The Influence of Fretting Parameters on Tribocorrosion Behaviour of AISI 304L Stainless Steel in Ringer Solution

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Medical applications where tribocorrosion has to be considered are orthopaedic and prosthetic implants, hip joints, amalgam restorative materials, and orthodontic brackets-archwire structures. In most cases, the degradation of biocompatible implant materials can lead to failure of medical therapy and cause a tissue inflammation. The dependence of the tribocorrosion of stainless steels AISI 304L orthodontic archwires sliding against corundum in Ringer's solution on applied normal force, and sliding velocity, has been investigated using in-situ electrochemical current-potential measurements. Applied normal force and sliding velocity were found to greatly affect current and potential during fretting-corrosion. An increase in normal force and sliding velocity induce an increase in current and a decrease in potential accelerating the depassivation rate of the tested stainless steels. Sliding wear affects the repassivation behaviour of stainless steel by increasing the anodic current in the wear track area.

Keywords: tribocorrosion, orthodontic archwire, stainless steel, AISI 304L, electrochemical noise, Ringer solution

Materials in a passive state ussualy have a very good corossion resistance in absence of wear, but their corossion resistance may significantly degrade under combined wear and corrosion since its passive layer could be destroyed by wear.

The synergistic effect may be significantly reduced by mitigating the effects of the wear and corrosion (fretting-corrosion) synergism requires a fundamental understanding of the mechanisms involved.

The term "fretting-corrosion" was first coined by Tomlinson in 1927 to cover the form of damage arising on steel surfaces under combined mechanical and electrochemical processes. In tribology, "fretting" is defined as a small amplitude oscillatory motion, usually tangential, between two solid surfaces in contact. The "fretting-corrosion" is a form of fretting wear defined as "wear in which chemichal reaction with environment is significant". Sometimes, corrosive wear is also called "tribocorrosion". The combined effect of wear and corrosion on materials failure was studied and recognized many years ago [1]. The combined action of corrosion and wear occur in a wide variety of engineering components ranging from bearings to surgical implants and orthodontic materials [2].

Generally, passive materials reacting with an aqueous environment exhibit an active-passive behavior [3].In such systems, corrosion and wear interactions are of great importance since the growth of an oxide film provides protection against corrosion while wear may brake up and remove that oxide film. Thus, depending on film properties (stability, adherence...) and repassivation kinetics, corrosion and wear interactions in these systems may accelerate the material loss [4]. The detailed description of corrosion-wear interactions is very complex. However, it is generally believed that rupture and removal of an oxide film from the surface lead to the exposure of active metal to the environment. This can be followed by a local dissolution or repassivation of the active metal depending on the material-electrolyte system and the loading conditions.

The aim of this study is to investigate the tribocorrosion behavior of AISI 304L stainless steel on sliding against corundum in a Ringer's solution. The effect of applied normal force and sliding velocity were investigated.

Materials and Investigations methods

The experiments were conducted on Katholieke Universiteit Leuven, Belgium laboratories,with austenitic AISI 304L stainless steel material. The AISI 304L (UGINE & ALZ Belgium NV, Gent, Belgium) cold rolled flat samples with a size of 25 . 25 . 1 mm^3 were polished to a mirror-like finish (R$_a$ <0.01 µm). The roughness was evaluated with a Rank Taylor Hobson profilometer. The ultimate yield strength for this material is 640 MPa. The nominal composition of that stainless steel is 0.03 wt% C, 17-19 wt% Cr, 8.5-10.5 wt% Ni, 1.0 wt% Si, 0.045 wt% P and balance Fe. The samples were covered with an electrically insulating adhesive tape prior to fretting tests leaving an area of 10^2 mm^2 exposed to the Ringer's solution. These samples were fixed at their ends in a polymer wire holder when immersed in a Ringer's solution of *p*H of 6.6, and mounted on the tribometer machine. The composition of this electrolyte is 8.402 g/L NaCl, 0.302 g/L KCl and 0.298 g/L CaCl$_2$. Polished corundum balls (Ceratec, The Netherlands) with a diameter of 10 mm, a hardness of 2000 HVN, and a surface roughness R$_a$ < 0.02 µm, were used as counterbodies. Prior to the fretting tests, samples and balls were degreased for 60 s with ethanol (naturalized ethanol + 5% diethyl ether) to remove oils or other surface adsorbed contaminants, and then dried in hot air.

