Suggestions for further study include the high-strength Beta III alloy, as well as continued work on pre-cracked specimens for SCC and corrosion fatigue crack propagation.

References


