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EFFECTS OF STATIC STRESS ON ANODIC POLARIZATION BEHAVIOR OF Ti-4.5Al-3V-2Mo-2Fe ALLOY

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ABSTRACT

Corrosion behavior of implant metals having applied stress must be quantified because these metals are often used under stress *in vivo*. The aim of the present study is to clarify the effects of static stress on corrosion behavior of Ti-4.5Al-3V-2Mo-2Fe alloy in a simulated physiological environment. An anodic polarization procedure was performed with applied static stresses in Ringer's solution at 37°C, from a free corrosion potential up to a potential of 4.0 V higher than the free corrosion potential. Then the potential was scanned in the cathodic direction. The specimen surfaces were observed using a Scanning Electron Microscope.

We conclude that constant compressive stress up to –800 MPa and tensile stress of below 100 MPa have little effect on corrosion behavior because both of the anodic polarization curves and the features of corroded surfaces were similar to those under zero stress. With applied static tensile stresses of 200 ~ 800 MPa, current density increased suddenly at about 4 V vs. SHE, which is about 1 V higher than the breakdown potential. Before the sudden current density increase, the corrosion reaction seems to be the same as the corrosion reaction under zero stress because the anodic polarization curves and the features of corroded surfaces were similar to those without an applied stress. The observations of corroded surfaces indicate that sudden current density increase at about 4 V vs. SHE is due to great dissolution in a localized area.

KEYWORDS

Titanium alloy, Biomaterial, Passivity, Corrosion resistance, Corrosion fatigue

1. INTRODUCTION

Corrosion of implant metal is detrimental for two reasons. First, corrosion fatigue is a major risk factor in fracture of implant metals [1]. Second, released metallic ions may be toxic [2]. Therefore, corrosion of implant alloys is a serious problem. Not only simple corrosion behavior but also corrosion behavior with applied stress must be clarified because implant metals are often used under stress *in vivo*. In recent years, titanium alloys have been widely used as biomaterials. Although the effects of cyclic load on corrosion behaviors of titanium alloys have been reported [3], no detail work has focused on the effects of static stress on its' corrosion behavior [4]. In the present study, to clarify the effects, anodic polarization tests were carried out in constant stress condition.

2. EXPERIMENTAL

2.1. Materials

A β rich, α+β type titanium alloy (Ti-4.5Al-3V-2Mo-2Fe; with the commercial name of SP-700) was used. This alloy was annealed at 800°C for 8 hours. The configuration of the test specimens is shown in Figure 1. The surfaces of the specimens were ground and polished electrolytically. To avoid preferential corrosion of edges, the specimens were covered with inert coatings, leaving an exposed surface area of 1 cm^2 (Figure 1).

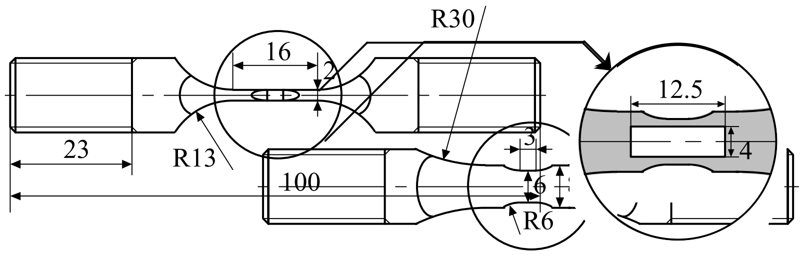

Figure 1: Configuration of the specimen

2.2. Corrosion test

Figure 2 shows the schematic of the corrosion test system; a platinum auxiliary electrode and an Ag/AgCl reference electrode were used. A Ringer's solution, a simulated physiological solution was used as the electrolyte. This solution was kept at a temperature of 37°C and was exposed to the atmosphere.

Fist, a specimen was mounted on a polarization cell and on the chuck of a servohydraulic test system. Then static stress was applied using the servohydraulic test system followed by filling the polarization cell with the solution. Cyclic, anodic, potentiodynamic polarization tests were carried out with an automatic polarization system. The open-circuit potential, i.e., the corrosion potential, was recorded after maintaining constant stress for 30 min. The potential was potentiostatically kept to the measured corrosion potential for 1 hour then scanned anodically at a scan rate of 0.167 mV/s, from the corrosion potential, up to the potential of 4.0 V higher than the corrosion potential. Then the potential was scanned in the cathodic direction at the same scan rate until the applied potential reached the corrosion potential. Such anodic polarization tests were conducted without an applied stress, with applied compressive stresses of –800 and –200 MPa, and with applied tensile stresses of 100 ~ 800 MPa. The specimen surfaces were observed using a Scanning Electron Microscope (SEM) to examine corrosion reaction of the samples.

