See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/238648149

# Mechanics and Chemistry of Solids in Sliding Contact †

ARTICLE in LANGMUIR · SEPTEMBER 1996					
Impact Factor: 4.46 · DOI: 10.1021/la951056n					
CITATIONS	READS				
61	26				

#### 1 AUTHOR:



Irwin Lee Singer

United States Naval Research Laboratory (re...

149 PUBLICATIONS 3,745 CITATIONS

SEE PROFILE

## Mechanics and Chemistry of Solids in Sliding Contact<sup>†</sup>

I. L. Singer<sup>‡</sup>

Surface Chemistry Branch, Code 6176, U.S. Naval Research Laboratory, Washington, D.C. 20375

Received November 20, 1995. In Final Form: February 26, 1996

Wear behavior of coated surfaces has been studied extensively over the past 20 years. Although the behavior can be discussed in terms of classical models, it is described more completely using third-body concepts. These concepts consider the processes that take place at a moving interface: deformation and particle detachment, third-body formation and kinematics, and particle ejection. Tribological and analytical studies of several practical surface treatments, including TiN hard coatings and MoS2 Jubricant coatings,  $will be \ presented \ to \ illustrate \ the \ influence \ of \ third \ bodies \ on \ friction \ and \ wear \ behavior. \ More \ fundamental$ aspects of solid lubrication have also been studied in an ultrahigh vacuum chamber using gases to lubricate well-characterized surfaces. These studies indicate how third bodies form, how they influence friction and wear, and why some surface treatments are better than others. They also point to the need for better understanding of (1) the physical protection afforded by surface films, (2) tribochemical processes, and (3) chemical and mechanical properties of third bodies.

#### **Background**

Surfaces of engineering materials (steels, Ti and Al alloys, etc.) used in moving mechanical assemblies (bearings, gears, shafts, etc.) lack the wear resistance needed to survive unlubricated sliding contact. Even if the rate of wear could be reduced to 1 atomic layer every thousand passes-clearly a low and "difficult to measure" wear rate—it, too, might be unacceptably high. For example, in an auto engine running at 3000 rpm, each piston ring slides along the cylinder liner 6000 times/min. If there were no lubricant to separate the ring from the liner and the wear rate were 1 nm/1000 passes, then wear losses would be 6 nm/min (=360 nm/h = 36  $\mu$ m/100 h) and the engine would fail in a few weeks! Oils and other liquid lubricants can often extend the life of engineering materials. But there are many circumstances in which liquid lubricants cannot be used (low speeds, high loads, extreme environments, etc.), and the only solution is to develop coatings or other surface treatments that reduce wear and lower friction.1

Today, one can find many recipes for surface treatments that combat wear and reduce friction.2 However, treatments that protect in one application can be fatal in others. For example, a hard coating like TiN can increase the wear life of tool steel in a cutting operation but, on a piston ring, might accelerate the wear of an iron cylinder liner (TiN is harder than iron and can abrade it). Surface treatments cannot be applied in "cookbook" fashion because tribological behavior is not governed by material properties alone; rather it depends on contact conditions (geometry, load, speed, etc.), atmosphere, and temperature<sup>3,4</sup> as well as materials<sup>5,6</sup> and their failure modes.<sup>7</sup> Classical tribology provides much of the basic vocabulary

fatigue removes layers by crack growth and propagation; (4) chemical wear, in which gases or liquids enter the surface, react with or otherwise weaken it, and cause material to be released. For those interested in the mechanical wear modes, I recommend the studies of Kato and his colleagues,8 who have performed pin-on-flat tests on a wide range of materials in a scanning electron microscope and provide both visualization and modeling of most of the wear modes described above. One aspect of wear that has often been ignored or overlooked is the role of detached particles. These particles often remain in the interface, either imbedded in the surface or as free particles. If this happens, then, technically, it is not accurate to say that the couple has worn (i.e., lost material). Moreover, this interfacial "debris" may be able to accommodate sliding and absorb deformation energy, resulting in reduced wear of the counterfaces. Several years ago, Godet9 and Berthier10 proposed an alternate way of describing wear behavior, one that takes into account these "third-body" materials

needed to discuss and model wear behavior. Briefly, it is generally accepted that stresses transmitted across an

interface during sliding contact cause particles to detach

by one of four modes: (1) adhesive wear, in which high

spots (asperities) on opposing surfaces adhere while the

weaker material shears below the surface, transferring a

particle of the weaker material to the stronger counterface;

(2) abrasive wear, in which a hard particle, imbedded in

one surface or free as a third body, plows loose counterface

material; (3) delamination or fatigue wear, in which cyclic

generated during sliding (and rolling) contact. The third-

body approach examines processes that take place at a

moving interface: deformation and particle detachment (via classical modes), third-body formation and kinematics

(particle morphology and flow within contact zone), and

particle ejection. The third bodies consist of two "screens"

or films attached to the two parent counterfaces and

unattached third-body particles between the counterfaces.

