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In-situ detection of hydrogen evolution in a lubricated sliding pin on disk test under high vacuum

Dominik Kuerten [a,1,*], Nicholas Winzer [a,2], Andreas Kailer [a,3], Wulf Pfeiffer [a,4], Reiner Spallek [b,5], Matthias Scherge [a,6]

[a] *Fraunhofer Institute for Mechanics of Materials IWM, Fraunhofer-KIT MicroTribology Center μTC, Wöhlerstr. 11, 79108 Freiburg, Germany*
[b] *Klüber Lubrication München SE & Co. KG, Geisenhausener Strasse 7, 81379 München, Germany*

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ABSTRACT

In the present study the decomposition mechanisms of a multi-alkylated cyclopentane (MAC) lubricant on a steel surface were investigated in a ball-on-disk sliding test under vacuum. The lubricant was analyzed in-situ using a mass-spectrometer to study possible tribochemical reactions with the metal surface. The degradation of the lubricant was correlated with the formation of gaseous reaction products including hydrogen and various alkanes and alkenes. An increased carbon concentration was detected using XPS up to a depth of 1 μm below the surface of the wear track. This was attributed to reactions between the lubricant and the metal surface involving carbon chain cracking and fragmentation of the lubricant. An oxidation reaction between the lubricant and metal oxides was also identified. From the sliding test results it was shown that the rate of formation of gaseous reaction products increased with increasing load and sliding speed. Flash temperatures were calculated according to the Kuhlmann-Wilsdorf model. Finally, a correlation between the frictional power density and the evolution of hydrogen was established.

1. Introduction

Brittle flaking represents a serious industrial problem affecting steel bearings of all sizes in a diverse range of applications. Despite there being a considerable body of literature, the mechanism for the generation and absorption of hydrogen is still unclear [1]. Numerous investigations were carried out in the 1960's and 1970's with the aim of evaluating lubricant contamination with water as a possible source of hydrogen. Cantley [2] attributed the correlation between the reduction in bearing lifetime and increased water content in the lubricant to the influence of hydrogen. Grunberg et al. [3] and Ciruna and Szieleit [4] evaluated the influence of water contamination on fatigue lifetime by using a four ball testing apparatus and measured the hydrogen concentration in the balls after the tests. Grunberg et al. [3] concluded that hydrogen plays an important role in the lifetime of the rolling elements and that the presence of water in the lubricant contributes to this effect. Ciruna and Szieleit [4], on the other hand, used oxidation tests to demonstrate that hydrogen is produced in an oxidation reaction of the lubricant with the steel surface. Additives such as water or glacial acetic acid influenced the quantity of hydrogen that was formed [4]. The generation of hydrogen as a product of some tribochemical reaction of the lubricant, even in the absence of water or additives, is now a common theme in the literature. Tamada and Tanaka [5] found that brittle flaking occurs in double-roller rolling contact fatigue (RCF) tests of specimens pre-charged with hydrogen. Based on these results, the authors proposed that brittle flaking was due to hydrogen produced by the reaction of the lubricant with the metal surface and absorbed by the steel body. Kino et al. [1] proposed that the critical factor affecting hydrogen generation is the local increase in temperature due to frictional heating.

Numerous researchers [6–9] have evaluated the mechanisms for hydrogen generation by performing ball-on-plate tribometer tests in a vacuum chamber and measuring the evolved hydrogen using a mass spectrometer; however, vacuum tribometer tests are limited to the evaluation of oils that are stable under vacuum.

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* Corresponding author.
E-mail addresses: dominik.kuerten@iwm.fraunhofer.de (D. Kuerten), nicholas.winzer@thyssenkrupp.com (N. Winzer), andreas.kailer@iwm.fraunhofer.de (A. Kailer), wulf.pfeiffer@iwm.fraunhofer.de (W. Pfeiffer), reiner.spallek@klueber.com (R. Spallek), matthias.scherge@iwm.fraunhofer (M. Scherge).
[1] Tel.: +49 761 5142 148.
[2] Tel.: +49 761 5142 247.
[3] Tel.: +49 761 5142 247.
[4] Tel.: +49 761 5142 166.
[5] Tel.: +49 89 7876 536.
[6] Tel.: +49 721 4640 750..

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Based on such tests, Kohara et al. [6] proposed that the lubricant decomposition reaction is catalyzed by the film-free steel surface, which is exposed by sliding contact. Lu et al. [7] correlated the sliding speed and load with the quantity of gaseous reaction products, which include H_2^+, CH_3^+, $C_2H_3^+$, $C_2H_4^+$, and $C_3H_7^+$, for vacuum tribometer tests using the multi-alkylated cyclopentane (MAC) lubricant Pennzane 2001A. The authors rationalized the results in terms of the removal of the oxide layer from the steel surface by rubbing. In two separate works [8,9] the same authors showed that the addition of 1 wt% di-tert-dodecyl disulfide to Pennzane 2001 A prolonged the period of time until the onset of decomposition. This delay was attributed to the coverage of the steel surface with iron sulfide and hydrocarbon sulfide, which poisoned the catalytic reaction and hindered the decomposition process. Another study of the decomposition of MAC under ultrahigh vacuum conditions was done by John et al. [10]. It showed that during a sliding test, the oxide layer of the steel surface was removed. The degradation of the lubricant involves tribochemical reactions on the oxide-free metal surface causing the formation of methane, which can be detected with a mass spectrometer. Analysis of the steel sample after testing showed the formation of graphitic-type carbon on the surface [10].

