Numerical Simulation of Tribocorrosion of CoCr Alloy and Ti with Galvanic Coupling in Simulated Body Fluid

Sayaka Miyabe*2, Norifumi Fujii and Shinji Fujimoto

Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

The artificial hip joints have galvanic couple between femoral head made of CoCr alloy and stem made of Ti or Ti alloy, and are subjected to high levels of mechanical stress. Therefore, tribocorrosion of artificial hip joints has been frequently reported. In this study, we performed the first electrochemical numerical simulation for CoCr alloy and Ti with friction in simulated body fluid. We constructed single metal model and galvanic couple model to investigate the effect of the cathodic reaction on the tribocorrosion behavior. In single metal model, CoCr alloy with friction is referred to as CoCr(Tribo.). In galvanic couple model, CoCr alloy with friction in contact with Ti is referred to as CoCr(Tribo.)–Ti. In single metal model, the current density of CoCr(Tribo.) was higher than that of Ti(Tribo.). For the CoCr alloy with friction, the current density of galvanic couple model (CoCr(Tribo.)–Ti) was higher than that of single metal model (CoCr(Tribo.)). The current density of both single metal model and galvanic couple model increased as the increase in area of the non-friction part increased. The current density of CoCr(Tribo.)–Ti was highest, and the rate of increase in current density with the increase in area was also highest.

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1. Introduction

Metallic materials are often applied as medical devices (implants) embedded in the human body because of their excellent mechanical properties. Currently, pure Ti and Ti alloys, CoCr alloys, Type 316L stainless steel, etc. are widely employed as biomedical materials. These materials exhibit high corrosion resistance, stemming from the passive film which is a thin and dense oxide film formed on the metal surface. When the passive film is damaged, the exposed surface is immediately recovered (repassivation) in the surrounding environment, thus corrosion resistance is maintained. However, inorganic ions (e.g. Cl−) and organic substances such as amino acids, proteins and cells comprising the living body suppress repassivation, then enhance the corrosion of the implant. Furthermore, these medical implants constantly undergo mechanical stress originating from the body weight and motion; for instance, artificial hip joints are repeatedly subjected to loads several times that of the body weight and to various types of degradation, such as wear, fatigue and stress corrosion cracking. When the passive film is breakdown by a repeated load, the repetition of exposure and recovery of new surface results in progress of the environmentally induced degradation. Particularly, the degradation originating from the simultaneous action of wear and corrosion is called tribocorrosion.

An artificial hip joint comprises a sliding bone head, typically consisting of wear-resistant CoCr alloys, and a stem inserted into the femur, usually made of bone-compatible pure Ti and Ti alloys; therefore, these dissimilar metallic materials are constantly in direct contact with each other. Different kinds of degradations, such as wear and crevice corrosion, have been reported to occur at the tapered part where the stem is inserted into the bone head. According to some reports, 0.5–4.0% of the implanted artificial hip joints had been failed at the tapered part. Previous tribocorrosion tests for CoCr and Ti alloys revealed that the larger current was observed for sample coupled with another kind of metal than that of a single metal. As tribocorrosion is affected by both the cathodic reaction at the non-wear part as well as the anodic reaction at the wear part, it is worth studying the effect of the cathodic reaction on tribocorrosion. However, the concurrent monitoring of the anodic and cathodic currents, both locally and separately during the experiments, is a highly challenging task. Although numerical simulation-based methods are capable of performing such complicated analyses, the numerical simulation on electrochemical reactions of tribocorrosion has not been performed yet. Considering the above mentioned facts, the present study utilized both experimental and numerical analytical models to investigate and comprehend the mechanisms underlying tribocorrosion in CoCr alloy and Ti galvanic couples, and especially the influence of cathodic reactions on the evolution of this phenomenon.