<sup>†</sup> Presented at the Workshop on Physical and Chemical Mechanisms in Tribology, held at Bar Harbor, ME, August 27 to September 1, 1995.

Tele (202) 767-2327; fax (202) 767-3321; e-mail singer@ ccf.nrl.navv.mil.

Abstract published in Advance ACS Abstracts, Sept. 15, 1996. (1) Singer, I. L. In New Materials Approaches to Tribology: Theory and Applications; Pope, L., Fehrenbacher, L., Winer, W., Eds.; MRS:

Pittsburgh, PA, 1989; p 215.
(2) Holmberg, K.; Matthews, A. Coatings Tribology; Elsevier: Am-

<sup>(3)</sup> Czichos, H. *Tribology: A Systems Approach to the Science and Technology of Friction, Lubrication, and Wear*; Elsevier: Amsterdam,

<sup>(4)</sup> Buckley, D. H. Surface Effects in Adhesion, Friction, Wear, and Lubrication, Elsevier: New York, 1981.

<sup>(5)</sup> Zum Gahr, K.-H. Microstructure and Wear of Materials; Elsevier: Amsterdam, 1987

<sup>(6)</sup> Hutchings, I. M. Tribology: Friction and Wear of Engineering (6) Hutchings, I. M. Tibology, Tricker and Materials, CRC Press: Boca Raton, FL, 1992.
(7) Ashby, M. F.; Lim, S. C. Scr. Metall. 1990, 24, 805.
(8) Kato, K. Wear 1992, 153, 277 and references therein.
(9) Godet, M. Wear 1984, 100, 437.

<sup>(10)</sup> Berthier, Y.; Brendle, M.; Godet, M. *Tribol. Trans.* **1989**, *32*, 490. Berthier, Y. Wear **1990**, *139*, 77.

Figure 1. A schematic representation of the wear process observed for the three low-friction, low-wear treatments during sliding in air.14

Table 1. Phases Identified by Electron Diffraction of Debris Stripped from Riders Slid against Surface-Treated Steels

treatment	rider	phase	ref		
TiN-coated steel	steel	FeTiO <sub>3</sub> /α-Fe <sub>2</sub> O <sub>3</sub>	19		
	sapphire TiO <sub>2</sub>	TiO <sub>2</sub> (rutile)	19		
TiC-coated steel	steel	FeTiO <sub>3</sub> /α-Fe <sub>2</sub> O <sub>3</sub>	20		
	sapphire	TiO <sub>2</sub> (rutile)	۵0		
$Ti^+$ - and $(Ti^+ + C^+)$ -implanted steel	steel	FeTiO <sub>3</sub> /α-Fe <sub>2</sub> O <sub>3</sub>	18		
	sapphire	FeTiO <sub>3</sub> /α-Fe <sub>2</sub> O <sub>3</sub>	10		
MoS <sub>2</sub> -coated steel	steel MoS <sub>2</sub> , FeMoO <sub>4</sub> , Fe <sub>2</sub> MoO		28,29		
	WC:Co	MoS <sub>2</sub> , CoMoO <sub>3</sub> , MoO <sub>3</sub>	20,23		

Third-body studies have generally emphasized the kinematics and mechanics, the "where" and "how" of velocity accommodation. Our studies at the Naval Research Laboratory have focused on the sliding behavior of "low-wear" surfaces in concentrated contacts; we have been interested mainly in how screens form on stationary counterfaces and "what" compositions and phases of the screens and third-body particles are produced. We perform wear tests at relatively low speeds, typically 0.1-100 mm/s, with sphere vs flat geometries at high normal contact stresses (0.5-1.5 GPa) in unidirectional or reciprocating sliding. Surfaces are characterized before and after wear tests, using all available techniques to analyze the topography, chemistry, and microstructure of coatings and treated surfaces. 11,12 In this essay, I will show how this approach has revealed both chemical and third-body contributions to the wear behavior of long-lived coatings. Selected results from case studies of well-known wear resistant and/or low-friction coatings such as TiN, diamond-like carbon (DLC), and MoS2 will be presented, and unresolved issues will be highlighted in italics. At the end, I will list six areas where improved fundamental understanding of mechanical and chemical processes in wear and friction are needed to increase the predictive capability of tribology.