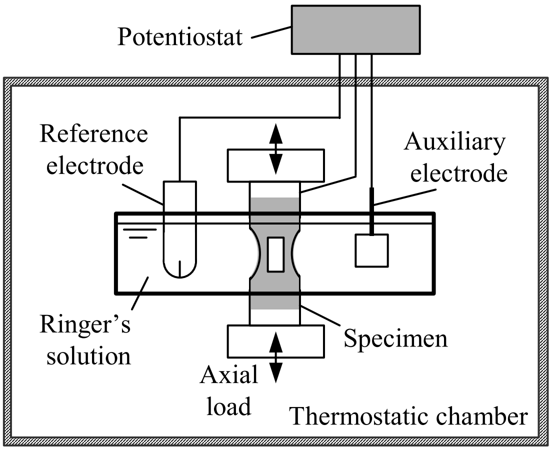

Figure 2: Schematic of the corrosion test system

3. RESULTS

3.1. Anodic polarization curve of the specimen without an applied stress

The solid line in Figure 3 (a) shows the anodic polarization curve of the specimen without an applied stress. It can be seen that passive current density is 3.0 μA/cm^2 (1 V vs. SHE) and breakdown potential is 2.5 V vs. SHE (We define the breakdown potential as the potential at which current density exceed 10 μA/cm^2). Above the breakdown potential, the current density increases significantly as the potential becomes more positive because pitting initiates and propagates. This region of the anodic polarization curve is called the transpassive region. The reverse sweep of the scan closely retraces the path of the forward scan. This indicates that the pitted region repassivates immediately. Consequently, Ti-4.5Al-3V-2Mo-2Fe alloy has a high corrosion resistance in Ringer's solution.

3.2. Anodic polarization curves of the specimens under applied compressive stresses

The Anodic polarization curves of the specimens with applied static stresses of –200 MPa (a dotted line in Figure 3 (a)) and –800 MPa were similar to the ones of the specimen without an applied stress. Figure 4 shows the passive current densities (solid squares) and breakdown potentials (open circles) of these tests. These values seem to be independent of stresses between 0 ~ -800 MPa. This implies that static compressive stress has no significant effect on corrosion behavior.

3.3. Anodic polarization curves of the specimens under applied tensile stresses

The anodic polarization curve of the specimen under an applied stress of 100 MPa is shown in the dotted line in Figure 3 (b). The curve is similar to the one without an applied stress. This suggests that static tensile stress of 100 MPa has no effect on corrosion behavior.

During the anodic sweep at below 3.8 V vs. SHE, the anodic polarization curve of the specimen under an applied tensile stress of 200 MPa (the broken line in Figure 3 (b)) is similar to the one of the specimen without an applied stress (the solid line in Figure 3 (a)). As shown in Figure 4, in this anodic polarization test, the passive current density (the solid square) and the breakdown potential (the open circle) are approximately the same as those of the specimen without an applied stress. However, at 3.8 V vs. SHE in a transpassive region, the current density suddenly increased to 200 mA/cm^2, and stayed at a high value during the cathodic sweep. Such sudden current density increase was also found with applied tensile stresses of 400 ~ 800 MPa at 3.8 ~ 4.1 V vs. SHE. These results suggest that static tensile stress of 200 ~ 800 MPa has no effect on corrosion behavior at below or about 4 V vs. SHE. However, this stress greatly accelerates dissolution at this potential in a transpassive region.