2. Analytical Model

Figure 1 illustrates the geometry of the two-dimensional tribocorrosion models studied herein. In the single metal model (Fig. 1(a)), a 7 mm area on the left side of electrode A was designated as the wear area; however, the actual friction mainly occurred in the central 1 mm region of the wear area. The right part (p mm) of electrode A was not subject to friction and was therefore designated as the non-wear area. Figure 1(b) illustrates a galvanic couple model. Electrode A, a part of which was subjected to friction as mentioned above, was connected to electrode B of another kind of metal with a length of p mm. For both models, the wear area of electrode A comprised a friction part (1 mm) in the center and two non-friction parts (3 mm each) adjacent to either side of the friction part. The single metal model (p = 0 mm) corresponds to the cross section (Fig. 2(b), dashed-dotted

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*2Corresponding author, E-mail: miyabe@mat.eng.osaka-u.ac.jp
line) perpendicular to the wear direction at the center of the disk sample used in the polarization test described in Section 3. An electrolyte layer with a thickness of 2 mm covered the electrodes.

In this study, the potential distribution was assumed to follow the Laplace equation. The current density \( i \) and the potential \( \varphi \) of the electrolyte were described as the following eqs. (1) and (2):

\[
\begin{align*}
    i &= -\sigma \nabla \varphi \quad (1) \\
    \nabla^2 \varphi &= 0 \quad (2)
\end{align*}
\]

A minimum essential medium Eagle, alpha modification (\( \alpha \)-MEM) simulated body fluid was used as an electrolyte medium in this study. The measured conductivity of this solution, \( \sigma \), was 1.5 Sm\(^{-1}\) at 37°C. The polarization characteristics of the electrodes required for the calculations were obtained from the potentiodynamic polarization curves described in Section 3. Hereinafter, the single metal model of electrode A (CoCr) (Fig. 1(a)) was referred to as CoCr(Tribo.), and the galvanic couple model of electrode A (CoCr) with electrode B (Ti) (Fig. 1(b)) was referred to as CoCr(Tribo.)-Ti.

The numerical simulation was conducted using the finite element method (FEM) simulation software COMSOL Multiphysics 5.3. In the present study, the steady state calculations were performed without considering the factor of elapsed time or the chemical reactions of ionic species in the solution.

### 3. Electrochemical Tests for Determining the Polarization Function

To measure the polarization characteristics of each electrode under wear or static states, electrochemical tests were performed using a pin-on-disc type friction player (FPR-2100, Rhesca). Figure 2 shows a schematic illustration of the equipment and the disk sample. A rod of ultra high molecular weight polyethylene (UHMWPE) with a diameter of 5 mm, length of 18 mm, and tip radius of 15 mm was used as the pin sample. The square-shaped CoCr alloy or pure Ti disk samples of 20 \( \times \) 20 \( \times \) 2 mm were mirror polished, and then insulated with silicone rubber and polytetrafluoroethylene (PTFE) tape, leaving an exposed area of approximately 1.8 cm\(^2\). Subsequently, the sample was autoclaved at 121°C for 15 minutes and then immersed in the \( \alpha \)-MEM solution for 1 day. A 1 kg load was applied to the pin sample, and the disk sample was reciprocally rotated with a rotation radius of 15 mm and rotation angle of 60° at 15 mm/s. Electrochemical measurements were performed in the \( \alpha \)-MEM solution at 37°C using a three-electrode cell with a Ag/AgCl (3.33 M KCl) as the reference electrode and a platinum wire as the counter electrode. In order to determine the potential range of the numerical simulation, the change in the open circuit potential after the start of wear was measured prior to the potentiodynamic polarization. Figure 3 illustrates the potential changes of the CoCr alloy and pure Ti for 2500 s after the start of wear. The static state potentials (before wear) of the CoCr alloy and pure Ti single metal models were approximately \(-0.086\) and \(-0.013\) V, respectively. Approximately 500 s after the start of wear, the potentials reached almost constant values (assumed as the steady state). The steady state potentials of the CoCr alloy and pure Ti single
metal models were determined to be $-0.35$ and $-0.22$ V, respectively. One hour or more after the start of wear (under wear state), the potentiodynamic polarization curve was measured from the open circuit potential to $+1$ V for the anodic polarization and to $-1$ V, for the cathodic polarization with a sweep rate of 1 mV/s. The polarization curve under static state (without friction) was obtained. As shown in Fig. 4, the current density in the anodic polarization curves under wear state was higher than that under static state. On the contrary, the cathodic polarization curves showed a relatively equivalent current density regardless of the friction.