### **Behavior of Hard Coatings**

The protective nature of many practical surface treatments can be traced back to a film that forms on the surface of a substrate.<sup>4,13</sup> Although the film wears away, on the average it wears very slowly; hence, there is ample time for a new film to regrow. In the meantime, the worn film evolves into a third body. We have observed that the third bodies generated from low-wear coatings, both hard and soft (discussed in the next section), form in three stages, shown schematically in Figure 1.14 At first, the surface film is removed from the substrate and transferred to the rider (pictured here as a sphere whose contact area never loses touch with the track). The "transfer" film can then react with the rider material and atmospheric gases, forming compounds with identifiable phases. As the transfer film thickens, it is extruded from the contact area and can break up, forming debris particles.

What do we know about transfer films and coating wear? The films are initially thin, perhaps only a monolayer or so thick, but can be detected by Auger electron spectroscopy and other surface sensitive spectroscopies long before wear is detected on the track. 15-17 Later, the transfer film grows to tens of nanometers thick, even though the coating wear is negligible. How is that possible? Suppose that a layer 1 nm thick, of fixed width, were removed from the coating surface along a length of track 5 mm long and all the material collected from the layer were deposited on the stationary contact to a length of 0.1 mm and the same width. By conservation of volume, the transfer film would be 50 nm thick. This layer-by-layer removal mechanism has been inferred from the shape and composition of transfer films examined by transmission electron microscopy. The films were generated during low-friction sliding of steel and/or sapphire against Ti-implanted steel, <sup>18</sup> TiN, <sup>19</sup> and TiC, <sup>20</sup> in air; they contained platelets, uniformly thin over distances of micrometers, which, we speculated, were sheared from the wear track. However, the actual mechanism of material removal from the wear track has not been identified.

Although transfer films originate from a "parent" material, not all films have the same composition or phase as the parent. In the three Ti-containing materials mentioned above, the compositions of the films were always oxides and their phases were either binary oxides of one of the metal counterfaces or ternary oxides of both metal counterfaces (see Table 1). The phases were, in fact, those predicted by equilibrium thermochemical calculations of the counterface materials plus oxygen. It may seem surprising that equilibrium phases are attained at room temperature during low-speed sliding ( $\approx$ 10 mm/s), especially since several of the phases, such as ilmenite  $(Fe_xTi_{1-x})_2O_3$  where  $0 \le x \le 1$ , require high temperatures to form in the bulk. 19 High temperatures are usually required to provide the diffusion kinetics needed to completely transform bulk materials in a reasonable time. With films, however, each layer "stripped" from the track

<sup>(11)</sup> Singer, I. L. Appl. Surf. Sci. 1984, 18, 28.
(12) Surface Diagnostics in Tribology; Miyoshi, K., Chung, Y. W., Eds.; World Scientific: River Edge, NJ, 1993.
(13) Iliuc, I. Tribology of Thin Layers; Elsevier: Amsterdam, 1980.
(14) Singer, I. L. Surf. Coat. Technol. 1991, 49, 474.

<sup>(15)</sup> Ehni, P. D.; Singer, I. L. In New Materials Approaches to Tribology: Theory and Applications; Pope, L., Fehrenbacher, L., Winer, W., Eds.; MRS: Pittsburgh, PA, 1989; p 245.

<sup>(16)</sup> Wahl, K. J.; Seitzman, L. E.; Bolster, R. N.; Singer, I. L. Surf. Coat. Technol. 1995, 73, 152.

<sup>(17)</sup> Wahl, K. J.; Singer, I. L. *Tribol. Lett.* **1995**, *1*, 59. (18) Fayeulle, S.; Singer, I. L. *Mater. Sci. Eng.* **1989**, *A115*, 285. (19) Singer, I. L.; Fayeulle, S.; Ehni, P. D. *Wear* **1991**, *149*, 375. (20) Fayeulle, S.; Singer, I. L. In *Wear Particles: Cradle to Grave* 

Dowson, D., Taylor, C. M., Godet, M., Eds.; Elsevier: Amsterdam, 1992; p 293.

**Figure 2.** Friction coefficient (solid line) and vertical deflection of the cantilever arm (dashed line) plotted against cycle for 52100 steel ball (rider) sliding on polished TiN-coated steel. Cantilever deflection scale was set to zero arbitrarily at the minimum deflection <sup>19</sup>

**CYCLE** 

is perhaps only nanometers thick. At room temperature, defect-enhanced diffusion should enable the kinetics to complete the phase formation across the layer in the time scale of the experiments (i.e., minutes). This, however, has not been proven and is only a rationalization for the observed phase formation.

