

FRETTING CORROSION OF IMPLANTS: AN ELECTROCHEMICAL APPROACH

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INTRODUCTION: Fretting corrosion of implants arises from micro motions occurring at the bone/implant interface. It is known to cause degradation of femoral stems of metallic implants leading to the release of wear particles and oxidized products into the body. Depending on their amount and size, wear fragments can lead to inflammation of the surrounding tissue and to loosening of the implant. The extent of fretting corrosion depends on many factors and synergistic effects between mechanical and electrochemical degradation mechanisms (called tribocorrosion) are of crucial importance [1].

The main mechanical factors are the contact pressure, slip amplitude at the interface and the frequency of movement, the latter depending on the age and activity of the patient. Osteoporosis affects the mechanical properties of bone and thus influences the stiffness of the contact. In addition, chemical parameters are critical. Indeed, the presence of a passive oxide film at the surface of the metallic implant is at the origin of the good biocompatibility of titanium alloys. However, the periodic removal and reformation of the passive oxide film under fretting conditions can lead to a significant increase in corrosion and in the rate of formation of wear fragments.

There is a need to better understand the mechanism of generation of wear fragments under tribological conditions typical for bone-implant interfaces. For this reason, an experimental apparatus has been developed which permits to carry out fretting studies under controlled mechanical and chemical conditions in simulated biological environments. In particular, the apparatus allows one to carry out experiments under potential control using the implant material as an electrode in an electrochemical cell.

METHODS: The apparatus consists in a rigid stainless steel structure with a mobile beam. When the mobile beam is moved upwards, the flat surface of the metal sample (usually Ti6Al4V) enters into contact with an alumina ball (or another material) used as antagonist. The normal force is controlled by a rotating screw pressing the contact along the z axis via a spring of variable stiffness. The oscillation of the metal sample is controlled by a piezo-actuator,

which allows for different amplitudes and frequencies. A force sensor monitors the evolution of the normal and the tangential forces. The contacting surfaces subjected to fretting are immersed in a liquid electrolyte as shown in Fig.1. The metal sample forms the anode in an electrochemical cell. Critical mechanical and electrochemical quantities are monitored in real time. The biological medium is simulated by a solution of 0.9 %wt NaCl. Although the experimental device offers temperature control of the solution, all experiments described here were performed at room temperature. An anodic potential of 0.5 V was applied with respect to the Ag/AgCl reference electrode.

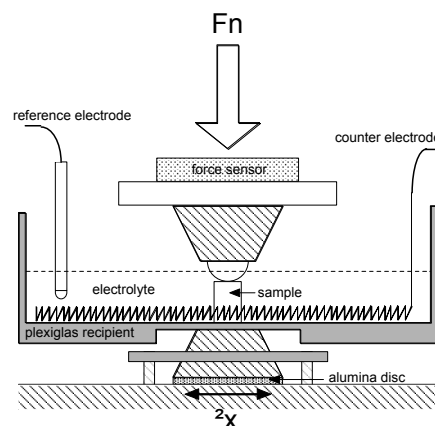


Figure 1: Schematic of the contact and the electrochemical cell.

RESULTS: As an illustration, Figure 2 shows the evolution (a) of the friction coefficient, (b) of the anodic current and (c) of the position of the antagonist with time. (amplitude: 150 μm , frequency: 1 Hz, normal force: 10 N, applied potential: +0.5 V). The monitoring of position of the antagonist permits to measure in situ the wear rate. In Fig. 2, rubbing starts at 300 s and stops at 900 s. To get more information on the nature of wear fragments formed under the present experimental conditions worn surfaces were observed with the scanning electron microscope. Fig. 3 shows a worn surface resulting from fretting for 5 hours at an amplitude of 150 μm , a frequency of 1 Hz, a normal force of 10N and an applied potential of 0.5 V

