Taiho Kogyo Tribology Research Foundation

Main report

Name: Joichi Sugimura and Monica Ratoi

Theme: Effect of lubricants on hydrogen embrittlement of steel

1. Progress and result of the research

The project investigated the influence of lubricant on preventing premature failure of bearing steel due to the ingress of atomic hydrogen while achieving reduced friction and wear of the components. The study involved novel methods for investigating rolling contact fatigue, hydrogen embrittlement and the role of lubricants in preventing them by employing a wide range of state-of-art technology.

The research focused on two main aspects: 1) the effect of the base oil chemistry in hydrogen permeation in different environments including air, argon and hydrogen, and 2) the effect of chemical reactions with antiwear additives

1. The effect of base oil
In the first study, high pressure rolling contact fatigue tests were conducted on bearing steel in controlled atmospheres lubricated with a synthetic polyaphaolefin (PAO32) oil. Bearings were tested until significant wear or failure was apparent and immediate thermal desorption spectroscopy (TDS) analysis was undertaken for hydrogen content evaluation. Wear loss was analyzed using Alicona optical profilometry and the wear track chemistry was determined with XPS analysis. Wear track sub-surface analysis was performed using traditional sectioning methods alongside a comparative investigation into the prospects of high energy micro-computed-tomography (Micro-CT/μ-CT) as a new non-destructive technique for sub-surface damage characterization. The aim of this work was to elucidate the role of lubricant in preventing wear and failure in different environments.

The study found that the lubrication environment influences the generation and characteristics of the tribofilm formed on the wear track, which can affect the wear mechanisms and the catalytic action of nascent surface on the generation of hydrogen through the decomposition of base oils. The tribofilm consists of iron oxide and solidified cracked/oxy-polymerized carbon species, and its thickness decreases in the order Air > H2 > Ar. In the inert argon atmosphere where no oxidation or hydrogenolysis of the hydrocarbon lubricant takes place, the tribofilm was thinner and contained less carbon and iron oxide. This led to extensive surface initiated spalling and pitting and therefore reduced service life. The impact of the tribofilm on the service life extension of steel becomes especially important in H2 environment where atomic hydrogen is generated from both the environment and lubricant and failure rates are high.

It was found that the use of Micro-CT as a non-destructive technique for investigating damage gives a reasonable crack depiction and is also capable of revealing 3D crack morphology. Replacing μ-CT with a monochoromatic synchrotron would help to avoid the problems associated with the high density of steel (such as noise) and the long duration of the scanning as it offers a more coherent light sources and much faster imaging.

In the next series of tests, three different types of synthetic oils: a polyalphaolefin (PAO32), a polyol ester - trimethyolpropane ester (POE) and a polypropylene glycol (PPG) were used. These oils were selected to have similar viscosities at the testing temperature but different chemistry. Test were run up to 10 hours during which the oils were condition monitored and their ability to form tribofilms on the wear track was related to the hydrogen content, wear and subsurface damage of specimens. The study revealed that oil chemistry plays an important role in hydrogen generation and permeation, and wear prevention of bearings. These effects are influenced by the ability of the lubricant to generate

tribofilms on the wear track as well as the likeliness of the lubricant to decompose. The results are summarized as follows.

1) The amount of hydrogen permeated into steel is relatively small with POE and PAO and it does not change with rolling time.
2) The chemical stability (oxidative) of the tested oils varied in the range POE >PAO>PPG
3) Hydrogen permeation is affected by the amount of water solubilized in oils
4) PPG contains relatively large amount of water, and cause larger amount of hydrogen in the steel
5) The formation of tribofilms (surface oxide film) suppresses hydrogen permeation
6) POE and PPG generate iron oxide films on the track, while PAO films are made of inorganic carbon
7) Essentially, the amount of hydrogen permeated in the steel during rolling depends on the formation of surface films at contacting surface and the water content in the oils.

2. Effect of additives
The effect of additive chemistry in generating a protective tribofilm against the permeation of hydrogen into steel substrates was studied. It was found that conventional phosphorous and sulphur based additives, such as trioctylphosphate and zinc dialkyldithiophosphate (ZDDP), show varying efficiency depending on their affinity/reactivity towards the substrate and the morphology/chemistry of the generated tribofilms. A thick, uniform film can induce lower hydrogen concentrations in the substrate after operation. This indicates that matching the chemistry of the lubricants to the experimental conditions of a specific application is important for a low hydrogen concentration in the samples and a longer fatigue life.