Surface films and their transfer products contribute to friction by establishing well-defined shear planes, sometimes called the "velocity accommodation plane", and by increasing the roughness of the sliding path. Initially, sliding occurs at an oxide-substrate interface (panel 1, Figure 1) or at the interface between the transfer film and the worn track (panel 2, Figure 1); in both cases, the sliding path is rather "flat". Friction, at this stage, is determined by the shear strength of these interfaces since roughness contributions to friction are small. However, as the transfer film thickens and breaks into debris, some of the debris can fall back onto the track. As debris builds up on the track, the sliding path roughens and the friction rises.  $^{19-21}$  This correlation is illustrated in Figure 2, which shows both the friction coefficient and the cantilever deflection vs cycles for a steel ball sliding against a polished TiN flat; the deflection gives the height difference between ball and flat during sliding. The *increase* in height (deflection) during the friction rise indicates a buildup of third bodies between ball and flat. The subsequent decrease in height at steady state friction ( $\mu = 0.6$ ) could be due to loss of debris from the contact or to wear of either surface (the actual cause was not investigated). However, it is clear that interfacial sliding no longer took place between the transfer film and the parent wear track; instead, it occurred between the transfer film and a debriscovered wear track. Invariably, this new velocity accommodation plane was rougher and of different chemistry than the earlier lower friction surfaces. The increase in friction is probably due to increased plowing contributions along the rougher surface and perhaps some increased adhesion as the transfer film and debris evolve in composition and morphology.

#### **Behavior of Solid Lubricating Coatings**

For most of the hard coatings studied, low-friction sliding was a relatively short lived phenomenon, often only 10-

100 cycles. However, diamond-like carbon (DLC) hard coatings can provide much longer periods of low-friction sliding, upward of 10<sup>6</sup> cycles, before failing.<sup>22–24</sup> As with the aforementioned hard coatings, DLC and the solid lubricant MoS2 rely on transfer films to sustain low wear and low friction. Here again, the chemistry of the transfer film depends on solid-solid and gas-solid reactions. For example, steel sliding against DLC in ultrahigh vacuum (UHV) generated a transfer film that was identified as an oriented, straight-chain hydrocarbon, 23,25 whereas Si<sub>3</sub>N<sub>4</sub> against DLC in moist air produced a film that contained oxidation products of Si and C.26 Transfer films from MoS2 coatings run in inert atmospheres were mainly basallyoriented  $MoS_2^{27,28}$  but, when run in air, included oxidation products of counterface materials (see Table 1).<sup>29</sup> Again, the oxidation products contain binary and ternary compounds predicted by equilibrium phase diagrams.

Friction coefficients of DLC and  $MoS_2$  coatings are generally lower ( $\mu < 0.1$ ) than those obtained from conventional hard coatings ( $\mu \ge 0.1$ ). Moreover, they are very sensitive both to the environment and to the contact pressures at which the tests are run. In dry environments, friction coefficients of both DLC<sup>30</sup> and  $MoS_2^{31}$  were shown to obey the following relationship

$$\mu = S/P \tag{1}$$

where S is a shear strength and P is the mean contact

<sup>(22)</sup> Enke, K.; Dimigen, H.; Hubsch, H. Appl. Phys. Lett. **1980**, 36, 291.

<sup>(23)</sup> Miyake, S.; Takahashi, S.; Watanabe, I.; Yoshihara, H. *ASLE Trans.* **1987**, *30*, 121. Sugimoto, I.; Miyake, S. *Appl. Phys. Lett.* **1990**, *56*, 1868.

<sup>(24)</sup> Grill, A. Wear 1993, 168, 143.

<sup>(25)</sup> Miyake, S. In *Surface Diagnostics in Tribology*, Miyoshi, K., Chung, Y. W., Eds.; World Scientific: River Edge, NJ, 1993; p 183. (26) Kim, D. S.; Fischer, T. E.; Gallois, B. *Surf. Coat. Technol.* **1991**, 49, 537.

<sup>(27)</sup> Fleischauer, P. D.; Bauer, R. Tribol. Trans. 1988, 31, 239.

<sup>(28)</sup> Fayeulle, S.; Ehni, P. D.; Singer, I. L. Surf. Coat. Technol. 1990, 41, 93

<sup>(29)</sup> Fayeulle, S.; Singer, I. L.; Ehni, P. D. In *Mechanics of Coatings*; Dowson, D., Taylor, C. M., Godet, M., Eds.; Elsevier: Amsterdam, 1990; p 129.

<sup>(30)</sup> Singer, I. L. *Fundamentals of Friction*; Singer, I. L., Pollock, H. M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; p 237.

<sup>(31)</sup> Singer, I. L.; Bolster, R. N.; Wegand, J.; Fayeulle, S.; Stupp, B. C. *Appl. Phys. Lett.* **1990**, *57*, 995.

pressure. For loads below the yield point of the substrate, in a ball-on-flat configuration, the friction coefficient fell from 0.2 to 0.01 as the contact pressure increased from 0.3 to 1.5 GPa. Instead of obeying Amontons' law-that the friction coefficient is independent of the load L—the friction coefficient varied as  $\mu \propto L^{-1/3}$ . This power-law dependence is consistent with the expected load dependence of an elastic (Hertz) pressure contact.<sup>31</sup> Moreover, implicit in eq 1 is that the area of contact A that carries the load is the same area that accommodates sliding.<sup>32</sup> The transfer film must have been very ductile yet cohesive in order for it to have spread fully over the contact area. Values of (interfacial) shear strength for both coatings, inferred from eq 1, were in the range of 20-80 MPa in air and as low as 1 MPa in UHV.30,33 To the author's knowledge, however, there have been no direct investigations of the mechanical properties (shear strength, elastic modulus, etc.) of transfer films.