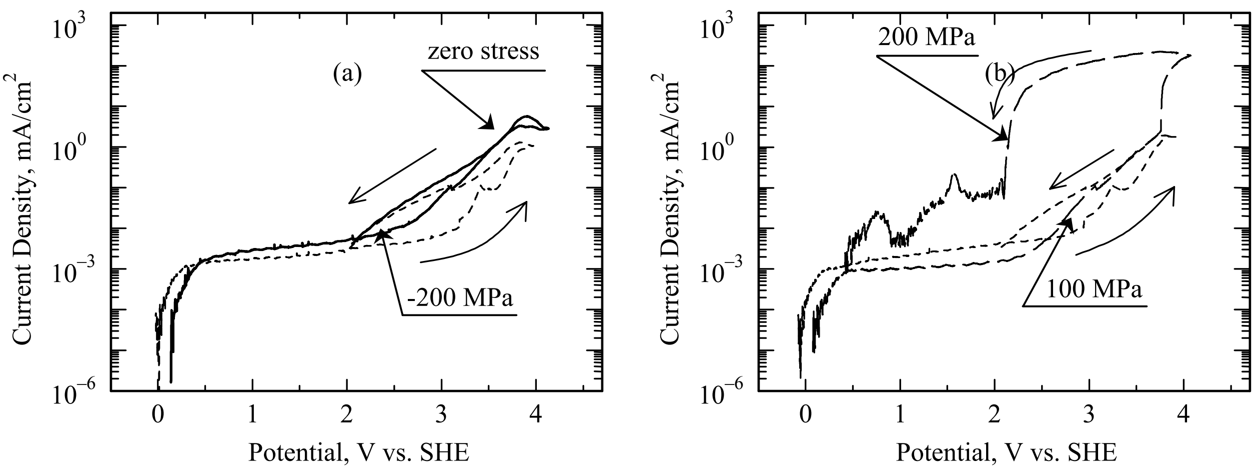

Figure 3: Anodic polarization curves for Ti-4.5Al-3V-2Mo-2Fe alloy in Ringer's solution at 37°C

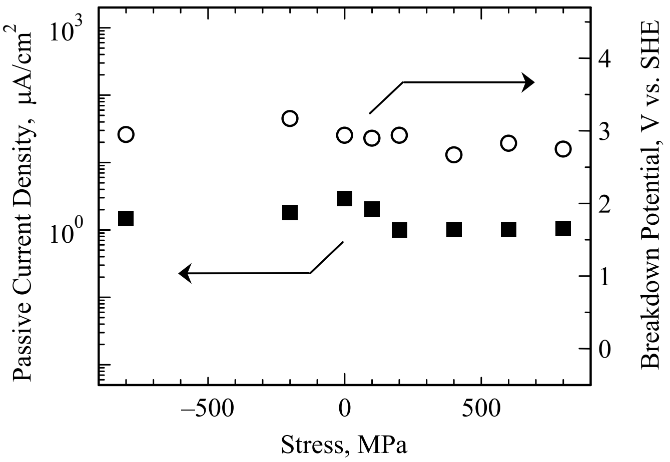

Figure 4: Passive current densities and breakdown potentials obtained by anodic polarization tests

3.4. Observation

In order to examine the corrosion reaction under tensile stress before the sudden current density increase at about 4 V vs. SHE, an anodic polarization test was conducted under an applied tensile stress of 400 MPa. After the current density reached 1 mA/cm^2, the test was terminated and the surface of the specimen was observed using SEM. A Typical feature of the corroded surface is shown in Figure 5. Dissolutions in the β-phase and corrosion products were found. Similar phenomena were also observed after the anodic polarization tests with compressive stress of –200 MPa and zero stress. Therefore, the corrosion reaction with either tensile stress or compressive stress turns out to be the same as the corrosion reaction under zero stress before sudden current density increase at about 4 V vs. SHE.

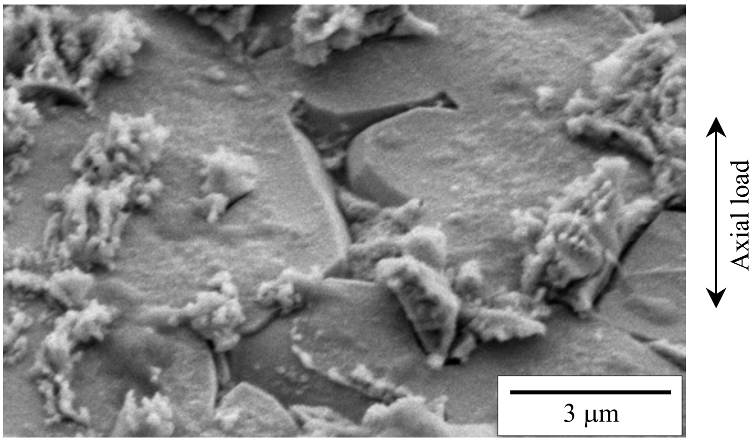

Figure 5: SEM observation of dissolutions in the β-phase and corrosion products

To explain the reason for the sudden current density increase at about 4 V vs. SHE, an additional anodic polarization test was carried out with a tensile stress of 400 MPa. The test was terminated 7 min after sudden increase, and the surface of the specimen was examined. Macroscopic damage at the center of the test surface was observed (Figure 6). However, the rest of the surface was similar to that of Figure 5. This means that the sudden increase in current density is probably because of a great dissolution in the localized area as shown in Figure 6.

Most of the test surfaces were damaged similarly and there was only one damage on one test surface after anodic poralization tests with constant stresses of 200 ~ 800 MPa.

