Bridging the Gap between Macro- and Nanotribology: A Quartz Crystal Microbalance Study of Tricresylphosphate Uptake on Metal and Oxide Surfaces

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We report a quartz crystal microbalance study of the nanodynamical properties of tricresylphosphate (TCP) reaction films formed on high purity Fe, Cr, Fe oxide, and Cr oxide surfaces at elevated temperatures. The data reveal trace levels of interfacial slippage, potentially in conjunction with viscoelastic effects, for reaction films characterized by very low macroscopic friction coefficients. In contrast, rigidly attached TCP reaction films are observed in systems characterized by high macroscopic friction coefficients.

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Introduction.—From the transport of granular food products to the slip of tectonic faults, the dynamical properties of dense materials undergoing shear determine ubiquitous phenomena that profoundly impact our everyday lives. Despite great progress in recent decades concerning the physics of such materials, an understanding from a microscopic point of view is still lacking [1]. We focus here on the physics of sheared solid lubricants [2], materials whose development is key to a myriad of modern technologies (such as extreme temperatures, space/vacuum applications, microelectromechanical systems).

The literature abounds with nanotribological studies of model lubricants [3], as well as suggestions of how physical properties probed by nanotribological techniques might be manifested macroscopically. C60, for example, has been proposed as an additive for macroscopic lubricants, based on surface forces apparatus reports of high interfacial slip levels for C60 molecules dissolved in toluene [4]. Other nanotribological measurements have indicated, however, that interfacial slippage of model lubricant films does not reduce friction [5]. The macroscopic significance of such measurements is a matter of some current debate, as friction coefficients measured by means of nanotribological techniques and macroscopic "tribotests" routinely differ by orders of magnitude [6]. Terms such as "superlubricity" nonetheless abound in the nanotribological literature [7], the tacit assumption being that extremely low friction coefficients and/or extremely high interfacial slip levels at the atomic level are linked in some manner to macroscopic lubricousness.

The quartz crystal microbalance (QCM) is an attractive technique for comparative studies of macroscopic and microscopic phenomena, owing to the high sliding speeds (up to 2 m/s) and shear rates at which the data are recorded [8]. It was employed here to study the nanodynamical properties of sheared tricresylphosphate (TCP) $[(CH_3C_6H_4)_3PO_4]$ reaction films at elevated temperatures and in ultrahigh vacuum conditions. TCP is a candidate material for vapor phase lubrication, an emerging technology targeted at extreme environment applications that preclude conventional liquid-phase lubricants [9]. TCP molecules fragment upon uptake on certain metals and oxides, forming thick polymeric reaction films above 200 °C through partial corrosion of the underlying substrate (Fig. 1). TCP reaction films on numerous metals and metal oxides have been evaluated by means of a very wide range of sliding and rolling contact friction test setups, as well as on actual machinery. Reaction films formed on iron oxide or on iron in the presence of oxygen are highly effective lubricants, but are ineffective lubricants when formed on iron, chromium, chromium oxide, or aluminum substrates [10]. Macroscopic friction coefficients for TCP reaction films formed on iron oxide or iron in the presence of oxygen are close to 0.02, with little or no associated wear. Friction coefficients for TCP films formed on materials that it does not lubricate are typically on the order of 0.8, with high wear rates also in evidence [10]. The aforementioned measurements have been performed by a variety of techniques, with a typical study involving pins and disks of like materials in sliding contact, the reaction film being formed on the disk in advance of the measurements.

Given the well-documented tribological attributes of TCP reaction films at the macroscale, one might well ask

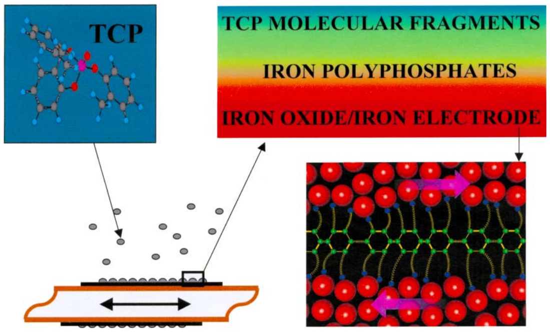

FIG. 1 (color online). TCP reaction films that form on the QCM iron electrodes in the presence of oxygen exhibit trace levels of nanoscale slippage in response to its oscillatory motion.

whether the lubricous reaction films formed on iron oxide exhibit distinctive nanodynamical properties. The QCM data reported herein provide the first documentation of such a link. Trace levels of interfacial slippage, potentially in conjunction with viscoelasticity, are present in systems characterized by very low macroscopic friction coefficients, while no interfacial slippage is detected in systems exhibiting high friction coefficients.