4. Polarization Functions

4.1 Polarization functions for the numerical modeling

To model the electrochemical process, numerical functions describing the relationship between the potential and current density of both the anodic and cathodic reactions were required. In this study, it was necessary to quantify both the anodic and cathodic polarization functions (with and without wear) for the CoCr alloy and pure Ti. The anodic and cathodic reactions exhibited overlap in the experimentally measured polarization curves, especially near the corrosion potential. Therefore, it was necessary to separate the cathodic and anodic currents from each polarization curve. The procedure followed to determine both the anodic and cathodic reaction rates as a function of potential from the polarization curves, is described in the following subsection.

4.2 Formulation of the cathodic reaction

As wear did not significantly affect the cathodic polarization patterns, the equation for the cathodic reaction was derived from the cathodic polarization curve under static state (Fig. 4). The superimposition of the anodic current on the cathodic current was almost negligible in the potential range from $-0.40$ to $-0.10$ V for the CoCr alloy and from $-0.25$ to $-0.15$ V for pure Ti. The correlation between the cathodic current and the potential in these potential ranges was approximated as an exponential function after averaging the current to eliminate noise. Then, the function was divided by the exposed area to obtain the cathodic current density function, $F_{ic}$, that of CoCr alloy and Ti are expressed in the following eqs. (3) and (4), respectively:

$$F_{ic} (E) = -0.011 \exp (-14.9 E) \quad (3)$$
$$F_{ic} (E) = -0.037 \exp (-11.1 E) \quad (4)$$

4.3 Formulation of the anodic reaction

The anodic polarization was also formulated using the polarization curve shown in Fig. 4. To compensate for the effects of the cathodic reaction on the anodic polarization curve under wear conditions, the anodic current obtained from the experiments was similarly approximated as an exponential function after subtracting the cathodic current calculated from eqs. (3) and (4) and then, divided by the area of the friction part to obtain the anodic current density function, $F_{ia}$, of the CoCr alloy and pure Ti on the wear parts are given by eqs. (5) and (6), respectively:

$$F_{ia} (E) = 9.305 \exp (4.62 E) \quad (5)$$
$$F_{ia} (E) = 3.870 \exp (2.17 E) \quad (6)$$

The anodic reaction rates both the non-friction part and the non-wear area were also formulated after subtracting the anodic current density using $F_{ia}$, the similarly obtained anodic current density functions, $F_{ia'} (E)$, of the non-friction
part and non-wear area for the CoCr alloy and pure Ti are given by eqs. (7) and (8), respectively:

\[
F_{i_a}(E) = 0.061 \exp(5.56E) \\
F_{i_a}'(E) = 0.046 \exp(2.64E)
\]

Equations (3)-(8) are plotted in Fig. 5 for the potential range under wear state.

5. Numerical Simulation of Tribocorrosion

5.1 Numerical simulation of single metal model

Figure 6 shows the calculated distribution of current density and potential in the electrolyte over the CoCr alloy and pure Ti single metal models subjected to local friction (Fig. 1(a), \( p = 0 \) mm). The numerical calculations for the friction part were performed by using the anodic (eqs. (5) and (6)) and cathodic (eqs. (3) and (4)) reactions under wear state, as well as the anodic (eqs. (7) and (8)) and cathodic (eqs. (3) and (4)) reactions under static state. Regardless of the metal species, the current density in the electrolyte was notably increased in the regions adjacent to the friction part, demonstrating a maximum at the boundary between the friction and the non-friction part. The current density of CoCr(Tribo.) was larger compared to that of Ti(Tribo.). Additionally, the potentials in the electrolyte were overall less noble in the areas surrounding the friction part, with CoCr(Tribo.) exhibiting a less noble potential than Ti(Tribo.): \(-0.33\) and \(-0.24\) V, respectively. These results corresponded well with the calculated steady state potentials under friction (\(-0.35\) and \(-0.22\) V, respectively) (Fig. 3). Therefore, the validity of the numerical simulation results was confirmed.

