ELECTROCHEMICAL APPROACH TO THE DEVELOPMENT OF A SIMULATING PHYSIOLOGICAL ENVIRONMENT FOR STRENGTH EVALUATION OF HARD TISSUE REPLACEMENT MATERIALS $B.\ J.\ Lee^*,\ J.\ Komotori^{**}\ and\ M.\ Shimizu^{**}$

To develop a simulating physiological environment for strength evaluation of femoral hip prosthesis materials (Ti-6Al-4V alloy), corrosion tests on Ti-6Al-4V alloy were carried out by means of applying a uniform current in order to accelerate the corrosion behavior in the simulated physiological environment. A potential difference was scanned to detect any variations of the resistance of specimens. Corrosion behavior was monitored by scanning potential differences, and an empirical formula was proposed in order to control the corrosion behavior of Ti-6Al-4V alloy.

INTRODUCTION

The modular femoral hip prosthesis consists of a titanium-alloy femoral stem and a cobalt-alloy femoral head. This type of prosthesis has been increasingly used as compared with a fixed head femoral prosthesis. However, corrosion has been reported to occur when different materials were used for the head and stem of the modular design implants (1). Such corrosion damage could limit the service life of the prostheses due either to tissue reaction to corrosion production, or to failure of the prostheses (2).

Therefore, it is very important to predict the expected service life of the prosthesis in the physiological environment. In our previous study, we observed a great number of corrosion pits on the surface of the modular femoral hip prosthesis which was retrieved 58 months after insertion (3). However, these effects on fatigue characteristics have not been well understood.

The aims of the present study are (i) to develop an accelerated laboratory corrosion testing method which simulates the physiological corrosion environment and (ii) to propose an empirical formula which represents the relationship of the maximum size of corrosion pit,

^{*} Graduate School of Engineering and Science, Keio University.

^{**} Department of Mechanical Engineering, Keio University.

applied current and corrosion time in order to control the corrosion behavior of Ti-6Al-4V alloy in this simulated physiological corrosion environment.

EXPERIMENTAL PROCEDURE

Ti-6Al-4V alloy (Table 1) was used for this study. The material was annealed at 900°C for 24hrs and machined into a simple cylindrical shape as shown in Figure 1. The exposed surface of the specimens was polished using emery paper. Every specimen was then vacuum-annealed at 600°C for 2hrs to eliminate residual stress due to machining. Then, the specimens were masked with insulating paint to prevent edging effects and to expose an area of 1cm^2 for testing.

The experimental apparatus consisted of a corrosion control part and a thermostatic chamber. This is illustrated schematically in Figure 2. All the tests were performed at 38 ± 0.5 °C in a Ringer's solution (Table 2).

The specimens were polarized by means of applying a uniform current density in order to accelerate corrosion behavior. Variations of potential differences during the tests were monitored and recorded using a computer. In order to limit galvanic corrosion effects, we used the same Ti-6Al-4V alloy for the specimen and the cathodic electrode.

TABLE I Chemical composition of Ti-6Al-4V alloy (wt. %)

C	V	Al	N	О	Fe	Н	Ti
0.01	4.00	6.07	0.01	0.17	0.13	0.001	Bal

TABLE 2 Chemical composition of Ringer's Solution (wt. %)

NaCl	KCI	$CaCl_2$	NaHCO ₃	H_2O
0.85	0.04	0.02	0.02	99.07

RESULTS AND DISCUSSION

The Relationship between Potential Differences and Corrosion Behavior

Corrosion tests were carried out at five different uniform current densities from 0.005mA/cm^2 to 10mA/cm^2 for 1hr. Figure 3 shows the variation curves of potential differences during the tests. In the cases of high current density $(0.1 \text{mA/cm}^2 \sim 10 \text{mA/cm}^2)$, the potential difference increases sharply after the first few seconds, and then drops rapidly. In this case, corrosion pits were observed on the surface of the specimen. However, in the case of low current density $(0.01 \text{mA/cm}^2 \sim 0.005 \text{mA/cm}^2)$, the peak of the variation curves of potential differences is not seen clearly. In the latter two cases, corrosion pits were not observed.

To understand the decrease in potential differences, additional tests were carried out using two different specimens with the same current density, 0.5mA/cm^2 : one was stopped after a decrease in the potential difference was observed (Figure 4, A) and the other was stopped before a decrease was observed (Figure 4, B). Corrosion pits were observed only in the former case. The reason for this may be explained as follows. Cl' ions destroyed passivity by displacing adsorbed O ions when a sufficient concentration corresponded to the critical potential (4). As the result of this, the resistance of the specimens is dropped, thus, potential differences are decreased.

From the results mentioned above, it is concluded that corrosion behavior of Ti-6Al-4V alloy can be monitored by scanning the variation of potential differences using voltmeter.

The Relationship among Maximum Size of Corrosion Pit, Applied Current and Corrosion Time

From previous results, total corrosion time can be separated into two parts: one is the induction period, T_s , for pitting which is the time required for supposed penetration of Cl ions through the oxide film (from a to b in Figure 5), and the other is the progress period for pitting, T_p , which is the time after the destruction of the oxide film to the end of the tests (from b to c in Figure 5).

