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Investigation of adsorbed protein and passive films on hydrodynamic lubricated steel slider surface

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ABSTRACT

The adsorbed bovine serum albumin (BSA) and passive tribofilms, which were formed on a hydrodynamic lubricated steel slider surface with BSA-PBS aqueous solutions, were investigated. The morphological features and chemical structure of the slider surfaces were analyzed using SEM, AFM and XPS. Results show that the protein adsorption is spread over the steel surface heterogeneously. The films are apparently characterized by two layers. The top layer is in the form of protein agglomerates embedded in a gel-like matrix, and the bottom layer contains $Cr^{+3}/Fe^{+2}/Fe^{+3}$-rich passive oxides. The relations between corrosion and adsorption are discussed. The BSA adsorption gets escalated due to the presence of corrosion. The organic-inorganic composite films can work as a solid lubricant to reduce friction.

1. Introduction

Water-based lubrication has drawn large amounts of attention due to its environmental friendly nature, also with other advantages such as higher thermal conductivity, fire-resistance and the potential for ultra low friction [1]. However, pure water can hardly be used as an effective lubricant for common engineering applications mainly due to its low-viscosity and corrosiveness. What is interesting is that, water with appropriate additives can meet most of nature's needs for lubrication, such as the synovial fluids in mammalian joints and tear droplets for blinking eyelids. Inspired by nature, aqueous lubricants with various additives have been being tested to overcome the weakness of pure water and fulfill tribological requirements. Actually, synovial fluids are aqueous electrolyte solutions containing different kinds of proteins, hyaluronic acid and lipids [2], among which proteins (such as albumin and globulin) are well known to play an important role on tribological performance. Although different studies may give different results, it is generally agreed that lubrication and anti-wear effects can be enhanced by the protein adsorption onto the tribopair surfaces [3–7].

When metallic surfaces are lubricated with protein aqueous solutions, tribofilms containing adsorbed protein and passive layers would grow on the surfaces due to mechanical and electrochemical effects. Lundin et al. [8] quantified the amount of protein adsorption and metal release (corrosion) from chromium metal and stainless steel using the techniques of GF-AAS and QCM-D. They pointed out that both the protein-induced metal release and the possible protective effect of the adsorbed tribofilm are interrelated. Wimmer and his co-workers [9–11] found that those adsorbed organic proteins, salts and tribochemical layers on bearing surfaces serve as a type of solid lubricant to avoid adhesion and reduce friction. Yan et al. [12,13] reported the organo-metallic formation on the surface of CoCrMo alloys and 316L stainless steel through bio-tribocorrosion process. They measured the friction coefficient, wear and corrosion signals at the same time, and found that the tribofilm can not only lubricate the contacts but also regulate ion release [14]. These protein based tribofilms as formed on a large variety of materials may show distinct compositions and they can probably affect corrosion resistance, lubrication behavior and thus applications [12,15]. Serro et al. [4] studied the adsorption of BSA on the surface of various kinds of materials using XPS and radio-labeling techniques. They found that albumin adsorbs on alumina as a mono-layer but as multilayers on metallic surfaces. For CoCrMo, the adsorbed films are organometallic in nature [16] and mainly consist of Cr^{+3} oxide with minor molybdenum oxides (Mo^{+4}, Mo^{+5}, Mo^{+6}) [12,17]. For 316L stainless steel, Cr^{+3} and Fe oxides are abundant in the passive tribofilm [12,18]. To understand lubricating film formation by aqueous lubricants, Mavraki and Cann [19], Fan et al. [20] and Myant et al. [21] measured the film thickness of bovine serum (BS) using 52100 steel and CoCrMo balls on an optical ball-on-disk EHL tester. They proposed a protein-aggregation lubrication mechanism to clarify the complex time-dependence of the lubricating film. They observed that wear occurred on the ball surface shortly after the start of the test, and attributed the wear to chemical polishing (corrosion).

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Furthermore, there have always been interests in water-based lubricants for industry applications, including studies in additives for a variety of purposes, such as friction modifier, anti-corrosion and anti-wear [22,23]. More recently, hydrophobin proteins have been studied as additives of water-based lubricants from engineering perspectives under the conditions of elastohydrodynamic and boundary lubrications [24,25]. Hakala et al. [25] found that some kinds of hydrophobins can work as additives in water-lubricated copper/DLC contacts and reduce friction by 13–30% compared to pure water lubrication but increase the amount of wear of the copper pin.

As has been stated that there was usually co-existence of protein adsorption, metal element release (corrosion) and passive film formation in tribo-pairs lubricated by protein aqueous solutions, and understanding fundamentals of their correlation and interaction is crucial for practical application. Most of the experiments in literature have been carried out under mixed lubrication conditions and wear usually occurs. The wear, in turn, influences the interactions among the three behaviors. On the other hand experiments under full film conditions enable the tribo-film generated without wear, and interactions occurs among protein adsorption, corrosion and passive film formation without external influence. Some of the present authors [26] conducted experimental studies on the hydrodynamic film formation in a slider-on-disk contact using BSA aqueous solutions. The large area of the contact enables easy observation of tribo-film formation on the slider surface and instrument characterization of the film. No large-size protein-aggregations at the inlet were found as those reported in Refs. [19–21]. The difference may be due to different kinematic running conditions of the two studies. Instead, on-line monitoring and post-test examination of the bearing surfaces revealed localized inlet corrosion and heterogeneous protein adsorption under hydrodynamic lubrication conditions. It would give further understanding of the lubrication of protein aqueous lubricants if more detailed information about the adsorbed films on the surface of the steel slider is known. This work was thus conducted to characterize the protein adsorbed film using X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscope (SEM) and Atomic Force Microscopy (AFM). The adsorbed film was formed on the surface of a steel slider bearing under hydrodynamic lubrication conditions using BSA aqueous solutions as the lubricant. Moreover, the tribological behavior of the protein adsorbed film on the steel slider surface was evaluated in a ball-on-plate configuration. The aim of this work is to reveal the formation mechanism of the tribofilm and the correlation of protein adsorption, corrosion and lubrication.