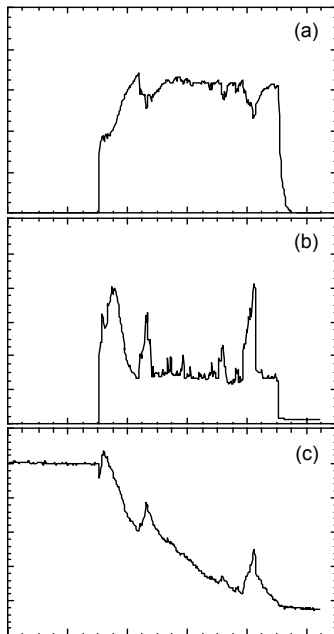


Figure 2: Friction coefficient (a), Current (b), Linear wear (c) measured during a fretting experiment ($150\ \mu\text{m}$, $1\ \text{Hz}$, $10\ \text{N}$, $+0.5\ \text{V}$). Rubbing starts at $300\ \text{s}$. and stop at $900\ \text{s}$.

DISCUSSION & CONCLUSIONS: At the onset of rubbing the current increases markedly. This confirms that rubbing damages the passive film and leads to anodic metal oxidation. This electrochemical contribution to material loss can be calculated by integrating the measured current and applying Faraday's law, assuming that titanium oxidation to the four valent state is the only anodic reaction. Calculations for experiments carried out at a slip amplitude of $30\ \mu\text{m}$ and an applied potential of $+0.5\ \text{V}$ show that the electrochemically oxidized material represents between 16 and 34 % of the total wear volume. Indeed, there seems to be a correlation between the current peaks, the friction coefficient variations and the wear rate shown in Fig. 2. These peaks can be explained by postulating that particles detach from the surface and form a third body. Their presence in the contact leads to a rise in the antagonist and a lowering of the friction coefficient. When these particles are ejected or disintegrate into smaller particles the contact behaves again as before. An explanation for the current increase would be that relatively large particles are formed at certain intervals due to fatigue wear. Detachment of such

plate like metal fragments from the surface would expose naked metal to the electrolyte. Reoxidation of the exposed metal surface would yield an anodic current peak. The plate like particles formed by fatigue may progressively be destroyed due to rubbing, and the small fragments formed may eventually be ejected from the contact.

The low magnification micrograph of Fig. 3a shows that wear fragments are present in the contact and distributed symmetrically at some distance around the contact. This confirms that wear particles are ejected during fretting. The high magnification micrograph of Fig. 3b suggests that the size of the ejected particles is on the order of a few micrometers, but they are in fact agglomerates of even smaller entities, of nanometer dimension. Wear particles of similar size and shape have been described previously in the literature and similar fragments have been observed in retrieved biological tissues. These observations support the idea that the present apparatus should be well suited for in-vitro simulation of physico-chemical phenomena at bone-implant interfaces.

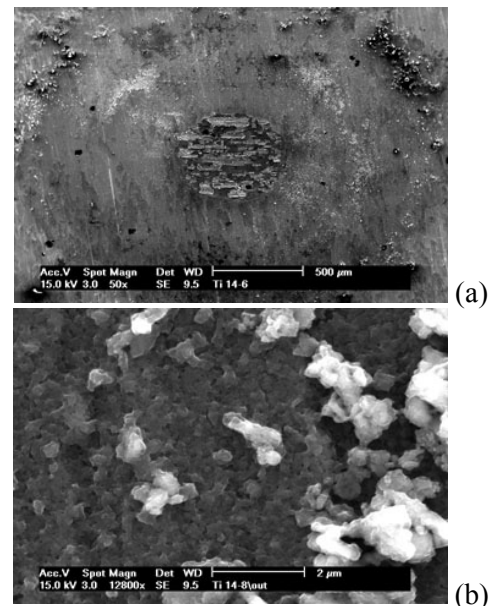


Figure 3: SEM Observation of wear particles formed after 5 hours ($150\ \mu\text{m}$, $1\ \text{Hz}$, $10\ \text{N}$, $+0.5\ \text{V}$). View of the wear scar (a). High magnification view of wear particles outside the wear scar (b).

REFERENCES: ¹S.Mischler, S.Debaud, D.Landolt, J.Electrochem, Soc., 145(3), 750-758 (1998)

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