MoS<sub>2</sub> coatings are also remarkable in that they continue to provide low-friction sliding despite the fact that the majority of the original coating can be worn away in the first 5–10% of the total sliding life. 17,27 Not only is this "early wear" behavior still a mystery but it also calls into question some long-standing ideas of how MoS<sub>2</sub> provides long life at low friction. It is generally believed that the wear of MoS<sub>2</sub> can be explained by the easy shear property of the SMoS layers in the MoS<sub>2</sub> coating. But continual shearing of a layered film could not account for the observed behavior; there are only so many cycles that a coating can be sheared before its thickness is reduced to a single layer. Consider for a moment that the coating is a deck of playing cards, with each card a single SMoS layer. If the deck has 52 cards, then it can only be "sheared" at most 51 times before the deck is reduced to a single card. This type of shearing, interlayer slip, probably occurs during the early, run-in stage of the coating and accounts for its thinning. However, our studies suggest that sustained low-friction sliding takes place by interfacial slip between some of the SMoS "cards" on the original coating and the "cards" transferred to the opposite counterface.

Although transfer films from MoS<sub>2</sub> coatings are often observed, 27-29 their role in the long life of  $MoS_2$ -coated components has usually been overlooked.<sup>34</sup> Over the last 40 years, most investigators have focused on wear modes of the MoS<sub>2</sub> coating itself.<sup>35</sup> The modes identified include deformation, fracture and reorientation of MoS<sub>2</sub> platelets, compaction and densification, oxygen-induced blistering, fatigue-induced blistering, fatigue of deformed surface layers, oxidative/adhesive wear plowing, and abrasion by foreign particles and oxidized third bodies. An alternative way of accounting for the long life of MoS<sub>2</sub> coatings, based on third-body concepts, has recently been suggested by Wahl and Singer.<sup>17</sup> They showed that, in reciprocating sliding, debris patches left at turn around points on the track serve as reservoirs of MoS<sub>2</sub>. In particular, they found that during the first 5% of sliding life, when most of the coating was worn from the track, MoS<sub>2</sub> transferred both to the counterface surface and to patches at the ends of the track. During the remaining 95% of the sliding life, the patches gradually became depleted, apparently replenishing the lubricant lost on both the counterface and the track. Although the material transport processes that

control replenishment have yet to be determined, the study suggests that the endurance of MoS<sub>2</sub>-coated systems is not simply a coating wear problem, but rather a flow problem involving third bodies, as suggested earlier by Godet.9

#### In-Situ Formation of Solid Lubricants by **Vapor-Phase Lubrication**

As we have seen so far, sustained low-friction sliding relies on transfer films of a low shear strength material like MoS<sub>2</sub> or on a low shear third-body product like that which forms from DLC. Unfortunately, transfer films lead to debris, and even small amounts of debris can interfere with the smooth operation of moving mechanical assemblies like gimbal bearings.36 Ultrathin films, like native oxide films on TiN, would form much less debris than thicker (ca. 1  $\mu$ m) solid lubricating films; however, such films provide low friction only during the short time that they are being sheared from a surface, not after debris is generated. How then might one produce an easilysheared, replenishable thin film whose third bodies sustain low-friction sliding yet minimize debris buildup?

One solution is vapor-phase lubrication, in which the vapor reacts with both counterfaces during sliding to form "slippery" surface films, hence minimizing wear to either counterface. We have recently investigated the thirdbody aspects of vapor-phase lubrication by performing friction testing and surface characterizations in a multianalytical UHV chamber containing a tribotester that can be operated at up to 1 Torr of selected gas.<sup>37</sup> Friction tests were performed with SiC pins and Mo disks cleaned in UHV and then slid against each other at gas pressures between 4 and 40 Pa of O<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>S; the sliding speed was 0.2 mm/s, and the initial mean contact pressure was 0.7 GPa. Surface films produced by gas exposures and sliding were analyzed in situ by X-ray photoelectron spectroscopy and Auger electron spectroscopy while thicker debris particles were characterized ex situ by scanning electron microscopy, energy-dispersive X-ray analysis, and transmission electron microscopy.

