Accessing Inaccessible Interfaces: *In Situ* Approaches to Materials Tribology

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Guest Editors

Abstract

The field of materials tribology has entered a phase of instrumentation and measurement that involves accessing and following the detailed chemical, structural, and physical interactions that govern friction and wear. Fundamental tribological research involves the development of new experimental methods capable of monitoring phenomena that occur within the life of a sliding contact. Measuring friction phenomena while the process is ongoing is a major improvement over earlier techniques that required the surfaces to be separated and analyzed, thereby interrupting the friction-causing event and modifying surface conditions. In the past, *MRS Bulletin* has highlighted how *in situ* approaches can greatly enhance our understanding of materials structure, processing, and performance. This issue highlights *in situ* approaches as applied to materials tribology, namely, the study of contacting surfaces and interfaces in relative motion.

Introduction

Tribology is a field of study that is focused on the fundamental investigations of friction and wear. As recently summarized in a report on the "Frontiers of Fundamental Tribology,"[1] new tools are needed to monitor tribological phenomena that are occurring within buried interfaces. These tools are essential for fundamental studies of friction and wear because they are not intrinsic properties of a material; rather, they are functions of the tribological system (which includes the contacting surfaces that are in relative motion, the local environment, the background temperature, the surface roughness and preparation, the sliding speeds and loads, and a host of other contributors). Over the past half century, tribological systems have been discussed and described in terms of three basic groups of thematically linked elements:[2] (1) the types of materials in contact and the contact geometry; (2) the operating conditions, including the gross motion, loads, stresses, and duration of operation; and (3) the environment and surface conditions, including the surface chemistry, surface topography, and ambient temperature. The incredibly large number of factors affecting tribological performance makes fundamental studies of materials tribology exceedingly difficult.

Energy and material losses in moving mechanical devices as a result of friction and wear impose an enormous cost on the national economy. Engineering tribology involves the designs of bearings, bushings, and a wide variety of interfaces that support our everyday mobility and often aims to simultaneously reduce both friction and wear. Practical solutions to mitigate friction and wear have traditionally been through the use of fluid lubricants such as oils and greases. However, there are a number of applications where traditional fluid lubrication strategies are either precluded or undesirable.[3,4] Materials tribology, and in particular solid lubrication, is an area of research that aims to control friction and wear through both the appropriate selection of known materials and the development of new materials and surface treatments.

The contact between macroscopic surfaces occurs on asperities, which are irregularly shaped protuberances that exist on all engineering surfaces.[5] Like fractals, these surface features occur across all length scales and define the distribution and shape of the real area of contact, which is orders of magnitude smaller than the apparent contact area.[6–8] Thus, friction and wear arise from microscopic contacts that are under tremendous stresses and might have contact lifetimes of microseconds. In macroscopic systems, these contact locations are unknown and are buried in an apparent area of contact that is typically inaccessible by most measurement techniques.

Most materials tribology studies have focused on the friction coefficient and the wear rate. As shown in Figure 1, the friction coefficient (μ) can be defined as the ratio of the friction force (F_f) to the normal force (F_n). The wear rate (K) is typically defined as the ratio of the volume of material removed (V) to the product of the applied normal load (F_n) and the distance of sliding (d). Both the friction coefficient and the wear rate are sensitive to the starting conditions, load, speed, temperature, and environment. The initial transients during the approach to steady-state sliding are usually monitored but not modeled, and many of the reported and tabulated values for friction coefficients and wear rates are for steady-state conditions.

To date, despite considerable efforts at understanding the origins of friction, there is no model capable of predicting friction coefficients from first principles. Similarly, there is no model for wear (which is often defined as the gradual removal of material from contacting surfaces in relative motion) that is based on first-principles arguments. Thus, careful and proven experimental techniques represent the most sophisticated and reliable approach for investigating, designing, and assessing the tribological worthiness of new materials. Fundamental studies of friction involve developing an understanding of the real area of contact, surface chemistry, adhesion, and shear strength of the interface, as well as the nature of

