TRIBOCORROSION EVALUATION
OF PROTECTIVE COATING

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INTRODUCTION

The study on tribocorrosion evolves to be an active research area, due to its wide existence in a variety of industries, such as mining, oil, automotive, food, nuclear, offshore marine and biomedical. Tribocorrosion is a surface degradation process resulting from simultaneous tribological and electrochemical actions in a corrosive environment [1-4]. Such a process cannot be simply predicted from the knowledge of isolated wear and corrosion behaviors of the material, since synergistic effects of these two processes can accelerate the mass loss in the tribocorrosion test. Tribocorrosion can cause material degradation, and affects the friction, wear and lubrication behavior of the tested materials [2].

IMPORTANCE OF USING TRIBOMETER FOR TRIBOCORROSION TESTING

The Tribocorrosion Module of the Nanovea Tribometer provides effective and efficient measurements for evaluating and developing cost-saving materials critical for corrosion and wear protection in various industrial applications. The purpose of tribocorrosion research is the minimization of losses resulting from wear and corrosion and the enhancement of production efficiency, application performance, and most importantly the cost savings to allow industrial growth.

MEASUREMENT OBJECTIVE

The tribocorrosion process of the commercial acrylic urethane paints applied as floor/automobile coatings is simulated in a controlled and monitored manner using the Nanovea Tribometer. In this study, we would like to use the industrial paint coatings as a selected example to showcase that Nanovea Tribometer is an ideal tool for evaluating the performance of materials used for wear and corrosion protection.
**TRIBOCORROSION TEST PRINCIPLE**

As shown in the schematic in Fig. 2, the tribocorrosion cup is fixed on a rotational stage. The conventional three electrode setup is used to monitor the change of voltage and current before, during and after the wear process. The sample is mounted against an O-ring (2.5 cm dia.) with a surface area of 4.91 cm² exposed to the electrolyte (see Fig. 1). The sample serving as the working electrode is connected from the back. A known force is applied on a pin, or ball, in contact with the sample surface to create the wear. The evolutions of coefficient of friction, COF, and open circuit potential, OCP, are recorded in situ. The volume lost allows calculating the wear rate of the material. Since the action performed on all samples is identical, the wear rate can be used as a quantitative comparative value for wear resistance.

![Fig. 2: Schematic of the tribocorrosion test.](image)

**TEST PROCEDURE**

**SAMPLE DESCRIPTION**

The sample for this study is a commercial acrylic urethane paint coating. It has a three layer structure: metal substrate/primer/topcoat. The bare steel substrate and substrate/primer samples were also tested for comparison. The top coating has a thickness of ~30 μm. The identifications of the tested samples in this report are listed in Table 1. Due to the agreement with the client, the detailed information of the coating and substrate is not disclosed in this report.
TRIBOCORROSION TEST

Tribocorrosion test at Open Circuit Potential
Nanovea Tribometer with the Tribocorrosion Module was applied to evaluate the tribocorrosion behavior, e.g. coefficient of friction, COF, and wear resistance. The sample was fixed against an O-ring with a surface area of 4.9 cm² exposed to 3.5 wt.% NaCl solution at room temperature. The sample, a platinum wire and a Ag/AgCl, NaCl (sat’d) electrode were used as working, counter and reference electrodes, respectively. A normal force of 10 N was applied using an Al₂O₃ ball of 6 mm diameter. The OCP was monitored by a potentiostat throughout the tribocorrosion experiments. The sample was first kept in the electrolyte for 1 h to obtain a stable OCP, followed by the tribocorrosion test for 10 min (1000 cycles). After the wear process, the sample was kept in the solution for another 10 min to allow surface repassivation. Dry wear tests were also performed at the same condition for comparison. The test parameters are summarized in Table 2.

Tribocorrosion test at Controlled Potentials
In order to investigate the effect of corrosion reactions on the tribocorrosion properties of the Coating, the wear tests were carried out under anodic and cathodic polarization conditions, while the other test parameters listed in Table 2 were kept the same. In the case of anodic condition, a +0.6 V potential vs. OCP was applied to the tested sample and accelerated the corrosion process, while in the case of cathodic condition, a -0.6 V potential vs. OCP applied to the sample could suppress the corrosion process. Under both conditions, the evolution of the current was monitored before, during and after the wear process.

The wear rate, $K$, was evaluated using the formula $K=V/(F\times s)=A/(F\times n)$, where $V$ is the worn volume, $F$ is the normal load, $s$ is the sliding distance, $A$ is the cross-section area of the wear track, and $n$ is the number of revolution. Wear track profiles were evaluated by the Nanovea Optical Profilometer, and the wear track morphology was examined using an optical microscope.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>bare metal substrate</td>
</tr>
<tr>
<td>Primer</td>
<td>substrate/primer</td>
</tr>
<tr>
<td>Coating</td>
<td>substrate/primer/topcoat</td>
</tr>
</tbody>
</table>

Table 1: Summary of samples for testing.