Vapor-phase lubrication produced low friction coefficients in all three gases; the steady-state friction coefficients in the SO<sub>2</sub> and O<sub>2</sub> were  $\mu \approx 0.1$ , whereas in  $H_2S$ , the friction coefficient fell to below 0.01. The surface films on Mo produced by the gas exposure alone were thin (<1 nm) and had compositions of  $MoO_2$  and/or  $MoS_2$ , consistent with compositions predicted by thermochemical calculations for the bulk reactions at room temperature. Analysis of wear features on the two counterfaces indicated three types of third-body products: particles and two films. Concerning the latter, one film was induced by rubbing (a tribochemical film) and the second removed from the opposing counterface (a transfer film). However, the third bodies formed in the two types of gases differed markedly, as shown in Table 2. In the two oxidizing gases, metallic Mo particles were found on both counterfaces and transfer films of Mo oxide and/or sulfide on the wear scar on SiC. In H<sub>2</sub>S gas, very few particles and no transfer films were found on either counterface; instead, tribochemical films covered the two counterfaces (Table 2).

The mechanics of friction and wear behavior can be accounted for by the classical adhesive junction model of Bowden and Tabor. According to the model, <sup>38</sup> if a junction forms at the interface between the two sliding counterfaces, it will shear when the interfacial adhesion is greater

<sup>(32)</sup> The friction coefficient is defined as the tangential force T divided the same area A, then  $\mu = (TA)/(L/A) = SIP$ . (33) Donnet, C.; Belin, M.; Auge, J. C.; Martin, J.-M. Surf. Coat. Technol. **1994**, 68/69, 626.

<sup>(34)</sup> Lancaster, J. K. ASLE Trans. 1965, 8, 146.

<sup>(35)</sup> For review, see: Singer, I. L.; Fayeulle, S.; Ehni, P. D. Wear **1996**, 195, 7.

<sup>(36)</sup> Loewenthal, S. H.; Chou, R. G.; Hopple, G. N.; Wenger, W. L. *Tribol. Trans.* **1994**, *37*, 505.

<sup>(37)</sup> Singer, I. L.; Le Mogne, T.; Donnet, C.; Martin, J. M. J. Vac. Sci. Technol. 1996, 45, 38; Trib. Trans. 1996, 39 (4), in press.

(38) Bowden, F. P.; Tabor, D. The Friction and Lubrication of Solids,

Part 2; Clarendon Press: Oxford, 1964; Chapter IV.

Table 2. Third-Body Products in the Sliding Contact Inferred from Auger Electron Spectroscopy, Energy-Dispersive X-ray Spectroscopy, and Transmission Electron Microscopy ( $2 \le x \le 3$ ; y and z = 1 or 2; C refers to graphite)<sup>37</sup>

			Third-body products on				
			Mo			SiC	
gas	friction coefficient	tribofilm	transfer	debris	tribofilm	transfer	debris
$\overline{SO_2}$	0.1-0.15	MoO <sub>x</sub> /MoS <sub>2</sub>	none	Mo	SiO <sub>v</sub> /SiS <sub>z</sub> , C	MoO <sub>x</sub> /MoS <sub>2</sub>	Mo
$O_2$	0.1	$MoO_X$	none	Mo	$SiO_y$	$MoO_x$	Mo
$H_2S$	≤0.01	$MoS_2$	none	none	SiS <sub>z</sub> . C	none	≈none

than the strength to shear the weaker material. Once sheared, the adhered junction becomes a transfer particle attached to the stronger counterface. The friction coefficient associated with shearing of the junction is given by  $\mu = \tau/P$ , where  $\tau$  is the shear strength of the weaker material and *P* is the contact pressure. For ideally-plastic junctions, with one counterface (metal) much softer than the other (ceramic),  $\tau \approx H/6$  and P = H, where H is the hardness of the softer contact. Hence,  $\mu \approx 1/6$ , approximately the value obtained for Mo vs SiC sliding in  $SO_2$  and  $O_2$ . Thus, in  $SO_2$  and  $O_2$ , the classical adhesive junction model accounts for the transfer of metallic Mo particles to the SiC pin and the magnitude of the friction coefficient. In H<sub>2</sub>S, sliding was accommodated between the two tribochemical films: MoS<sub>2</sub> on the Mo disk and Si sulfide/graphite on SiC pin. Thermochemical calculations in the pentenary MoSSiCH system indicated that these tribochemical films are coexisting phases (i.e., they do not react with each other). Interfacial sliding also resulted in a smoothing of the softer Mo. The ultralow friction coefficient in  $\tilde{H_2}S$  ( $\mu < 0.01$ ) may therefore be attributed to the near absence of chemical and mechanical interactions across the sliding interface. Thus, H<sub>2</sub>S lubrication of a Mo/SiC junction provides a model system of an easilysheared film formed on both counterfaces with a minimum of wear or debris on either counterface. The challenge for practitioners is to predict the vapor-phase lubricant that will produce ultralow friction and minimal third-body particles for arbitrary counterface materials.