Experimental.—Overtone-polished AT-cut (transverse shear mode) quartz crystals with resonant frequency 8 MHz and quality factor near 10^5 were employed for these studies. Metal film electrodes evaporated onto their two major faces served as the substrates for reaction film formation. The iron (chromium) electrodes were 1000 Å (1170 Å) thick, deposited at 0.5 Å/s (0.15 Å/s) by *e*-beam evaporation of 99.999% pure material in ultrahigh vacuum.

After performing Auger electron spectroscopy to verify chemical purity, samples were transferred within the vacuum chamber, at a base pressure of $\approx 2 \times 10^{-10}$, to a temperature controlled location where they were electrically connected to an external oscillator circuit. The temperature was then adjusted to the desired value and the frequency allowed to stabilize. Some of the samples were exposed directly to TCP vapor [11], while others were first exposed to 100 mTorr oxygen gas for 10—20 min to form an oxide layer. Still other samples were exposed to TCP before exposure to oxygen. The latter procedure was motivated by the fact that TCP reaction films are in practice continually worn and replenished, so that iron may be exposed to TCP and oxygen in either order. Data for pressure, temperature, frequency, and vibrational amplitude were recorded versus time during the gas exposure. Quality factor shifts were obtained from the amplitude shift data through calibration with nitrogen gas adsorption, after completion of the TCP uptake measurements [12].

Shifts in frequency f and quality factor Q of a quartz crystal are routinely analyzed within the framework of an acoustic impedance $Z = R - iX$ presented to an oscillating planar surface. The "mechanical resistance" R is proportional to the average energy dissipation per unit time, and the "mechanical reactance" X is associated with the inertia of the oscillator. For film adsorption on, or fluid exposure to two sides of the quartz crystal [13],

$$\delta(Q^{-1}) = 2\left(\frac{R}{\pi f \rho_q t_q}\right), \qquad \delta f = -2\left(\frac{X}{2\pi \rho_q t_q}\right), \tag{1}$$

where $\rho_q = 2.65\ \mathrm{g/cm^3}$ is the density of quartz and t_q is the quartz crystal's thickness (0.021 cm for $f = 8$ MHz).

In the thin film limit with no associated energy losses,

$$R = 0, \qquad X = \omega(m/A) = \omega \rho_f t_f, \tag{2}$$

where $\omega = 2\pi f$ and $m/A = \rho_f t_f$ is the mass per unit area of a deposited film with thickness t_f and density ρ_f.

Equations (1) and (2) can be combined to obtain the common expression for the frequency shift associated with deposition of a thin, nondissipative film on a QCM:

$$\frac{\delta f}{f} = -\frac{2(m/A)}{\rho_q t_q} = -\frac{2\rho_f t_f}{\rho_q t_q}. \tag{3}$$

A QCM's frequency and Q are also affected by temperature, ambient gas pressure, and stresses generated by the deposited film. Frequency and amplitude shifts arising from residual gas pressure, as well as temperature drift, were negligibly low in the present work. Frequency shifts attributable to surface tensile stresses generated by the reaction films were observed in certain cases, as discussed below.

Results.—Figure 2 presents frequency and Q shift data for systems characterized by high macroscopic friction coefficients. These include TCP on pure iron (300 °C, 400 °C) and chromium (400 °C) surfaces, TCP on previously oxidized chromium (300 °C), and oxygen uptake on a TCP reaction film formed previously on chromium (300 °C). The most distinctive feature of the Fig. 2 data sets is the lack of a detectable shift in Q ($\delta Q^{-1} < 10^8$), indicative of a rigidly attached film that dissipates no energy. Frequency shifts for the Fig. 2 data sets are relatively small in magnitude, and tend to reverse sign as time progresses. The sign reversal is attributable to tensile stresses, of order 5–10 GPa, generated within the films [14].

Figure 3 presents frequency and Q shift data for combinations of TCP and oxygen uptake on iron, systems that TCP is known to effectively lubricate that are characterized by low macroscopic friction coefficients. These include TCP on oxidized iron surfaces (300 °C, 400 °C) and oxygen uptake on a TCP reaction film formed on iron (300 °C). Frequency shift data for these systems are relatively large in magnitude and do not reverse sign at

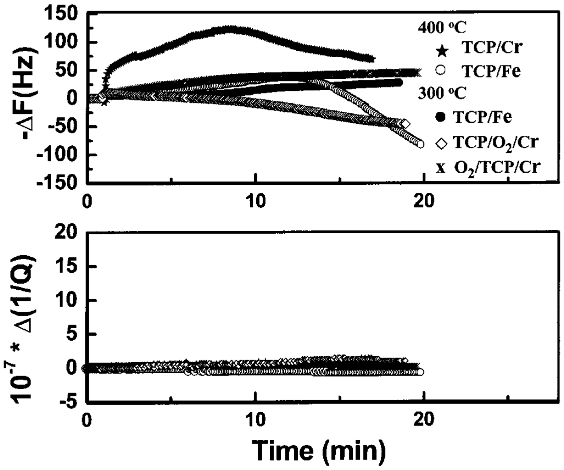

FIG. 2. Frequency and Q^{-1} shift data for TCP reaction film systems that exhibit high friction coefficients and high wear rates at the macroscale, with exposure beginning at $t = 1$ min. The films are rigidly attached within experimental resolution.