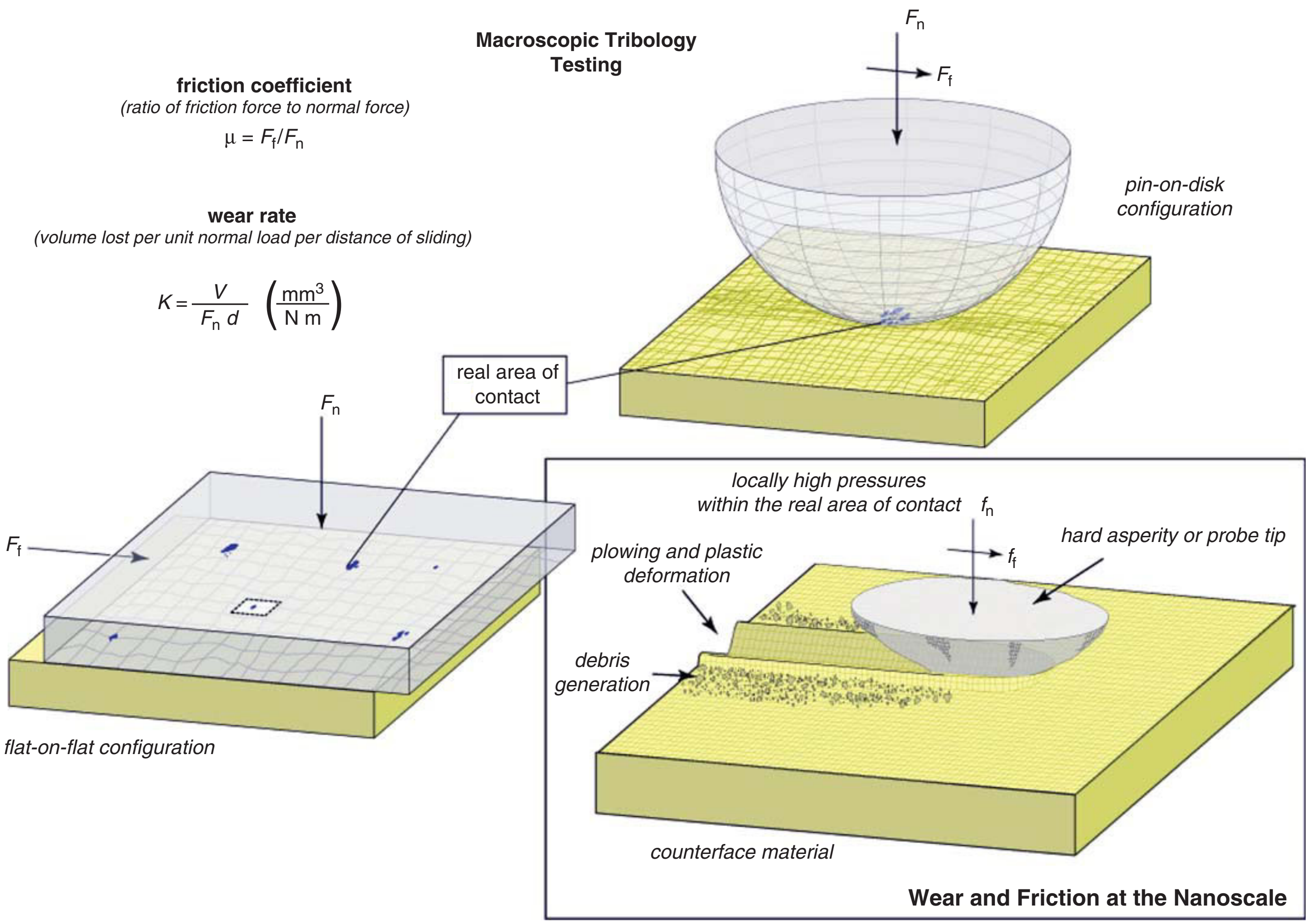

Figure 1. Tribology measurements for friction coefficient (μ) are traditionally made dynamically through force transducers that record both the lateral, or friction force (F_f) and the normal force (F_n). Whether a spherically tipped pin or a flat countersurface, the real area of contact (shown in blue) is a very small component of the apparent or projected contact area. The wear rate (K), defined as a ratio of the volume of material removed (V) to the product of the normal load (F_n) and the sliding distance (d), is rarely measured under dynamic conditions. As shown in the inset (lower right), the contact pressures at the asperity level (f_f and f_n, where $F_f = \Sigma f_f$ and $F_n = \Sigma f_n$) are typically large and approach the flow stress of the softer material. Single-asperity tribology measurements of friction can be accessed using atomic force microscope probes, and the deformation and structural transformation at this scale can be studied using tools such as *in situ* transmission electron microscopy.

deformation and energy dissipation occurring at the asperity junctions.

State of the Art

There are no standard reference samples (such as the standard kilogram prototype maintained by the International Bureau of Weights and Measures) in materials tribology because the specimens are consumed during testing. Thus, friction and the progression of wear must be monitored by sensitive force and displacement measurements and with periodic interruptions to examine the contacting surfaces. As illustrated in Figure 2, two common *in situ* approaches are used to follow and link chemical, structural, and physical interactions with friction and wear processes.