We have also investigated the effect of temperature on the reactivity of ZDDP, the most common additives used in high pressure contacts. At low temperatures the additive is not reactive enough to generate a uniform film in the contact, allowing hydrogen to generate and permeate into the steel substrate. However, very high temperatures promote high reactivity but large corrosive wear of the substrate. These results suggest that an optimum temperature is required for each additive in order to maximize the coverage of the film and reduce the amount of hydrogen in the substrate.

The importance of the structure and chemical composition of the tribofilm is summarized as follows. When no additives are used, the surfaces are only protected by a thin oxide film that is removed during sliding. On the other hand, the additive reacts with the steel substrate and generates the film on the contacting surfaces. This reduces the amount of catalytic metal surfaces available and inhibits the degradation of hydrogen-containing molecules. The chemical composition of the film is responsible for its resistance under the high loads employed.

2. Subjects remain to be solved in future/Subjects required further investigation

1) We have shown the hydrogen generation in rolling contact in terms of the amount of hydrogen diffused in steel. It is necessary to look at hydrogen that reacts on the surface or diffuses into oils in order to establish a whole picture of hydrogen behaviour in future research.

2) We have tested some representative base oils in this study, but there are some other practically important base oils including naphthenic and phenyl ether oils that have different molecular structures. We have started collaboration with oil companies to study these oils, and have obtained some interesting findings.

3) Future research will also have to investigate how the tribofilm forming additives including ZDDP influence the hydrogen permeation when dispersed in different types of base oils. The polarity of base oils may affect chemical reactions with the additives due to the competition in adsorption and reaction.

4) Future research will also have to improve the 3D observation of structural change in steel.

3. Plan and past presentation or publication of your research results

Oral Presentations:

1) Hiroki Fukuoka, Hiroyoshi Tanaka, Monica Ratoi, Joichi Sugimura
Formation of surface film and hydrogen permeation under rolling/sliding contact"
JAST Tribology Conference, Niigata, October 2016
2) Monica Ratoi, Joshua Seetanah, Brian Mellor, Hiroyoshi Tanaka, Joichi Sugimura
Lubricant Environments and Rolling Contact Fatigue Performance
International Hydrogen Energy Development Forum, Hydrogenius & I2CNER Tribology Symposium, February 2017
3) Monica Ratoi, Joshua Seetanah, Brian Mellor, Hiroyoshi Tanaka, Joichi Sugimura
The Effect of Lubricant Environments on Hydrogen Embrittlement
STLE Annual Meeting, Atlanta, May 2017
4) Vlad B. Niste, Hiroyoshi Tanaka, Joichi Sugimura
The importance of additive chemistry in generating tribofilms efficient at preventing hydrogen permeation in rolling contacts
World Tribology Congress 2017, Beijing, September 2017
5) Vlad B. Niste, Hiroyoshi Tanaka, Joichi Sugimura
The effect of temperature on generating ZDDP tribofilms efficient at preventing hydrogen permeation in rolling contacts
International Colloquium, Esslingen, January 2018
6) Vlad B. Niste, Hiroyoshi Tanaka, Joichi Sugimura
Controlling hydrogen permeation in bearing steel - effect of base oil polarity on ZDDP film growth
STLE Annual Meeting, Minneapolis, May 2018
7) Hiroyoshi Tanaka, Joichi Sugimura
Generation and permeation of hydrogen in rolling contact of steel
JAST Tribology Conference, Tokyo, May 2018

Publications:

1) Hiroyoshi Tanaka, Vlad Bogdan Niste, Yuta Abe. Joichi Sugimura
The Effect of Lubricant Additives on Hydrogen Permeation Under Rolling Contact
Tribol Lett (2017) 65:94
DOI 10.1007/s11249-017-0877-x
2) Vlad Bogdan Niste, Hiroyoshi Tanaka, Joichi Sugimura
The importance of temperature in generating ZDDP tribofilms efficient at preventing hydrogen permeation in rolling contacts
Tribology Transactions on line 2018.7
https://doi.org/10.1080/10402004.2018.1447180
3) Monica Ratoi, Hiroyoshi Tanaka, Joshua Seetanah, Brian Mellor, Joichi Sugimura
The Effect of Lubricant Environments on Hydrogen Embrittlement
submitted to RSC Advances
4) Monica Ratoi, Hiroyoshi Tanaka, Joichi Sugimura
Formation of surface film and hydrogen permeation under rolling/sliding contact: The role of synthetic oils in controlling hydrogen embrittlement in RCF
to be submitted