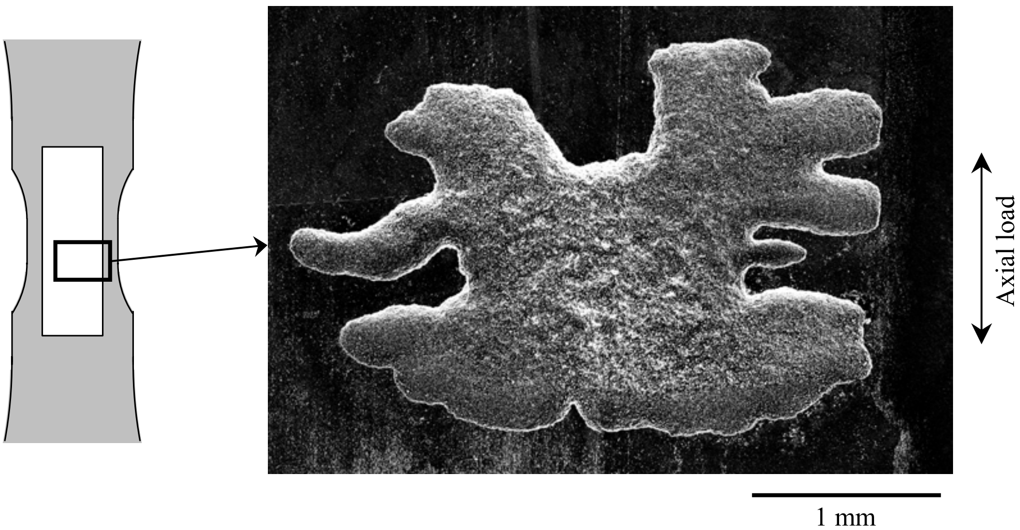

Figure 6: SEM observation of large damage at the center of test surface

4. DISCUSSION

In this study, the effects of static stress on corrosion behavior of Ti-4.5Al-3V-2Mo-2Fe alloy were investigated. We conclude that constant compressive stress and tensile stress of below 100 MPa have little effect on corrosion behavior because the anodic polarization curves and the feature of the corroded surfaces were similar to the one under zero stress (Figures 3 (a), and 4).

With applied static tensile stresses of 200 ~ 800 MPa at below or about 4 V vs. SHE, the anodic polarization curves and the surface feature were also similar to those without an applied stress (Figures 3, 4, and 5). Thus, we conclude that the corrosion reaction with static tensile stress of 200 ~ 800 MPa at below or about 4 V vs. SHE is the same as those under zero stress.

On the other hand, with static tensile stresses of 200 ~ 800 MPa, current densities increased suddenly at about 4 V vs. SHE in a transpassive region (Figure 3 (b)). To investigate the reason, anodic polarization with an applied stress of 400 MPa was conducted and terminated 7 min after sudden current density increase. Macroscopic damage was observed on the test surface (Figure 6) while the rest of the surface was similar to the one without an applied stress. From these results, static tensile stress of 200 ~ 800 MPa makes great dissolution in a localized area at about 4 V vs. SHE in a transpassive region. The shape of the damage (Figure 6) suggests that microscopic damage spread to the macroscopic damage. With these stresses, current densities kept at a high value after sudden current density increase and there was only one damage on each test surface after the anodic polarization tests. These results suggest that localized macroscopic damage propagates over most of the test surface.

In conclusion, static tensile stress of 200 ~ 800 MPa greatly accelerates dissolution at about 4 V vs. SHE in a transpassive region. This phenomenon might be the cause of corrosion fatigue and toxicity *in vivo*. Further study of the influence of stress on corrosion behavior of titanium alloy is needed to examine whether this phenomena would take place *in vivo*.

5. CONCLUSIONS

In the present study, anodic polarization tests were carried out in constant stress conditions to clarify the effects of static stress on corrosion behavior of Ti-4.5Al-3V-2Mo-2Fe alloy in Ringer's solution at 37°C. We conclude as follows.

Static compressive stress up to -800 MPa and tensile stress of below 100 MPa appears to have little effect on corrosion behavior.

With applied static tensile stresses of 200 ~ 800 MPa, current density increases suddenly during the anodic polarization tests at about 4 V vs. SHE, which is about 1 V higher than the breakdown potential for pitting. At below or about 4 V vs. SHE, the corrosion reaction is the same as the corrosion reaction under zero stress. On the other hand, great dissolution takes place in a localized area at about 4 V vs. SHE, while the rest of the test surface is similar to the one below this potential.

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