Fretting-corrosion experiments were performed at room temperature using a reciprocating ball-on-flat contact configuration. *In-situ* electrochemical noise measurements were used to monitor electrochemical parameters before, during, and after fretting tests (fig. 1). An Ag/AgCl (3 M KCl) reference electrode coupled to the working electrode was used to record the change in potential, while a Pt micro-

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electrode cathode connected to the working electrode was used to record the variation in current. Sliding conditions were established by rubbing the corundum ball against the stationary, horizontally mounted stainless steel samples. Corundum balls were loaded on top of the stainless steel samples at normal forces of 1 N, 2 N, and 5 N. These normal forces correspond to a maximum hertzian contact pressure of 493, 621, and 842 MPa respectively. Linear peak-to-peak displacement amplitude of 200 µm was applied to the tribocorrosion system and the sliding frequencies of 1 and 10 Hz were used. These experiments resulted in gross-slip fretting conditions. The tests were performed for 2 . 10^4 cycles and were triplicated.

The number of cycles, the tangential force, the normal force, the displacement amplitude, and the coefficient of friction, were acquired at equally spaced time increments of 6.6 sec over the whole test duration.

The test materials were exposed to the Ringer's solution for 1800 s before the start of the fretting-corrosion tests in order to reach a stable potential and a low background current. The corundum ball was loaded on top of the sample 400 sec before the start of the fretting tests. This static contact between corundum counterbody and samples was kept for 600 sec and then the fretting-corrosion test was started. After 20,000 fretting cycles, the fretting was stopped, and the ball was lifted away from the stainless steel samples.

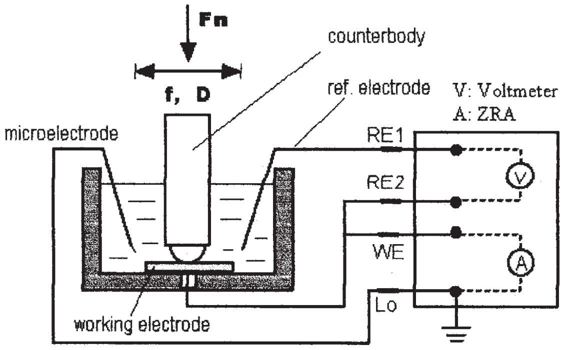

Fig. 1. Schematic set-up for electrochemical noise measurements on a working electrode (WE) sliding against a counterbody. RE is a reference electrode, V a voltmeter, and A a zero resistance ammeter (ZRA)

Electrochemical potentiodynamic polarization measurements were performed using a three-electrode set-up consisting of stainless steel samples as working electrode, a commercial Pt electrode as counter-electrode, and Ag/AgCl (3M KCl) as reference electrode. A potentiostat type Solartron electrochemical interface model 1287 was used. Potentiodynamic anodic and cathodic polarization curves were acquired on stainless steels AISI 304L before and during fretting wear, after an immersion period of 30 min in a Ringer's solution. The open-circuit potential measured before each test was set as the potential in applying either anodic or cathodic polarization. The potential scan was set at 1 mV/s. The potential range scanned was from –0.8 to 0.35 *vs.* Ag/AgCl. The potential scan was reversed – 0.8 V *vs.* Ag/AgCl once a current of 1 mA was reached during the scan.