An analysis of the decomposition process of Pennzane 2001A oil was conducted by Bertrand [11,12]. Bertrand [11] postulated that the fragmentation of the multi-alkylated cyclopentane (MAC) into volatile and non-volatile alkanes and alkenes is the first step in the decomposition process. The experimental results showed that the degradation of MAC fluids due to the emission of triboelectrons produced due to wear in both steel and hybrid bearings under vacuum conditions is insignificant [11]. The presences of a fresh metal surface produced by wear and chemical reactions on the surface have a more significant effect on lubricant degradation in these applications [11]. Bertrand [12] analyzed the wear-induced chemical decomposition of MAC fluids in bearing tests carried out under a vacuum pressure of 10^{-8} Torr. The lubricant was analyzed with infrared spectroscopy and gel-permeation chromatography. The results showed that the oil reacts with the fresh metal surface produced by wear. Both methods were used to detect the fragmentation of the oil into radicals (alkanes and alkenes). Such alkane and alkene radicals could react to form larger molecules like oligomers or even polymers [12]. They may also react with the oxide layer and debris, which contain oxide and iron particles and form acid on the surface resulting in its reaction with the oxide-free iron surface and the formation of carboxylate salt [12]. Bertrand [12] found this salt in the lubricant after the bearing test. Mori et al. [13] analyzed the decomposition of formic acid, which is the simplest carboxylic acid, and deuterated formic acid on a nascent steel surface. Scratching tests were carried out in a vacuum chamber under various loading conditions, whilst the decomposition products were analyzed using a mass spectrometer. H_2 and CO_2 were detected during the test; it was proposed that these were products of the decomposition of formic acid on the nascent steel surface. Deuterated formic acid was also used to clarify the influence of chemisorbed water on hydrogen evolution during scratching. The reaction products CO_2^+, HD^+, and D_2^+ were measured during the test. The formation of HD^+ was dependent on the water concentration on the steel surface and decreased with scratching time. The evolution of D_2 was nearly constant over the scratching time. Mori et al. [13] concluded that the evolution of H_2 and CO_2 was much lower than the chemisorption rate of formic acid on the steel surface. Cheng and Strair [14] conducted in-situ Raman analysis during a sliding of a steel ball on a sapphire plate lubricated using Krytox (a fluorine-containing lubricant) and Pennzane 2001A (MAC fluid). In both cases, a layer of amorphous carbon was formed on the steel surface, with that formed using Krytox being stronger than that formed using Pennzane [14]. Markowska et al. [15] and Kajdas et al. [16] carried out sliding tests using a ball and disc made of 100Cr6 bearing steel and lubricated using n-hexadecane. Aldehydes, alcohols and carboxylic acid were detected, indicating a tribochemical reaction on the steel surface. The possible presence of carboxylates was also documented. It was argued that the tribochemical reaction on the steel surface was activated by frictional energy [15]. Kajdas et al. [16] conducted an analysis of reaction products in wear tracks on steel surfaces; it was proposed that the decomposition of n-hexadecane led to the formation of salts and chelates (Fe–O bonding), carbonyl compounds and iron carbide [16]. Kajdas et al. [17] analyzed the decomposition of n-hexadecane in a ball-on-disk sliding test with different materials. The ball was always made of 100Cr6 steel whereas the disks were made of 100Cr6 steel, PA6 aluminum, MO58 brass and B101 bronze. Complex compounds (chelates) were formed on the wear track edges of all materials during the test. This was attributed to lubricant degradation. Lockwood and Klaus [18,19] analyzed the oxidation reaction of esters in a micro-oxidation test. Products of the ester oxidation were reported to react with the iron surface at temperatures ranging from 448 K to 523 K [18]. The oxidation of the ester is accompanied by an increase in molecular weight and by polymerization, which was enhanced by the reaction with the metal surface [19].

Przedlacki and Kajdas [20] investigated the decomposition of the fluorinated lubricants perfluoropolyether (PFPE), Z-Dol 2500 and perfluorooctanol. It was found that the decomposition of the PFPE oil on the metal surface produced a carboxylic acid salt. This is produced in an oxidation reaction of the hydroxyl group to a carboxyl group or due to the cracking of the polyether chain. The carboxylic acid is formed during hydrolysis of the acid fluoride, which is produced in a catalytic reaction with metal oxide. Using XPS-analysis, a metal oxide fluoride layer was detected under a film of carboxylic acid salt. The decomposition of the PFPE-oil during sliding contact produced a fluoride layer on the metal surface, which originated from a reaction of the evolved COF_2 with the metal surface [20].

The aim of the present study was to investigate the possible sources of hydrogen evolution in tribological contact under lubricated conditions by studying a model tribological system under vacuum and analyzing the lubricant decomposition products using various methods.

2. Methodology

2.1. Experimental

Ball-on-disk sliding tests were carried out under high vacuum (10^{-5} mbar) with the samples lubricated with either a thin film of Pennzane 2001A (MAC fluid) from Nye Lubrication with a viscosity of 108 cSt (40 °C) or perfluoro-poly-ether (PFPE) from Klüber Lubrication with a viscosity of 100 cSt (40 °C). The MAC fluid is a 1,2,4-Tris (2-octyl-1-dodecyl) cyclopentane (Fig. 1). The PFPE oil is a hydrogen-free lubricant in which all hydrogen atoms are substituted by fluorine atoms (Fig. 2).

The 100Cr6 disks had a diameter of 35 mm and a thickness of 2.6 mm. The diameter of the 100Cr6 balls was 10 mm (Fig. 3). Prior to testing, the samples were degreased with acetone and n-hexane in an ultrasonic bath. The disk was covered with a thin layer of the lubricant before testing. During the test the ball was brought into contact with the disk while simultaneously applying a constant normal load. In each test, loads of 25 N, 50 N, 75 N and 100 N were applied in the normal direction at consecutive intervals. The period between each loading interval was 1 h. Tests using the