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High-Temperature Vapor Phase Lubrication Using Carbonaceous Gases

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Abstract Following the pioneering work of Prof. James Lauer, the ability to provide continuous solid lubrication through vapor phase delivery of carbonaceous gases has been successfully demonstrated on a pin-on-disk contact at the temperatures of 650 °C. Results from tribological experiments under 2 N normal load and 50 mm/s sliding speed showed an over 20× reduction in friction coefficient. The samples were silicon nitride (pin) versus CMSX-4 (disk) and the experiments when run in a nitrogen environment with an acetylene admixtures. Two repeat experiments gave average friction coefficients of $\mu = 0.03$ and $\mu = 0.02$. The process was robust and provided low friction for the entire 500 m of sliding. Using focused ion-beam milling, high-resolution transmission electron microscopy, and confocal Raman spectroscopy, the resulting solid lubricant was found to be oriented micro-crystalline graphite.

Keywords Vapor phase lubrication · High-temperature tribology · Solid lubrication

1 Introduction

High-temperature lubrication continues to be a limitation for a wide variety of applications. In power generation, for example, there are tremendous efficiency gains that can be realized only if the operating temperatures are raised. The thermal limits of conventional lubrication strategies remain a daunting obstacle to these design concepts. As outline by Lauer and Bunting [1]:

> Several possibilities exist for high temperature lubrication. They are each listed here with a major drawback which needs to be overcome.

Synthetic fluids:	500 °C maximum use temperature
Solid lubricants:	replenishment
Molten glass:	Solid at room temperature

> Only solid lubricants show any promise of operating from ambient to above 500 °C.
> Solid lubricants would have to be replenished in order to provide long life and reliable operation at high temperatures. Various types of replenishment systems have been suggested, and they include such methods as:

1. Stick or Powder Feed
2. Gaseous or Liquid Suspension feed
3. Incorporation in pockets or retainers
4. Gaseous materials which react at the surface.

> An example of this last method, which is the subject of this paper, would be to chemically form the lubricant directly on the bearing surfaces from a gaseous feed material.

Lauer's pioneering work with vapor phase lubrication began with a hypothesis that the exposure of the nascent surfaces through wear would catalyze reactions with the ambient environment. In the 1988 paper by Lauer and Bunting [1], they were able to show that friction coefficients as a low as $\mu = 0.10$ were able to be achieved at

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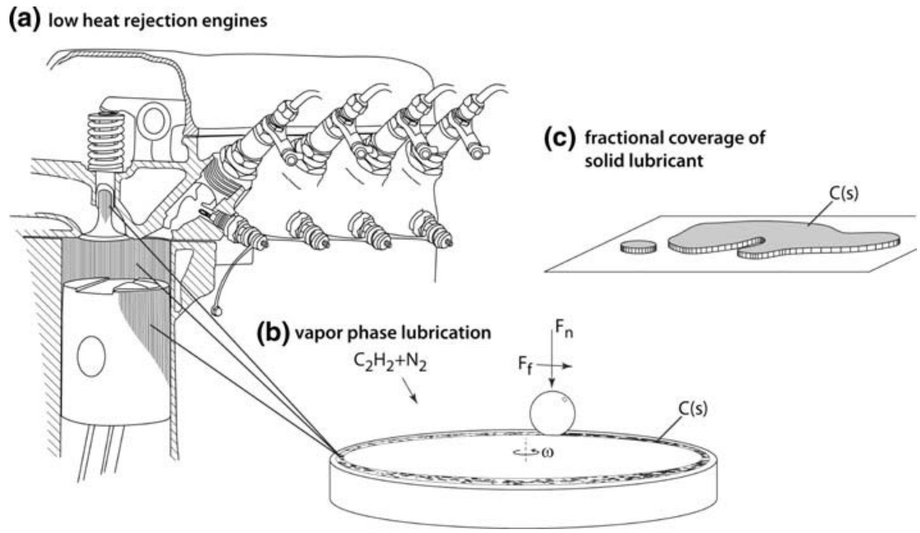

Fig. 1 An illustration of Lauer's high-temperature vapor phase lubrication (VPL) concept. As shown in (**a**) the injection of an appropriate gas admixture would lead to the deposition of thin and lubricous solid lubricants that could be continuously replenished during operation. In pin-on-disk experiments conducted in the laboratory (**b**), the admixture of gases such as acetylene would provide a replenishment of the carbonaceous solid lubricant on the wear track during exposure to the environment. The films have recently been observed and modeled as fractional (**c**) with regions of solid lubricant coverage on top of nascent surfaces

temperatures of 500 °C using ethylene as a feed gas for carbonaceous lubricating films (one of the initial choices of a substrate material was a nickel containing alloy that was thought to promote a "catalytically generate(d) carbon" film. This technique of using chemical reactions to build a solid lubricating film even as the existing film is being worn away became widely referred to as vapor phase lubrication.