The most common *in situ* tribology approach has been to perform detailed measurements on the surface of the sample within the environment but outside the contact. The tribofilms and surface topography that develop during testing can be carefully studied between contacts; postprocessing of the data enables cycle-by-cycle analysis that can be used to link data from the current cycle with the friction and wear measurements of the previous cycle. The advantage here is that the testing of the samples can take place under the appropriate tribological system conditions in an environment that is not varying during observation and experimentation. Full-scale engineering components down to devices on the scale of microelectromechanical systems can be analyzed in this way. A serious limitation is that the analytical measurements are not carried out within the contact, so inferences need to be drawn between the observations outside the contact and the probable dynamics (chemical and mechanical) that exist within the contact.

In situ approaches that enable measurements within a contact are ideal. However, such approaches frequently require compromises of sample composition, geometry, and testing environment to be made. For example, transparent materials enable observations of the intimate contact areas but are often not the traditional counterface material for the application. Additionally, spherical or pla-

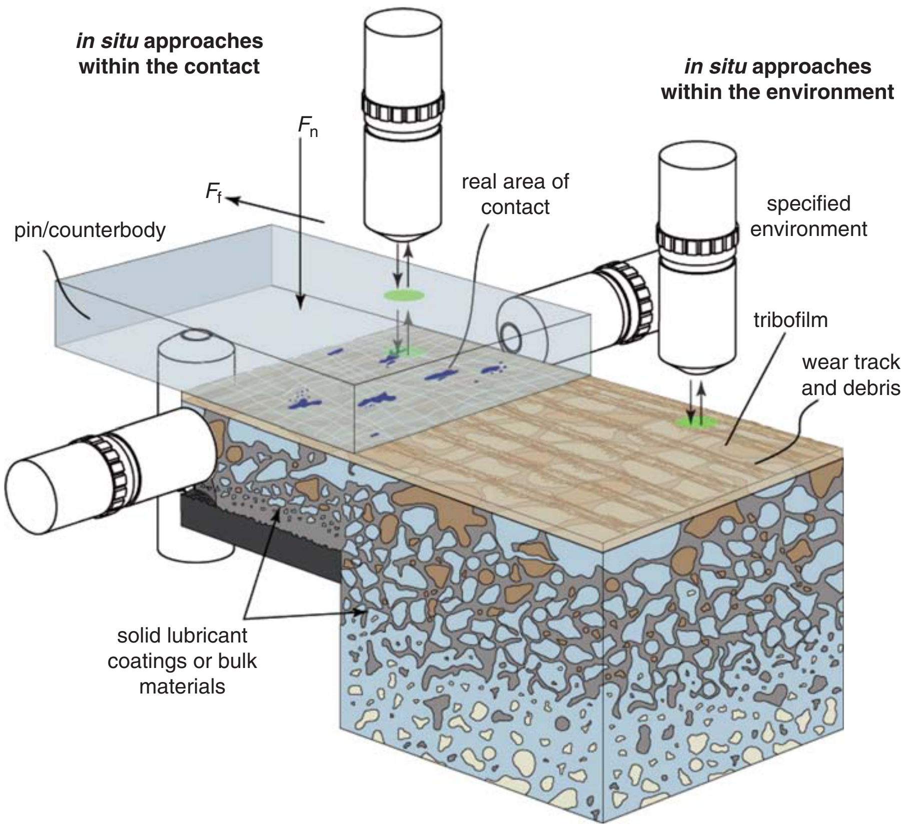

Figure 2. Various *in situ* approaches have been employed in tribological studies. Fundamental measurements of the real area of contact, the interfacial film or tribofilm chemistry, and the wear track morphology and wear rates are common goals. Here, microscope objectives illustrate pathways for *in situ* studies. The most common approach is to examine the surfaces emerging from a contact within the specified environment. A more complex scenario is to perform the measurements within the contact, as illustrated by the objectives looking through a transparent counterbody from above, below, or the side. Some compromise of the sliding contact (for example, materials, geometry, or scale) is typically required to achieve an *in situ* measurement of this type.

nar geometries are frequently selected for their suitability to the measurement rather than to the application. A number of analytical techniques have been employed for *in situ* tribology studies. Many of these techniques are listed in Table 1, with examples of the measurement application, resolution, and limitations.

The miniaturization of force and displacement measurement technologies have enabled a new suite of tribological test equipment that can be relatively easily integrated within a variety of existing surface analytical instruments. In other cases, advances in surface-science instrumentation have enabled these tools to be integrated with existing tribological equipment. Together, the merging of surface analytical instrumentation and careful tribological instrumentation is providing new and exciting opportunities to study the fundamentals of friction and wear.