Results and discussions

The typical potential-current noise response recorded before, during, and after fretting tests performed on AISI 304L stainless steel sliding against corundum in a Ringer's solution is shown in figure 2. Under unloaded conditions, the potential variations are quite small and stable. When the ball is loaded on top of the sample, a small decrease in potential was noticed. At the start of the fretting-corrosion test, the potential of the stainless steel sample undergoes a significant negative shift of about 16 mV. After a running-in phase, the potential fluctuates as long as the fretting-corrosion test was going on. When fretting was ended and the corundum ball was lifted away from the worn surface, the potential of the working electrode returned progressively to the value recorded before the start of the fretting test.

The evolution of the current during the electrochemical noise measurements is in phase with the evolution of the potential. A background current of 6 nA is recorded before the fretting-corrosion test was initiated. A significant rise in the anodic current through to the stainless steel samples is noticed at the start of the fretting-corrosion tests. After a running-in phase, the current fluctuates during the fretting-corrosion. At the end of the fretting-corrosion tests, the current returns to the level noticed before the start of the fretting test. Similar results have been reported by Oltra et al. [5, 6] for pure Fe immersed in a 1 M mixture of H_2SO_4 and Na_2SO_4 and irradiated by a laser beam. According to these authors, a potential drop or current increase was related to the depassivation of the surface on laser irradiation. A progressive potential rise or current decrease was related to the repassivation of an active surface. Fluctuations in potential and current during fretting-corrosion on AISI 304 stainless steel immersed in 0.5 M H_2SO_4, 0.5 M NaCl, and Na_3PO_4 were related by Wu *et al.* [7, 8] to an oxide film removal (depassivation) and re-growth (repassivation) [6]. Accordingly, the potential and current variations in figure 2 suggest that the tested stainless steel sliding against corundum under the considered test conditions, mainly undergo a removal of their passive surface film at the start of fretting. They remain partly active during the sliding test, and finally progressively repassivate on unloading.

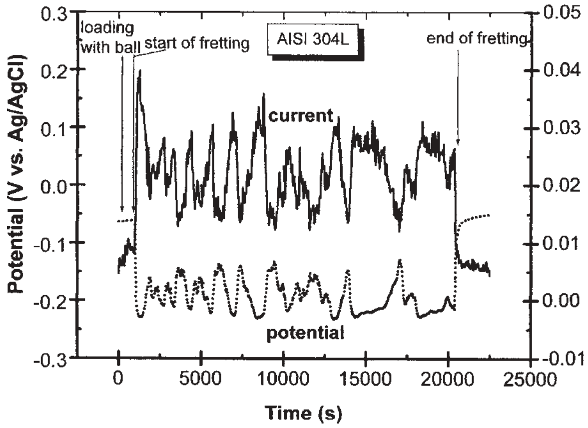

Fig. 2. Electrochemical noise measurements recorded before, during, and after a fretting test on AISI 304L stainless steel sliding against corundum in a Ringer's solution at 1 N, 1 Hz, displacement amplitude of 200 µm, and for 20,000 cycles

Effect of normal force and sliding velocity

The effect of normal force and sliding velocity on potential and current evolution were tracked during fretting tests on stainless steel AISI 304L (figs. 3 a and b) sliding against corundum in a Ringer's solution. These tests were performed at normal forces of either 1, 2 or 5 N and at a constant sliding frequency of 10 Hz. From these figures, it appears that the lowest potential and the highest current were recorded at the highest normal force.

Sliding velocity also affects potential and current fluctuations during fretting on AISI 304L (figs. 4 a and b) sliding against corundum. Tests were performed at either 40 µm/s or 400 µm/s corresponding to sliding frequencies

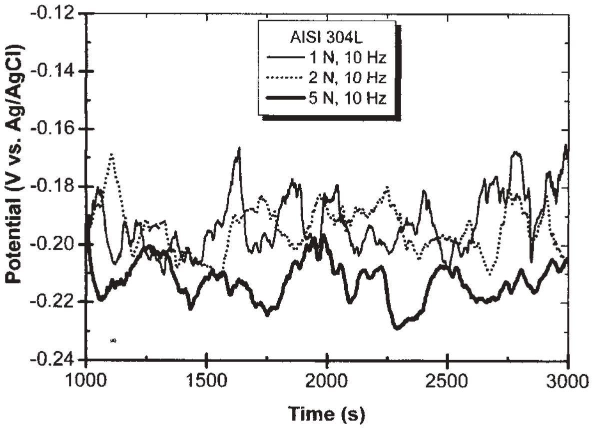

Fig. 3 (a). Potential variation (a) recorded on AISI 304L stainless steel during fretting-corrosion against corundum in a Ringer's solution at 10 Hz, 200 µm, 20000 fretting cycles under different applied normal forces