2. Experiments

2.1. Tribofilm generation under hydrodynamic lubrication

A custom-made optical slider bearing tester [27] was used in the study. All the tests were run under steady state and isothermal conditions. As schematically illustrated in Fig. 1, the lubricated contact pair consists of a fixed-incline steel slider and a transparent rotating BK7 glass disk. A thin lubrication film can be generated once the disk rotates. The surface of the glass disk in contact with the slider was coated with a semi-reflective Cr coating for the formation of high-contrast interference images. The slider inclination angle α can be known exactly through the number of fringes formed in the contact. The prescribed inclination angle α is set and locked by the bolts located on the load arm. The lubricating film thickness can be measured accurately via interferometry [28]. The term "film thickness" here is referred to the minimum film thickness h_0 at the outlet of the slider bearing, as depicted in Fig. 1.

The slider is made of AISI 52100 steel, and its chemical composition is shown in Table 1. The sliding surface was 4×9 mm^2 in size (length × width) and precisely polished to roughness Ra around 9 nm. Prior to a test, the slider was cleaned ultrasonically with high purity alcohol for 10 min, and then rinsed with acetone and left to air dry.

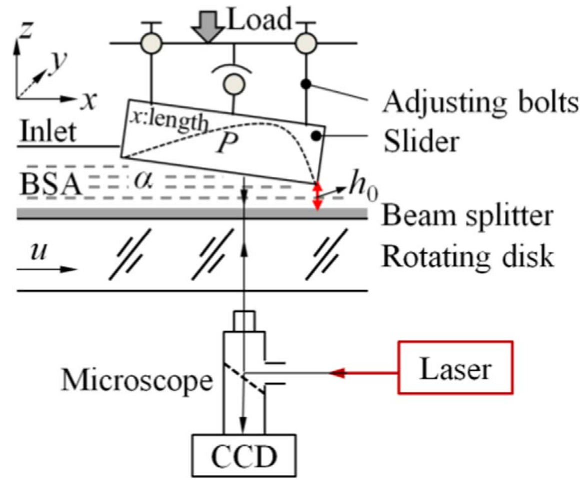

Fig. 1. Schematic diagram of the slider-on-disk test rig.

Albumin is the most abundant protein in synovial fluids as well as in serum and it is usually employed as a model protein in studying surface-protein interactions. The albumin solution used in the experiments was purified BSA (Bovine Serum Albumin, Fraction V, Roche) at 25 wt% concentration dissolved into a 0.01 M PBS (Phosphate Buffered Saline, pH=7.0–7.1) solution. Fresh BSA-PBS solution was stored at 4 °C and used within three days. The properties of the solution are listed in Table 2. The BSA molecule is well-characterized showing an oblate ellipsoid structure with a dimension of $14\times4\times4$ nm^3 and its molecular weight is approximately 65 kDa [29]. The BSA molecules are net negatively charged in the prepared solution as the solution PH is larger than the isoelectric point of BSA in water (pI=4.7) [30].

It has been known that proteins are abundant in natural synovial fluids (SF) and there is competitive adsorption among those proteins. A simple protein solution does not provide total information about the complex fluid behavior. All components of a complex fluid can affect each other and generate behaviors different from those from a single component. Nevertheless, the knowledge of the effect or the role of individual component can help to understand the behaviour of a complex fluid. Thus, the authors find the interest in studying the role of an important component BSA.

To prepare the surface tribofilm, the steel slider was lubricated with the BSA-PBS solution for 45 min at 20 °C and at 60 ± 5% relative humidity. The angle of slider inclination α was fixed to 8.9×10^{-4} rad. The load was 2 N (average pressure of 55.6 kPa) and the sliding speed was 20 mm/s. During running, interference images were saved every five minutes to record the growth of the tribofilm. After that, the slider was rinsed in deionized water to remove unbounded proteins and other ions, and then air dried.

After having conducted the lubrication experiment for 45 min, BSA size in the used solution was measured by a dynamic light scattering particle size analyzer (Zetasizer Nano ZS, Malvern).

2.2. Tribofilm characterization

The generated tribofilm on the slider surface was examined with optical microscopy (PMG3, Olympus) and SEM (JSM5600, JEOL) to get basic structural information. Furthermore, AFM (AutoProbe CP, Park Scientific Instruments) measurements were performed to scan an area of 20×20 μm^2 in tapping mode under ambient conditions, such that the profile of the surface film can be described in detail.

Surface chemical composition analysis was performed using XPS (PHI5820, Physical Electronics). The power source of XPS was in AlK_α (1486.6 eV) mode and set at 250 W. Spectra analysis was carried out in an area of 800 μm in diameter at the inlet zone of the slider. Wide