In this chapter, an empirical formula, which represents the relationship among maximum size of corrosion pit, applied current and corrosion time, is proposed.

In the first step, the relationship between current density, i, and induction period for pitting, T_s , was determined experimentally (Fig. 6). They satisfy the equation

$$T_S = C_1 i^{-\alpha} \qquad \dots (1)$$

where C_1 and α are experimental constants. In this investigation, C_1 =36.6 and α =1.

Next, in order to obtain a correlation between corrosion pit size and corrosion time, the value of $\sqrt{\text{area}_{\text{max}}}$ (which is the maximum size of the square root of the projected area of corrosion pits onto the maximum principal stress plane) was measured by using a scanning laser microscope.

The relationship between the progress period for pitting, T_p , and \sqrt{area}_{max} in each applied current density is shown in Figure 7, where the logarithm of \sqrt{area}_{max} is plotted as a function of the logarithm of T_p . The equation for \sqrt{area}_{max} can be expressed as

$$\sqrt{\text{area}}_{\text{max}} = f_1(i) \text{ Tp}^{1/3}$$
(2)

Total corrosion time, T. calculated from the sum of Eq.1 and Eq.2, is expressed as

$$T = C_1 i^{-\alpha} + f_2(i) \left(\sqrt{area}_{max} \right)^3 \dots (3)$$

where $f_2(i)$ is the function of the logarithm of the applied current density, i, as shown in Figure 8. Thus, $f_2(i)$ is given below,

$$f_2(i) = C_2 i^{-\beta}$$
(4)

where $C_2 = 2.4 \times 10^{-4}$, b = 0.45.

Using Eq (4), the total corrosion time, T, becomes

$$T = C_1 i^{-\alpha} + C_2 i^{-\beta} \left(\sqrt{area}_{max} \right)^3 \qquad (5)$$

Eq (5) can be used for the prediction of the corrosion pit size within a given period of time.

CONCLUSIONS

- (1) Corrosion behavior of Ti-6Al-4V alloy in a simulated physiological environment can be monitored by scanning the variations of potential differences with an accelerated laboratory corrosion testing system which has been developed in this study.
- (2) An empirical formula, which represents the relationship of the maximum size of corrosion pits, applied current density and corrosion time, is proposed in order to predict the maximum size of corrosion pits produced in a simulated physiological environment.

REFERENCE

- Jill S. Kawalec, Stanley A. Brown, Joe H. Payer, and Katharine Merritt, J. of Bio medical Materials Research. Vol. 29-7., 1995, pp. 867-873.
- (2) S. A. Brown, C. A. C. Flemming, J. S. Kawalec, and H. E. Placko, J. Applied Biomaterials, Vol. 6., 1995, pp. 19-26
- (3) Lee, B.J., Komotori, J. and Shimizu, M. "Corrosion Damage in Retrieved Femoral Hip Prosthesis", ICM&M'97, Tokyo, Japan, "Environment Effect". Edited by H. Nakamura, JSME Press, 1997.
- (4) H. Leckie, H. Uhlig, J. the Electrochemical Society, Vol. 113, No. 12, 1966, pp. 1262-1267.

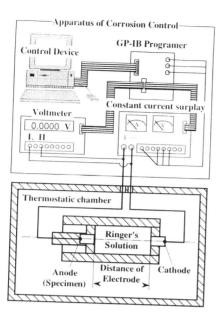


Figure 2 Schematic illustration of accelerated laboratory corrosion testing system

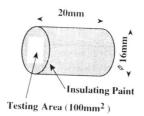


Figure 1 Schematic illustration of specimen

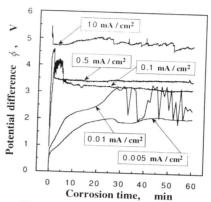


Figure 3 Variation curves of potential differences during the tests

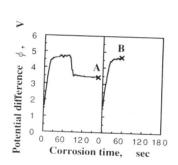


Figure 4 Variation curves of potential differences in 0.5mA/cm²

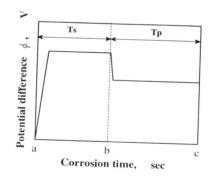
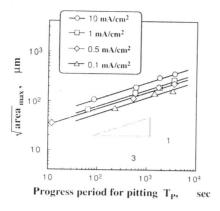
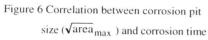


Figure 5 Schematic illustration of induction period and progress period for pitting





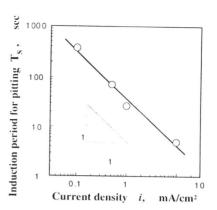


Figure 5 Effect of current density on induction period for pitting

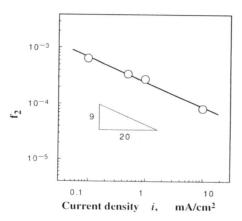


Figure 7 Relationship between f₂ and current density