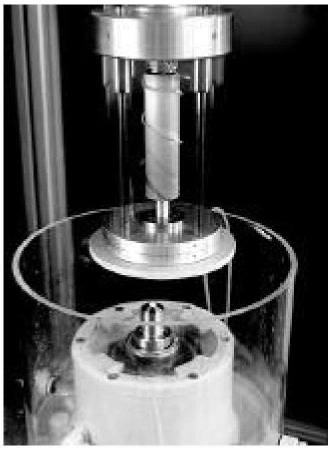
Tribocorrosion - Combined effects of wear and corrosion in aqueous environments

Dirk Drees
Falex Tribology NV, Leuven, Belgium
Jean-Pierre Celis
Dept. MTM, Katholieke Universiteit Leuven, Belgium



Research into tribological phenomena in an aqueous environment is a relatively new challenge, because historically most problems with friction and wear of materials were solved using organic lubricants. Growing environmental awareness as well as technological limitations are increasingly putting pressure on the use of these products. Theoretically, lubrication and cooling by water is possible and an elegant alternative to organic lubrication. But lubrication in water introduces the possibility of corrosion mechanisms, or more broadly, electrochemical reactions on the surface. This places us before an engineering challenge: to find materials that are both corrosion resistant under wear and that provide low wear and friction in water.
There will be a competition or a synergetic effect of both surface phenomena: wear and corrosion. To understand these mechanisms and to be able to control them favourably, there must be a better understanding of what is happening on the surface. This presentation shows the experimental tool that has been used for this research at the Department of Materials Engineering in Leuven, proposes a wear model for TiN coatings, which is generally applicable to passivating metals and highlights some of the practical results of the research.

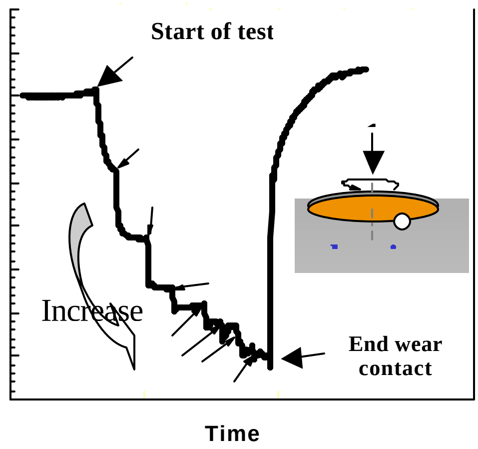
1. Experimental set-up

A pin-on-disk geometry was chosen as a compromise between a simple geometrical situation and easy production of test materials. In the pin-on-disk contact, a point contact evolves to small area contact. Speed is unidirectional so there are no effects of acceleration and speed reversal as in reciprocating tests. Speeds can be relatively high (up to 2 m/s). From the point of the disk material, the counter body (ball) is contacting every position in the circular wear track repeatedly and with the same frequency as the rotation speed.
As in any conventional pin-on-disk test, the friction can be measured but at the same time this set-up allows to retrieve another type of information from the surface during a test. The disk can be electrically connected as the working electrode of an electrochemical test cell. Adding a reference electrode allows us to measure the electrochemical potential of the disk surface, which contains information on both localised events (by the wear action) and the electrochemical condition of the whole surface (corrosion mechanisms).

2. Wear mechanism of TiN in water, in the pin-on-disk geometry.

TiN was chosen as the primary research material because of its industrial importance. Even today, when many variations of hard coatings exist, still about 50% of all commercially sold coatings are TiN. They are widely used for cutting applications, where already aqueous solutions with only small amounts of oil are used for cooling and lubrication.

The electrochemical potential of such a coating changes quickly in a wear test against an oxide ball. With increasing rotation speed, the electrochemical potential of the coating lowers, indicating that at least part of the coating becomes electrochemically 'active'. This experiment reveals that TiN, like stainless steels, owes its good corrosion resistance to a very thin native oxide layer that can be disrupted by a mechanical contact. A further study of this phenomenon and correlating it to the friction behaviour and wear volume of TiN in water has led to the proposal of a wear mechanism for TiN that appears to be valid for sliding conditions, both in water and in 'dry' sliding (humid air).