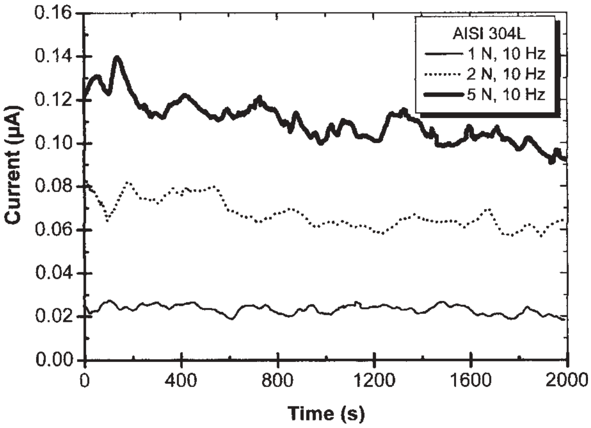

Fig. 3 (b): Current variataion recorded on AISI 304L stainless steel during fretting-corrosion against corundum in a Ringer's solution at 10 Hz, 200 µm, 20000 fretting cycles under different applied normal forces

of 1 and 10 Hz respectively for displacement amplitude of 200 µm. The fluctuations of current and potential are more pronounced at 10 Hz than at 1 Hz.

The mean values of potential and current during fretting-corrosion are summarized in table 1. The lowest mean potential values and the highest mean current values are observed for fretting tests performed at the highest normal force, i.e. 5 N, and the highest sliding velocity, i.e. 10 Hz.

Potentiodynamic polarization scans before and during fretting-corrosion were recorded. These results are plotted in figure 5 for fretting tests performed at 5 N, 10 Hz, and 200 µm displacement amplitude. Without any fretting (figs. 5 a), the open-circuit potential (zero-current potential) is about -0.23 V *vs.* Ag/AgCl. The passivation of the tested material occurs at potentials between –0.19 and +0.17 V *vs.* Ag/AgCl. At higher potentials, the transpassivation is induced. In this transpassive region, pits form on the stainless steel surface. The assumed pitting potential is about +0.17 V *vs.* Ag/AgCl. On reversing the potential scan the repassivation potential is about +0.008 V *vs.* Ag/AgCl.

Under fretting-corrosion conditions (fig. 5 b), the open-circuit potential of the stainless steel undergoes a negative shift of about 0.10 V in comparison to purely corrosive test conditions, i.e. -0.13 V *vs.* Ag/AgCl.

The open-circuit potentials measured during potentiodynamic scans under fretting-corrosion conditions are far from the potentials measured during fretting-corrosion tests performed under open-circuit test conditions (table 1).

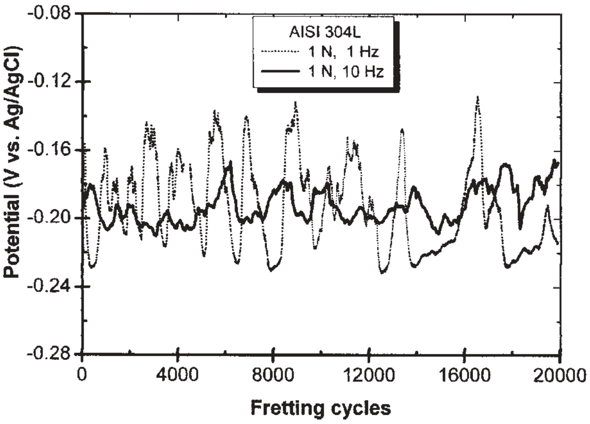

Fig. 4 (a). Potential variation recorded on AISI 304L stainless steel during fretting-corrosion against corundum in a Ringer's solution at 1 N, 200 µm, 20000 fretting cycles under different contact frequencies