In This Issue

In this issue of *MRS Bulletin*, we highlight the possibilities of applying *in situ* methods to the study of buried sliding interfaces found in tribological contacts. We have selected topics describing the state of the art in five areas ranging from the propagation of interfacial slip along crack fronts that simulate geological interfaces relevant to earthquakes to nanoscale single-asperity contacts probing how small collections of atoms accommodate, and are transformed by, sliding. Whereas previous *MRS Bulletin* issues tackling materials tribology[9–11] have highlighted a combination of parallel experimental and computational methods, the focus of this issue is on the development of experimental approaches allowing direct probing of materials mechanics and chemistry active in sliding contacts. Two of the articles address fundamental studies of liquid and solid lubrication using a range of *in situ* microscopy and spectroscopy approaches. The article by Cann reviews the application of infrared and Raman microscopy to liquid-lubricated contacts, showing how the relationship between molecular conformation, pressure, additives, and lubricant degradation can be correlated to friction performance. The article by Wahl and Sawyer reviews *in situ* approaches to understanding solid lubrication phenomena. Examples are provided to illustrate how optical and interference microscopy, Raman microscopy, and electron microscopy are applied to link real-time changes in interfacial film chemistry, morphology, and rheology to friction and wear events.

The remaining three articles address the state of the art in examining tribological contacts controlled by asperity-scale interactions. Marks et al. describe advances in *in situ* transmission electron microscopy to understand asperity–asperity interactions. The tools for controlling indentation and sliding of nanoscale contacts within the field of view of an electron microprobe provide unprecedented opportunities to observe atomic-scale tribological deformation processes in real time. The article by Bennewitz and Dickinson reviews another aspect of the state of the art in *in situ* atomic-scale measurements of wear. In this case, carefully prepared surfaces and controlled chemical environments allow examination of the role of defects and chemistry in the initiation of wear and its relation to atomic-scale friction. The last article, by Rubenstein et al., describes *in situ* optical measurements of the onset of sliding that show that the crack front motion comprises velocities from sluggish (tens of meters per second) to beyond the shear wave speed (>1,000 m/s). These direct observations indicate how the onset of sliding is influenced and controlled by these unusual crack propagation modes.

These articles illustrate a subset of the wide range of possibilities for applying *in situ* experimental methods to the challenge of understanding the materials and interface science of buried sliding interfaces. The *in situ* approaches could confirm or refute commonly accepted lubrication models and will allow closer comparison with molecular simulations of friction processes. Progress in materials tribology will depend on developing a detailed understanding of what is happening in buried sliding interfaces.

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Table I: *In situ* approaches used for tribological interface studies

Technique	Measurement	Spatial Resolution	Limitations
Optical microscopy	Tribofilm formation and motion, contact size	~ 1 μm	One counterface must be optically transparent.
Interferometry (contact)	Contact separation	~ 1 μm	One counterface must be optically transparent.
Interferometry (wear track)	Wear	~ 1 μm	Index of refraction or reflectivity changes can distort results.
Raman microscopy	Composition/chemistry, film thickness	~ 1 μm	One counterface must be optically transparent.
ATR-FTIR spectroscopy	Chemical bonding	mm to cm (width of crystal)	One counterface must be IR-transparent.
TEM + EELS + AFM/ nanoindentation	Microstructural transformation, interfacial film formation composition, chemistry	0.1 nm	Interface region must be electron-transparent; vacuum environment
SEM/EDX	Surface morphology, composition	10 nm	Contact charging, contamination in low vacuum environments
SEM + FIB	Cross section of sliding surfaces w/o separation	0.1 nm	Potential beam damage from FIB sectioning
SFA + x-ray diffraction or neutron relativity	Structure	μm's	Requires synchrotron access
AFM	Friction, surface topography, contact stiffness, wear	~ 1 nm	Difficult to ascertain contact size, chemistry
AES	Composition	10 nm	Cannot probe inside contact zone
XPS	Composition, chemical state	10s of μm	Cannot probe inside contact zone
Contact resistance	Coating thickness, damage, interfacial film formation		

Note: ATR-FTIR, attenuated total reflection Fourier transform infrared spectroscopy; TEM, transmission electron microscopy; AFM, atomic force microscopy; EELS, electron energy loss spectroscopy; SEM, scanning electron microscopy; EDX, energy dispersive x-ray spectroscopy; FIB, focused ion beam; SFA, surface force apparatus; AES, Auger electron spectroscopy; XPS, x-ray photoelectron spectroscopy.

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