<table>
<thead>
<tr>
<th>Test parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal force</td>
<td>10 N</td>
</tr>
<tr>
<td>Rotational speed</td>
<td>100 RPM</td>
</tr>
<tr>
<td>Duration of wear</td>
<td>10 min</td>
</tr>
<tr>
<td>Wear track radius</td>
<td>3 mm</td>
</tr>
<tr>
<td>Revolutions</td>
<td>1000</td>
</tr>
<tr>
<td>Ball Diameter</td>
<td>6 mm</td>
</tr>
<tr>
<td>Ball Material</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>3.5 wt.% NaCl</td>
</tr>
<tr>
<td>Temperature</td>
<td>24°C (room)</td>
</tr>
<tr>
<td>Humidity</td>
<td>40%</td>
</tr>
</tbody>
</table>

Table 2: Test parameters of the tribocorrosion measurement.
RESULTS AND DISCUSSION

Tribocorrosion test at Open Circuit Potential

The COF was recorded in situ during the wear tests at different conditions as shown in Fig. 3. It can be observed that the COFs at different test conditions show a comparable value of ~0.2 in the first 600 revolutions. The sample tested in the dry environment exhibits an increased COF of ~0.4 in the following cycles, possibly due to the formation of coating debris in the wear track. In comparison, the tests performed in the electrolyte show a relatively stable COF throughout the wear process, which may be related to the turbulence generated by the rotation of the corrosion cell during the pin-on-disk wear process. Such fluid movement can continuously flush away the wear debris during the tests. However, the presence of the corrosive electrolyte substantially accelerates the mass loss due to the synergistic effect of corrosion and wear.

Fig. 4 and Fig. 5 shows the cross section profiles and micro images of the wear tracks after the pin-on-disk tests at different conditions, and Fig. 6 summarizes the wear rate and wear track depth. As shown in Fig. 4, the Coating tested in a dry environment exhibits a narrow wear track. Although the topcoat was removed during the wear process, the primer underneath is still present and protects the substrate. On the other hand, the Coatings tested in the corrosive media all exhibit large wear tracks with the metal substrates exposed to the wear and corrosion attack. Compared to a wear rate of ~18 mm³/N m for Coating after dry wear tests, the sample tested at OCP exhibits nearly twice of the wear track depth and four times of wear rate. This finding illustrates that the corrosive media plays an important role in weakening the protective coating system during the tribocorrosion process.
Fig. 4: Images of wear tracks after the pin-on-disk tests.

(a) Dry wear:
(b) Wear at OCP:
(c) Wear at +0.6 V vs. OCP:
(d) Wear at -0.6 V vs. OCP:

Fig. 5: Cross section profiles of wear tracks after the wear tests at different conditions.
Evolution of the OCPs before, during and after wear tests on the Coating and Primer is presented in Fig. 7. The OCPs of the Coating and Primer maintain a high value above -0.5 V at the beginning of the wear process, indicating that the protective coating/primer system is still protecting the substrate from the tribocorrosion attack. Once the protective layers fail (at 650 s for Coating and 400 s for Primer), the OCPs abruptly drop to a value below ~-0.6 V, indicating the failure of the protective coating and the exposure of the substrate underneath to the corrosive media. The topcoat enhance the wear resistance by delaying the coating system failure by 250 s compared to the Primer sample. The steel substrate immediately repassivates when wear ceases.

Fig. 6: Wear rates and wear track depths of the Coating after wear tests at different conditions.
Tribocorrosion tests at Anodic/Cathodic Potential

In order to further emphasize and demonstrate the contribution of corrosion in tribocorrosion, the tribocorrosion tests were performed at anodic/cathodic potentials. At an anodic potential (+0.6 V vs. OCP), the rate of corrosion process is increased by the accelerated removal of electrons and dissolving of metal, whereas a cathodic potential (-0.6 V vs. OCP) suppresses the corrosion reaction. In these two tests, the potential of the surface subject to wear was held constant and the evolution of the current was monitored before, during, and after the wear test as shown in Fig. 8. In the first 200 s before wear begins, the anodic/cathodic currents were 0 A, demonstrating that the Coating acts as an excellent barrier for the transportation of electrons. It prevents the corrosive media from infiltrating to attack the substrate when wear is not involved. The coating remains to be protective in the first 100 s wear process at anodic potential, followed by a significant jump of the anodic current to 0.15 A. As the wear process continues, the anodic current progressively increases to 0.25 A, indicating the accelerated corrosion process due to the increased wear track size caused by wear. The synergistic effect of severe corrosion and wear leads to the formation of a substantially larger wear track (see Fig. 4 and Fig. 5), and the wear rate in this process is ~339 mm$^3$/N m, compared to ~68 mm$^3$/N m for that in OCP condition. In contrast, the tribocorrosion test performed at a cathodic potential exhibits a lower wear rate of ~57 mm$^3$/N, showing the importance of corrosion suppression for tribocorrosion protection.
Fig. 8: Evolution of the anodic/cathodic current on Coating before, during and after the wear process.

Other than the tribocorrosion measurements presented in the above session, the corrosion analysis including potentiodynamic polarization and optional electrochemical impedance spectroscopy (EIS) tests can also be performed using the Tribocorrosion Module of Nanovea Tribometer as illustrated in Fig. 9 as examples.
CONCLUSION

Nanovea Tribometer provides well-controlled quantifiable and reliable tribocorrosion assessment that can ensure reproducible evaluation and quality control of the industrial paint coatings. Moreover, the capacity of in-situ COF, potential and current measurements allow users to correlate different stages of wear process with the evolution of COF, potential and current, which is critical in improving fundamental understanding of the wear/corrosion mechanism and tribological characteristics of the coatings.

Based on the comprehensive tribocorrosion analysis in this study, we show that the tested Coating acts as an excellent barrier for the transportation of electrons and provides superior protection to the substrate against corrosion when wear is not involved. However, the synergistic effect of corrosion and wear can substantially accelerate the coating failure and mass loss to the substrate. This tribocorrosion assessment allows us to evaluate and select the best candidate that serves in environments that involve wear and corrosion attacks at the same time.

Nanovea Tribometer offers precise and repeatable wear and friction testing using ISO and ASTM compliant rotative and linear modes, with optional high temperature wear, lubrication and tribocorrosion modules available in one pre-integrated system. Optional 3D non-contact profiler is available for high resolution 3D imaging of wear track in addition to other surface measurements such as roughness.

Learn more about the Nanovea Tribometer or Lab Services

REFERENCES