#### **Mechanics and Chemistry of Protective Films**

How can one predict whether two surfaces in sliding contact will (1) adhere and form a junction which will later shear in the weaker material or (2) shear along the original, but chemically-modified, interfaces? Clearly this is a competition between chemical and mechanical processes. An order of magnitude estimate of contributions from the two processes can be made using dimensional analysis. The "chemical contribution" to adhesion is estimated as the change in the Gibbs free energy  $\delta G$  before and after the two surfaces A and B come into contact. The free energy  $\delta G$  is in units of energy/mole, but by dividing it by Avogadro's number  $N_0$ , we can get an "adhesion energy"  $\delta G/N_0$ , in units of energy/atom. An equivalent "mechanical energy" can be computed from the yield strength  $\sigma$ , where  $\sigma$  is in units of force/area. We multiply  $\sigma$  by the atomic volume (volume/atom)  $V_0$  and get an expression for the mechanical energy  $\sigma V_0$ , in units of energy/atom.

Values of adhesion and mechanical energies for SiC and Mo in the three gases are shown in Table 3. The  $\delta G$ values for 50/50 mixtures of SiC and Mo in 1 mol of gas were calculated with two different computational thermochemical programs;39,40 values for each of the three

Table 3. Calculation of Adhesion Energy vs Mechanical Shear Energy of SiC vs Mo in Two Gases (see text for details)a

reaction gas	$\delta G$ (kJ/mol)	$\delta G/N_0$ (J/atom)	$\sigma V_0$ (J/atom)
$O_2$	600	$10\times10^{-19}$	$1.6  imes 10^{-20}$
$SO_2$	400	$6.7 imes10^{-19}$	
$H_2S$	100	$1.6 imes10^{-19}$	

<sup>&</sup>lt;sup>a</sup>  $\delta G$  calculated at T = 298 K and 1 mol of gas at 13 Pa of pressure.

agreed to better than 2%. We see that adhesion energies in the two oxygen-containing gases are 4-6 times greater than that in H<sub>2</sub>S. The yield strength of Mo is about 1 GPa = 1  $\times$  10<sup>9</sup> J/m<sup>3</sup>, and  $V_A$  was calculated from the atomic weight and density of Mo,  $V_0 = 1.6 \times 10^{-29} \,\mathrm{m}^3/\mathrm{atom}$ . Hence,  $\sigma V_0 = 1.6 \times 10^{-20}$  J/atom, which is 10 times smaller than the lowest adhesion energy. If the mechanical energy had a value of  $\sigma V_0 = 3 \times 10^{-19}$  (i.e., higher than the adhesion energy of H<sub>2</sub>S but lower than that of the oxygencontaining gases), then one might have predicted that (1) adhesion was less favorable than interfacial shear in  $H_2S$ , but (2) Mo would bond to SiC in the oxygen-containing gases and shear would have to take place in the Mo junction. Perhaps a more rigorous analysis than the dimensional analysis presented here can help to sort out the competition between chemical and mechanical processes. With such a model, we should be able to predict what gas/material combinations would avoid adhesive wear processes.

While thermodynamics provides a handy tool for calculating the energy of reactions and predicting gas reaction and tribochemical films, it does not provide a satisfying physical mechanism for how films protect surfaces. Tabor<sup>41</sup> suggested protective films must keep atoms on counterface surfaces at least 2 Å apart, the distance at which only the weaker van der Waals forces begin to dominate. The surface science literature provides an alternate explanation for why the films formed on Mo in  $O_2$  do not protect as well as the films formed in  $H_2S$ . Studies of the structures of single-crystal Mo surfaces exposed to oxygen or sulfur indicate that oxygen penetrates the surface leaving Mo atoms exposed whereas sulfur adsorbs entirely on the surface. 42 It is believed that oxygen penetrates the Mo lattice because of its small radius (0.77 A) but that sulfur does not because of its larger radius (1.04 Å). Marchon et al.<sup>43</sup> have imaged S-terminated Mo by scanning tunneling microscopy in air and demonstrated that sulfur can passivate a Mo surface so completely that it remains inert to common atmospheric reactants like O<sub>2</sub> and H<sub>2</sub>O.

#### **Final Comments**

This essay has focused on the importance of third bodies on providing and sustaining low friction and low wear. Several issues related to improved fundamental under-

<sup>(39)</sup> Pelton, A. D.; Bale, C. W.; Thompson, W. T. *Equilibrium product calculation* of the F\*A\*C\*T SYSTEM, Version 21 Feb 94; thermfact LTD/LTEE: Montreal, 1986.