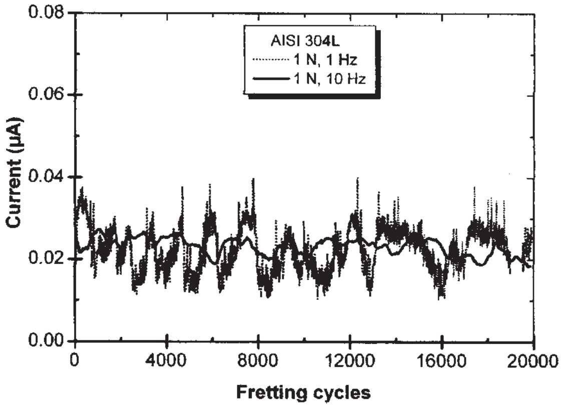

Fig. 4 (b): Current variation recorded on AISI 304L stainless steel during fretting-corrosion against corundum in a Ringer's solution at 1 N, 200 µm, 20000 fretting cycles under different contact frequencies

Table 1

INFLUENCE OF FRETTING TEST PARAMETERS ON CURRENT AND POTENTIAL MEAN VALUES MEASURED DURING FRETTING-CORROSION

Fretting test parameters		Mean values of potential (V)	Mean values of current (µA)
1N	1Hz		
	10Hz	-0.192 ± 0.026	0.022 ± 0.005
	1Hz	-0.193 ± 0.010	0.023 ± 0.002
2N	10Hz	-0.193 ± 0.021	0.023 ± 0.006
	1Hz	-0.194 ± 0.008	0.067 ± 0.006
5N	10Hz	-0.223 ± 0.013	0.026 ± 0.003
		-0.232 ± 0.006	0.110 ± 0.009

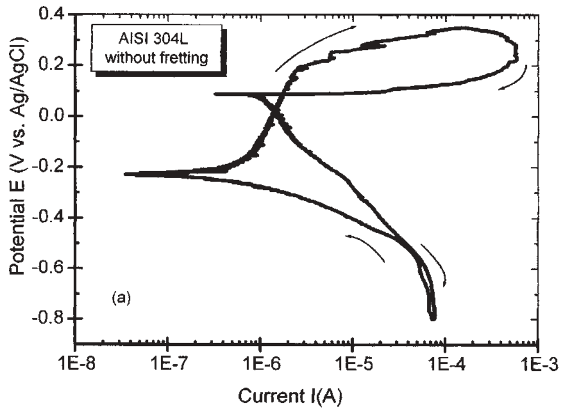

Fig. 5 (a). Potentiodynamic measurements without fretting on AISI 304L stainless steel in Ringer solution

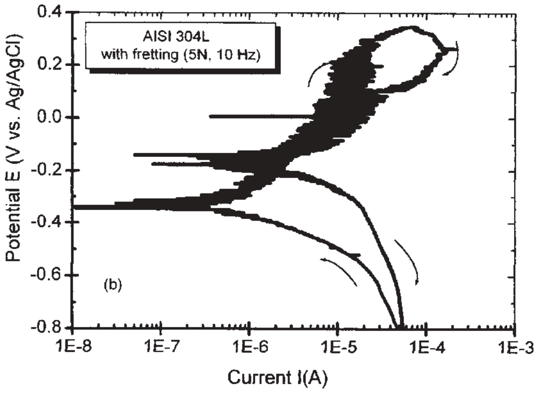

Fig. 5 (b): Potentiodynamic measurements with fretting on AISI 304L stainless steel in Ringer's solution for test performed at 5 N, 10 Hz, 200 μm and 20,000 fretting cycles

Furthermore, in the passive region higher current are noticed in the case of fretting-corrosion than in the case of corrosion. The polarization curve in the passive region is characterized by fluctuations due probably to active-passive transitions taking place in the wear track. An increase of the anodic current in the passive region by about 15 μA appears on AISI 304L. The repassivation potential is also affected by fretting-corrosion. The repassivation potential is shifted towards lower values. That potential shift is about 0.076 V *vs.* Ag/AgCl.