It is a mechanism of mild oxidational wear (cfr. mild oxidational wear of steel, Quinn) : the native oxide on TiN grows by the energy input caused by sub sequential contacts with the counter body until it reaches a critical thickness where it can no longer carry the load. The oxide breaks of, causing material loss thus wear, and leaving a part of the TiN unprotected from corrosion. This part is called the 'active area'. Immediately, the active area commences to repassivate (reformation of the oxide film) and the cycle starts again.
According to this mechanism, the rate of material removal is entirely controlled by the rate at which the oxide film reaches the critical thickness under which it breaks of as a wear particle. Thus, in the absence of a third body, the wear rate of TiN is controlled by it's oxidation rate in a pin-on-disk geometry.

3. Practical results with TiN

A series of experiments were carried out to confirm and substantiate this wear mechanism.
First, it was observed that the wear rate in water, when related to the dissipated energy, is lower in water than in humid air. TiN can oxidise by two mechanisms: low temperature oxidation by oxygen and electrochemical repassivation. The low temperature oxidation is the dominant mechanism in air where it is very fast due to the availability of oxygen. In water, dissolved oxygen is less than 10 ppm, so the oxidation rate slows down, reducing the wear rate. By electrochemical anodic polarisation, the electrochemical repassivation can be enhanced and we find indeed an increase of wear rate under anodic polarisation (+1 or +2 V).
Reducing the amount of available oxygen in the aqueous environment, by means of an oxygen scavenger (H_2SO_3), reduces the wear rate of the TiN coating considerably and also lowers the friction force, thus lowering the amount of energy dissipated in the contact. Unfortunately, this acid also attacks the steel substrates through the pores in the TiN coating and can not be used for practical purposes. A compromise is reached by using an H_3PO_4 addition, which protects steel from corrosion and lowers the friction and thus the absolute wear rate.

The mild oxidational wear mechanism was derived for the pin-on-disk geometry and by extrapolation may be considered for unidirectional sliding contacts. A case study, comparing two different pin-on-disk geometries with a reciprocating test set-up shows that the wear rate results show a similar tendency of lowering friction and wear by acid additives in all geometries, but the relative improvement is much larger in the unidirectional sliding geometry than in the reciprocating motion geometry. In reciprocating motion, wear particles can stay in the contact and start to play a determining role. Clearly, depending on the practical application, the correct simulation method must be used to predict the effects of additives on the wear rate of TiN coated tools or components.

4. Practical results with DLC coatings

Meanwhile, this experimental set up was used to investigate the combined effects of corrosion and wear on a variety of materials : oxidized magnesium for turbine blades, sliding bearing materials for water lubricated bearings, stainless steel, oxidized TiN, TiAlN etc.

The most surprising results came in a study of DLC coatings. Both CVD and PVD deposition techniques were used to prepare 6 different DLC type coatings. All these coatings exhibit an excellent wear resistance in the pin-on-disk configuration in humid air, with the CVD coatings far superior to PVD coatings. However, under water, all the CVD coatings (pure DLC) failed in less than 1% of the lifetime in air. The PVD coatings (usually alloyed with metals as W or Ti) showed no marked decrease of wear resistance and even some improvement of wear resistance in water over humid air. The reason for this behaviour is until now not solved, but it probably is linked to the behaviour of a transfer film of carbon that is thought to be responsible for the very low friction of DLC against many materials. Further investigation into this topic is required to fully understand this difference.

5. Conclusions

With this test set-up and research method, we are obtaining fundamental information about the electrochemical surface condition of a material subjected to wear. As such, the wear mechanism of TiN was identified under the experimental conditions. TiN wears by a mild oxidational wear mechanism. This model can be used to predict the effects of additives in an aqueous environment on wear and on corrosion behaviour of the coating.

This method and modelling principles have also been applied to a study on stainless steel. This study has allowed to determine the limits of mild wear of stainless steel in aqueous environments and to calculate wear in such conditions from the electrochemical properties of the steel and the expected loading conditions.

The same methods can be used to investigate the wear and friction behaviour of any material in water, notably a study of DLC coatings resulted in a surprising discrepancy between PVD and CVD type of DLC coatings