<sup>(40)</sup> Poine, A. Outokumpu HSC Chemistry for Windows, Version 2.0; Outokumpu Research Oy, Pori, Finland, ARSoftware: Landover, MD,

<sup>(41)</sup> Tabor, D. J. Lub. Technol. 1981, 103, 169. (42) Clarke, L. J. Surf. Sci. 1981, 102, 331.

<sup>(43)</sup> Marchon, B.; Bernhardt, M. E.; Bussell, G. A.; Somorjai, S. M.; Siekhaus, W. Phys. Rev. Lett. 1988, 60, 1166.

standing of low-wear sliding contacts have already been highlighted. A more extended list, extracted in part from an earlier overview on friction,44 is given below:

- (1) What are the particle detachment mechanisms? delamination by fatigue? junction plucking due to adhesion? atom-by-atom removal?
- (2) What are the *tribochemical processes*? Tribochemistry can be beneficial if it produces "protective" layers that reduce adhesion and minimize adhesive wear or provides an "easy shear" plane that lowers friction. However, it can be harmful if it promotes material loss
  - (a) H<sub>2</sub> or O<sub>2</sub> embrittlement that leads to fracture,
  - (b) enhanced diffusion that leads to stress gradients into a surface
  - (c) formation of surface films that enhance adhesive
- (3) Can the *dynamics of third-body formation* be modeled? (a) What are the mechanics and particle dynamics that create and stabilize transfer layers and other third
  - (i) Are there stability criteria?
  - (ii) Is there an equilibrium state (i.e., a zero-wear state where losses equal gains)?
  - (b) What are the mechanical properties of third bodies? (i) hardness, elastic modulus, thermal conductivity,
    - (ii) deformation behavior
  - (c) What are the chemical properties of third bodies?
    - (i) structure
    - (ii) chemical reactivity
- (4) Can friction coefficients be predicted?
  - (a) Can we develop quantitative relationship between measured "shear strength" and interface chemistry, along the lines suggested above?
  - (b) Can we measure junction shear strength in gaseous atmospheres (e.g., using a technique similar to that developed by Agrait et al.), 45 recognizing the effects of environment and size scale on the strength of materials?46

- (c) Can we create three-dimensional models of friction and molecular interactions at interfaces, along the lines of Landman,47 Harrison,48 and Israelachvili?49
- (5) What analytical tools can be used to examine sliding at buried interfaces? One of the main obstacles to studying friction and wear experimentally is that sliding takes place at a buried interface. Here we need advances in in situ spectroscopy and in situ mechanical testing.<sup>50,51</sup> A good example of combining both would be to perform analytical studies of film structure during sliding between monolayer films in a surface force apparatus.
- (6) What experimental techniques can be used to probe short time and length scales? Another major obstacle is that friction and wear processes occur at much shorter time and length scales than we can now measure using traditional friction and wear apparatus.44,52 Future solutions will require clever physics and chemistry experimentation.

In addition, there are two areas in which knowledge of the friction and wear of low-wear surfaces can impact practical tribology of moving mechanical assemblies:

- (1) How can we tailor lubricants so that the third bodies generated are either "lubricating" or, at worst, benign, to reduce friction and minimize wear?
- (2) What technologies can be developed to provide realtime monitoring of friction and wear behavior? Such technologies will allow us to schedule maintenance of moving mechanical assemblies based on actual needs rather than the more conservative, more costly routine maintenance approach.

**Acknowledgment.** I wish to thank past and present collaborators for their contributions to this essay: S. Fayeulle, P. Ehni, R. Bolster, J. Wegand, L. Seitzman, I. Hayward, T. LeMogne, J. M. Martin, Ch. Donnet, and K. Wahl.

#### LA951056N

<sup>(44)</sup> Singer, I. L.; Pollock, H. M. Fundamentals of Friction; Singer, I. L., Pollock, H. M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; p 569.

<sup>(45)</sup> Agrait, N.; Rubio, G.; Vieira, S. Langmuir 1996, 12, 4505.
(46) Nabarro, F. R. N. Theory of crystal dislocations, Dover: New York, 1987.

<sup>(47)</sup> Landman, U.; Luedtke, W. D.; Gao, J. Langmuir 1996, 12, 4514.

<sup>(48)</sup> Perry, M. D.; Harrison, J. A. Langmuir 1996, 12, 4552.

<sup>(49)</sup> Berman, A. D.; Ducker, W. A.; Israelachvili, J. N. Langmuir

<sup>(50)</sup> Bair, S.; Green, I.; Bhushan, B. J. Tribol. 1991, 113, 547.
(51) Cann, P. M.; Spikes, H. A. Tribol. Trans. 1991, 34, 248.
(52) Singer, I. L. J. Vac. Sci. Technol. 1994, A12, 2605.