Abstract

In conventional tribological experiments that study friction and wear behavior of materials, the contact interface is hidden by the contacting bodies. The physical or chemical phenomena taking place at the interface must then be examined through intermittent tests. These kinds of postmortem studies have remained speculative and model based. The inadequacy of such analysis has long been recognized. For a fundamental understanding of interfacial phenomena, it is important to study interactions in real-time. The present work attempts to overcome this hidden-interface problem by developing a tribometer using optically transparent surfaces which can carry out real-time tribological experiments under a microscope equipped with a Raman spectrometer. Such a micro-Raman system enables combined optical imaging capability with chemical mapping and is consequently a promising tool for *in situ* studies in tribology.

Chapter 2 describes the development of a novel *in situ* total internal reflection (TIR) Raman tribometery, a technique based on TIR Raman spectroscopy combined with tribological experiments. The *in situ* TIR-Raman tribometer test rig is based on a ball-on-flat geometry. The rotating ball is immersed in an oil bath and carries a film of lubricant while rotating as it rubs against a flat (transparent) surface. Raman spectra of the lubricant are recorded from the contact region through the transparent window as a function of load, time, and velocity.

A unique advantage of the TIR technique is that the sample can be analyzed from a known depth beneath the interface using evanescent waves. The capabilities of this TIR Raman tribometer have been demonstrated by carrying out experiments with known solid lubricant material molybdenum disulfide (MoS2).

MoS2 is known for its solid lubricant properties. Nanoparticles of MoS2 are used as an anti- wear additive in engine oil. The commissioning of the tribometer rig was carried out using MoS2 nanoparticles to lubricate a steel-steel contact. Before carrying out *in situ* Raman tribometry on MoS2 nanoparticles, a set of characteristic friction and wear data was obtained from MoS2 nanoparticle-lubricated steel- steel contact (chapter 3) and compared with the data obtained from a commercial tribometer. In addition, friction characteristics of dry MoS2 and MoS2- hexadecane lubricated steel-steel contact were studied as a function of temperature. The friction in the dry particle lubrication was found to increase with temperature while the friction in wet condition was found to decrease with increasing temperature. Micro-Raman and FTIR spectroscopy are used to explore the roles of environmental moisture and chemical degradation of oil on the formation of antifriction films on the steel substrate.

Ex situ optical and Raman analysis revealed the formation of an anti-friction film on the steel substrate. To understand the underlying mechanism of nanoparticle lubrication, *in situ* Raman tribometry was performed and results are presented in Chapter 4. By combining *in situ* optical imaging and Raman spectroscopy, the sliding history in friction-induced material transfer of dry 2H-MoS2 particles in a sheared contact was studied. Video images in contact showed the fragmentation of lubricant particles and build-up of a transfer film. Contact imaging was used to measure the speed of fragmented particles in the contact region. Total internal reflection (TIR) Raman spectroscopy was used to follow the build-up of the

MoS_2 transfer film. The combination of *in situ* and ex-situ analysis of the mating bodies was used to understand the mechanism of transfer film formation in the early stages of sliding contact.
Application of *in situ* TIR Raman tribometry for the study of liquid lubricants was demonstrated by using PAO to lubricate SF10 glass – silica contact and results are discussed in Chapter 5. It is well established that under high shear rates, synthetic base oils undergo shear thinning. Earlier studies of shear thinning relied mainly on viscosity measurements from which it is not possible to obtain information on molecular alignments or ordering. In the present study, TIR Raman spectra were used to estimate the thickness of the lubricant film under sliding conditions and polarized Raman data was used to study the alignment of molecules during shear thinning. The experimentally obtained film thickness data was superposed with theoretical calculations and a transition from Newtonian to non-Newtonian behavior was observed at high shear rates. Also, the effect of additive molecules on the shear thinning behavior of poly alpha olefin lubricant was studied.

The *in situ* TIR Raman tribometer is a powerful tool to detect the physiochemical changes lubricants undergo at the hidden interface under sliding conditions. The capability of this technique in enabling tribological processes to be observed dynamically in real time with concomitant chemical changes at the interface has the potential to make it an indispensable tool in fundamental studies of tribological interactions. The application of total internal reflection resulted in significant signal enhancement which makes the technique developed in this study an important addition to the already available ones for future tribological studies. The information and insight generated in a range of tribological phenomena taking place at the hidden interface of contact will be useful in developing new lubricant materials.