5.2 Numerical simulation of galvanic couple model

Numerical simulations were also performed for the galvanic couple models (Fig. 1(b)), under the conditions that the p-length of the electrodes A and B were both 7 mm and that the electrode reactions were the same as those described in Section 5.1. Figures 7(a) and 7(c) show the calculated current density distributions for the CoCr(Tribo.)–Ti and Ti(Tribo.)–CoCr galvanic couple models, respectively. The CoCr(Tribo.)–Ti and Ti(Tribo.)–CoCr galvanic couple models current density distributions of the single metal models (\( p = 7 \) mm, Fig. 1(a)), CoCr(Tribo.) and Ti(Tribo.) are presented in Figs. 7(b) and 7(d) for comparison. The
CoCr(Tribo.)–Ti and Ti(Tribo.)–CoCr galvanic couple models demonstrated current densities of 7.6 µA/cm² and 3.0 µA/cm² at the centers of their corresponding function areas (Figs. 7(a) and 7(c)), respectively. This means that the current density at the friction part of CoCr(Tribo.)–Ti in the galvanic couple model was larger than that of Ti(Tribo.)–CoCr. Furthermore, the current density at the center of the friction part of CoCr(Tribo.) in the single metal model (Figs. 7(a)) was 7.0 µA/cm², which was slightly lesser than that of CoCr(Tribo.)–Ti in the galvanic couple model. On the other hand, the current density of the friction part of Ti(Tribo.) in the single metal model (Fig. 7(d)) was 3.3 µA/cm², which was larger than that of Ti(Tribo.)–CoCr in the galvanic couple model (Fig. 7(c)).

In order to investigate the effect of the non-wear area on tribocorrosion, a numerical simulation was performed for the part including the wear area, while changing the length of the non-wear part (p mm, Figs. 1(a) and (b)) from 0 to 140 mm. Figures 8(a) and (b) respectively demonstrate the changes in current density and potential at the center of the friction part as a function of the area ratio (p/7). By comparing the results for the same area ratio, the largest current density was observed for CoCr(Tribo.)–Ti, followed by CoCr(Tribo.)–Ti(Tribo.), and Ti(Tribo.)–CoCr. This behavior suggested that pure Ti contributed to the corrosion of the friction part more than the CoCr alloy, regardless of the material on the friction part (CoCr or Ti). While the corrosion potential of pure Ti under static state was nobler than that of the CoCr alloy (Fig. 3), the potential of the friction part (regardless of the material) was nobler when the adjacent non-wear area consisted of pure Ti (in comparison with CoCr alloy) (Fig. 8(b)). Namely, the current density of the friction part accompanied by the non-wear area of Ti was larger than that by the non-wear area of CoCr alloy, owing to the augmented anodic reaction at higher potential (Figs. 4 and 5). Furthermore, in any case, the current density increased along with the increased area ratio, p/7. As the area ratio was raised from 0 to 20, the current densities of Ti(Tribo.) and Ti(Tribo.)–CoCr increased by 1.5 times and 1.3 times, respectively, whereas the current densities of CoCr(Tribo.)–Ti and CoCr(Tribo.)–CoCr increased by 2.5 times and 2 times, respectively. In particular, the friction part of the CoCr alloy exhibited a significantly increased current density compared to that of pure Ti. This result was in good agreement with the higher anodic reaction rate of the CoCr alloy (compared to that of pure Ti) under wear state (Fig. 5). Namely, the notably increased current density at the friction part of CoCr(Tribo.)–Ti with the increasing area ratio, p/7, was derived from the enhanced anodic currents induced by the cathodic reactions in both the wear and non-wear areas. Thus, it was concluded that the tribocorrosion rate was highly affected by both the material and the surface area that was connected to the metal and/or alloy subjected to wear. In particular, the tribocorrosion rate of the CoCr alloy was significantly stimulated by the connected pure Ti with a larger surface area.
6. Conclusion

(1) The numerical simulation for electrochemical reactions of tribocorrosion was performed for the first time. The calculated potentials of the CoCr alloy and pure Ti single-metal models that were partially worn within an α-MEM electrolyte were consistent with the corresponding experimental results, verifying the validity of the simulation results.

(2) In the single metal model, the CoCr alloy exhibited a larger current density at the center of its friction part, compared with that of pure Ti. The corresponding current density at the center of the friction part of galvanic couple model for the CoCr alloy was slightly larger than that of the single metal model.

(3) The anodic current density of the friction part increased along with the increased non-wear area for both the single metal and galvanic couple models. The largest current density was observed at the friction part of CoCr alloy connected to pure Ti as the non-wear part. Furthermore, the maximum tribocorrosion rate was confirmed by the increasing the non-wear area of pure Ti.

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