time progresses. This feature is consistent with a lack of stress buildup within the film. The saturating nature of the frequency shift data for these systems is consistent with the "parabolic" growth curves observed in prior studies, attributed to systems where cation diffusion is the uptake rate-controlling step [15]. The oxygen uptake measurements are distinctive in that mass uptake starts slowly, with a substantial increase in uptake rate after 1 min. Dissipation effects moreover lag the mass uptake in the 300 °C data set, reminiscent of a static friction effect; i.e., the reaction film appears to remain rigidly attached until it acquires a certain critical mass. The most distinctive feature of the Fig. 3 data sets is, however, a substantial shift in Q, indicative of either slippage of the reaction film in response to the oscillation of the underlying substrate or to viscoelastic effects within the film itself. In the following section we examine whether slippage, viscoelasticity, or a combination of the two is giving rise to the observed dissipation. We conclude that trace levels of slippage, possibly in conjunction with viscoelastic effects, must be present in these systems.

Analysis.—The oxygen/TCP/iron system at 300 °C is selected for a detailed analysis, as the chemical nature of the adsorbate is apparent. In contrast, TCP uptake on iron oxide involves molecular fragmentation, with some of the constituents desorbing. The origin of the Q shift data for the oxygen/TCP/iron data set is moreover simpler to analyze, as the underlying TCP/iron substrate is nondissipative (Fig. 2). Our analysis approach is to consider the limiting cases of energy dissipation arising solely from slippage and then energy dissipation solely from viscoelastic effects. The properties of the reaction films obtained under these limiting assumptions are then examined to assess whether they are physically realistic. While our analysis is quite detailed, and some estimated values are employed for the physical parameters, our primary conclusion is quite robust: *The physical parameters obtained in the limiting cases would need to vary by 2 orders of magnitude in order for the outcome to vary.* Our analysis is meanwhile accurate to within a factor of 2.

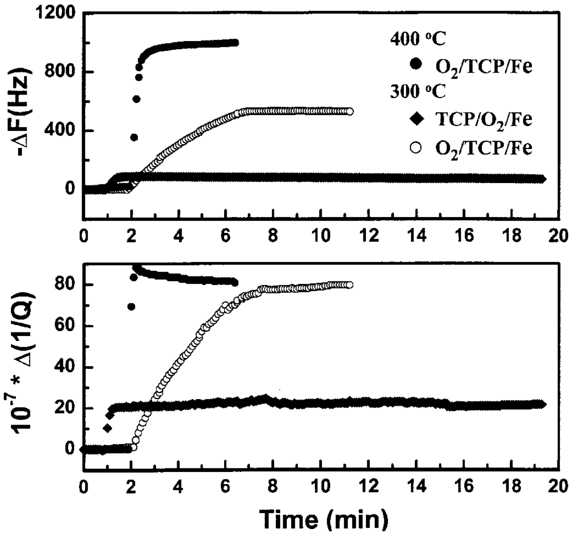

FIG. 3. Frequency and Q^{-1} shift data for TCP and O_2 uptake on Fe, systems that are lubricious at the macroscopic scale, with exposure beginning at $t = 1$ min. A frequency shift of -100 Hz corresponds to a mass uptake of 3.4×10^{-7} g/cm^2 on each electrode.

For the first limiting case of film slippage with no internal mechanisms for energy dissipation, friction is characterized by a "slip time" $\tau = (m/A)/\eta$, where $\eta = \sigma/v$ is the friction coefficient that relates an applied shear stress σ to the film's sliding speed v [13]. The resistive and reactive components of the impedance of an adsorbed film that exhibits slippage are

$$R = \frac{(m/A)\omega^2\tau}{1+\omega^2\tau^2}, \qquad X = \frac{\omega(m/A)}{1+\omega^2\tau^2}, \tag{4}$$

which in combination with Eq. (1) yields

$$\delta(Q^{-1}) = -4\pi\tau\delta f. \tag{5}$$

Employing the values $\delta(Q^{-1}) = 80 \times 10^{-7}$ and $\delta f = -500$ Hz obtained from the oxygen/TCP/iron data set recorded at 300 °C, Eq. (5) yields in the simplest scenario the value $\omega\tau = 0.06$. Since the mechanical reactance tends towards $X = \omega(m/A)$ in the limit $\omega\tau \ll 1$, Eq. (3) is highly accurate for determining the mass per unit area of the oxygen that has adsorbed on each of the QCM electrodes, $(m/\mathrm{A})_o = 1.7 \times 10^{-6}$ g/cm^2.