Results and discussions

The simultaneous action of corrosion and wear during fretting-corrosion lowers the open-circuit potential, increases the current and also the anodic current in the passive range, as shown in figure 5. These effects are, in general, consistent with the formation and the subsequent removal of a passive surface film. Thus, the sharp potential drop and the current increase observed in this study at the start of fretting-corrosion are due to the removal of an oxide layer and the subsequent exposure of fresh active material to the environment [6]. This can be explained as follows. In these conditions, a galvanic coupling takes place between the active wear track area (anode), where the passive film is removed by the sliding action of the counterbody, and the remaining surface in passive state (cathode). Thus, the low open-circuit potential and the high anodic current measured during fretting-corrosion are characteristic of the active state of the worn surface.

The dependence of the potential drop and the current increase during fretting-corrosion on the applied force can be understood by considering the contact geometry between the two sliding surfaces. In general, the real contact area depends on the topography of the surface, the material properties of the two solids in contact, and the force applied onto the mating surfaces [7]. When asperities are elastically deformed, the contact area is proportional to the third power of the normal force, *F*. At high normal forces, when plastic deformation of the asperities dominates, the real contact area, A_r is directly proportional to the normal force:

$$Ar = k \,.\, F^m$$

with *k* a constant. Under plastic deformation, $m = 1$, while under elastic deformation, $m = 0.67$.

An increase of the applied normal force from 1 to 5 N results thus in a 1 to 3 fold increase in A_r when the asperity contact is elastic, and in a 1 to 5 fold increase in A_r when the asperity contact is plastic. The increase in A_r could result in the removal of oxide films from a larger area, and subsequently could increase the exposed active material area leading to a lower potential and a higher anodic current. Since the normal force is transmitted at various asperity contact points, an increase in normal force will increase A_r whereas the contact stress at each asperity contacts should not change significantly. Higher normal loads produce sufficient stress at local asperity contacts to cause an oxide film removal since a substantially lower potential is then observed during fretting (table 1). It may thus be expected that the potential will decrease with increasing normal force till the oxide layer is removed from the entire apparent contact area. This means that once the entire apparent contact area has become active, a further increase of the loading at the asperities will not induce a further decrease of the potential, and thus a potential limit is reached.

Similarly, the effect of sliding velocity on tribocorrosion behavior of the tested material can be explained by considering the repassivation process. At increasing sliding velocity, more active material is exposed to the electrolyte for a lesser duration in between two contact events. At a given repassivation kinetics, the activation of the surface areas in the wear track during fretting will result in a lower potential increase and a higher current increase, which may enhance the anodic dissolution of the material. This is supported by the fast and easy removal of the oxide debris generated by fretting.

Conclusions

The tribocorrosion behavior of stainless steels AISI 304L sliding against corundum in a Ringer's solution was investigated in a ball-on-flat contact configuration combined with *in-situ* electrochemical noise measurements. The effect of applied normal force, and sliding velocity on corrosion-wear of the tested material were determined. Applied normal force and sliding velocity were found to greatly affect the current and potential during fretting-corrosion. An increase in the normal force and the sliding velocity induce an increase in current and a decrease in potential accelerating the depassivation of the stainless steels. The fluctuations in potential and current during fretting become larger at increasing sliding frequency than at increasing normal force.

During fretting-corrosion, sliding promotes the dissolution of stainless steel due to the removal of the oxide surface film and the exposure of active material to the electrolyte. This dissolution process is revealed by an increased anodic current. A subsequent repassivation of active material takes place during fretting-corrosion creating a dynamic evolution of the material surface conditions in the wear track.

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Manuscript received: 9.10.2007