We now take into account the fact that the oxygen reacts with the substrate rather than remaining on top of it. Based on the work of Saba and Forster [10], whereby similar reaction film compositions were reported as 50% Fe, 30% O, 15% C, and 5% P, we represent the reaction film chemical formula as $Fe_{10}O_6C_3P$. An oxygen mole balance is then performed to determine the mass per unit area of the reaction film:

$$\left(\frac{m}{A}\right)_f = \left(\frac{m}{A}\right)_o \left(\frac{M_{Fe_{10}O_6C_3P}}{6M_O}\right) = 1.3 \times 10^{-5}\ \mathrm{g/cm^2}, \tag{6}$$

where M_O and $M_{Fe_{10}O_6C_3P}$ are, respectively, the molar weights of atomic oxygen and the film composite. The effective frequency shift that is associated with $(m/\mathrm{A})_f = 1.3 \times 10^{-5}$ g/cm^2 is -3765 Hz [from Eq. (3)]. This, in combination with $\delta(Q^{-1}) = 80 \times 10^{-7}$, yields $\eta \approx 100\,000$ g cm^{-2} s^{-1} for the reaction film composite. This is about 1000 times greater than that of a physisorbed rare gas monolayer adsorbed on a noble metal surface [16], but close to that expected for chemisorbed layers [17]. Since the reaction film is in fact chemically bound to the substrate, the data are consistent with slippage in response to the oscillatory nature of the substrate. It is important to note, however, that only trace slippage levels are present. The fact that they are detected at all arises from the atomic-scale sensitivity of the QCM technique.

We next consider the case of a nonslipping film, with all dissipation arising from viscoelasticity within the film. Viscoelastic films are routinely parametrized by a frequency dependent complex modulus $G(\omega) = G'(\omega) + iG''(\omega)$ that relates the applied shear to the resultant stress. The complex modulus is composed of a real (elastic) component G', termed the storage modulus, and an imaginary (viscous) component G'' termed the loss modulus. The acoustic impedance of a viscoelastic film, $Z = (\rho_f G)^{1/2} \tanh(i\omega t_f \sqrt{\rho_f/G})$ [18], simplifies to

$$R = \frac{\rho_f^2 \omega^3 t_f^3}{3|G|^2} G'', \qquad X = \omega \rho_f t_f \tag{7}$$

in the thin film limit, defined by $|G| \gg \omega^2 t_f^2 \rho_f$ [19].

To establish whether the thin film limit is applicable here, we first estimate the thickness of the reaction film: Of the iron oxide compounds whose densities are known, FeO ($\rho = 5.7\ \mathrm{g/cm^3}$) has the closest chemical composition to the reaction film. (Pure iron has density $\approx 8\ \mathrm{g/cm^3}$, and the actual density will be in the range 6–8 $\mathrm{g/cm^3}$.) Setting $\rho_f = 5.7\ \mathrm{g/cm^3}$ for calculation purposes, we obtain $t_f = (m/\mathrm{A})_f/\rho_f = 22$ nm, which for realistic values of $|G|$ (1 MPa to 1 GPa) [18,19] easily satisfies the thin film limit. Utilizing $\rho_f = 5.7\ \mathrm{g/cm^3}$, $t_f = 22$ nm, and $\delta(Q^{-1}) = 80 \times 10^{-7}$, Eq. (1) in combination with Eq. (7) yields $G''/|G|^2 = 3.6 \times 10^{-7}\ \mathrm{cm^2/dyn} = 3.6 \times 10^{-6}\ \mathrm{m^2/N}$. For the physically reasonable condition that the film's elastic modulus is much greater than its loss modulus, the resulting G' is 100 kPa or less while G'' is 10 kPa or less. These values are excessively low [20]. A combination of viscoelasticity and film slippage is not, however, ruled out as the value obtained for the film modulus would in fact be artificially low if slippage were not taken into account in the analysis. In this scenario, the slippage levels would remain trace, their upper limit being that obtained in the slip-only analysis.

Discussion.—We conclude that slippage of the reaction film, potentially in conjunction with viscoelasticity, is the only physically realistic interpretation of the experimental results. The slippage does not appear to be at a level that would allow the reaction film to slip out of the interface in an actual tribological contact. The intriguing issue of whether increased slip levels would further lower macroscopic friction coefficients thus remains open.

Fortunately, the materials studied here are well suited for study by a myriad of alternate nanoscale tribological techniques both in vacuum and in ambient conditions [21–23], and further studies are readily attainable. The information to be gained will be highly complimentary to the existing body of literature on the chemical nature of TCP reaction films [24], and will strengthen the path that we have forged between macro- and nanotribology.

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