An illustration of Lauer's vision for a vapor phase lubrication approach of a low heat rejection ("adiabatic") diesel engine is shown in Fig. 1. As Lauer and Dwyer described in a 1991 paper [2],

> the authors have been injecting a carbonaceous gas, such as ethylene, continuously into the conjunction region of the tribosurfaces. A well-adhering lubricating carbon film is formed and replenished after wear. The authors' approach is essentially not destructive of the solid wear surface…

Over the years, vapor phase lubrication with a number of different carbonaceous gases and tribological materials has been successfully demonstrated in the laboratory. The range of materials includes high performance ceramics (nitrides [3–6], carbides [2, 3], oxides [2, 3]) and high-temperature metals and alloys (bearing steels [3, 7, 8], stainless steels [3], and nickel super alloys [1, 3]). The range of gas chemistries include a wide variety of hydrocarbons (ethane, ethylene, acetylene, benzene, propane, and 1-propanol) [1, 2, 5, 9–11] as well as mixtures of carbon monoxide and hydrogen, and a simulated rich burn exhaust gas [4, 6].

The ability to provide low friction in pin-on-disk, rolling four-ball, and combined rolling-and-sliding contacts was a commonplace during the 1990s in the 5th floor laboratory of the Jonsson Engineering Center at Rensselaer Polytechnic Institute, where much of this work was performed. During this time, a number of different high-temperature tribometers were developed and equipped with vapor phase delivery systems, and the carbonaceous gas with the most efficacies for high-temperature vapor phase lubrication turned out to be acetylene. Working with acetylene (which is reportedly an intrinsically unstable compound that will readily decompose explosively) as an efficient, vapor phase additive seems in some ways contrary to Lauer and Dwyer's [9] discussion in their 1990 manuscript on the topic:

> After all, what could be simpler than injecting a gas,…, and converting it into a solid lubricant (graphite like) right on the wear surface?

A glimpse into some of the complexity of this approach can be found in a rather innocuous description of the safety measures [11] that were implemented in the home-built high-temperature tribometer used in these studies.

> …as illustrated…the present apparatus retains the two chambers…the inner one where the tests are actually carried out and the outer one that provides the safety shield by being filled with argon or another inert gas. The top of the outer chamber is not attached so that it can lift in case of an explosion.

These little explosions were not actually as uncommon as one might hope. During undergraduate research in the laboratory, one of the authors of this manuscript (W.G.S.) often set a large adjustable wrench on the lid such that after the explosions the lid would fall back into place on the tribometer and not travel too far; this method enabled experiments to continue (even if the graduate students were a little startled). In later designs of high-temperature tribometers, PTFE seals and baffles were used to prevent leaks and maintain positive pressures within the chambers, which eliminated the occurrence of explosions during testing.

Recently we have performed high-temperature vapor phase lubrication on a pin-on-disk high-temperature tribometer with acetylene feed gas. At the conclusion of these experiments, we flooded the inner-chamber with nitrogen gas in an effort to provide rapid cooling and retain the "graphite-like" surface films. This provided an opportunity to perform detailed microscopy characterization and spectroscopic analysis on the surface films and the near surface region of the substrates.

2 Experimental Procedure

2.1 High-Temperature Tribometer

Following the designs of Lauer and co-authors [11] and Blanchet et al. [4], a commercially available high-temperature pin-on-disk tribometer (CSM) was modified to have dual chamber design (the inner chamber was at elevated temperature and contained acetylene and nitrogen gas, whereas the outer chamber acted as a nitrogen dilution/safety chamber). The tribometer schematic is provided in Fig. 2. The outer chamber was made of acrylic and had feedthroughs for environmental control. A continuous flux of ~0.6 L/s of gaseous nitrogen was supplied to the outer chamber and was sufficient to maintain a positive pressure. An oxygen sensor (Delta-F Corp., model 310) was used to measure and ensure ppm levels of O_2 were maintained inside the acrylic chamber during testing. An additional flux of N_2 was also injected into the inner chamber. Finally, a stainless steel tube was inserted through the spindle housing lid and pointed at the central region of the disk; it was this tube that carried acetylene to the contact.

The sample surfaces for these studies were maintained at 650 °C. Normal load was applied through dead-weights and counterbalances, and the rotary motion was controlled *via* a belt-driven spindle and servo motor with a coupled rotary encoder. This spindle design could provide rotation speeds in the range 0.3–500 rpm. The friction forces were measured using a calibrated flexure and linear motion transducer sensitive enough to measure into the mN range. The radius of the wear track was controlled and measured with a calibrated micrometer stage, and for all experiments performed in this study were in the range 5–20 mm.

Custom data acquisition software was made to operate the tribometer using LabVIEW (National Instruments). The software controlled motor speed, oven temperature, and sample loading and unloading. The program also monitored and recorded analog input voltages for friction force, oven, and sample temperatures, the angular position of the disk, and motor RPM that were then averaged at 1-s intervals and recorded. The program saved the raw data for three full revolutions of the disk every ten or hundred seconds (user defined), which, when coupled with the measured angular position of the disk, made it possible to correlate friction coefficient with a given location on the wear track.

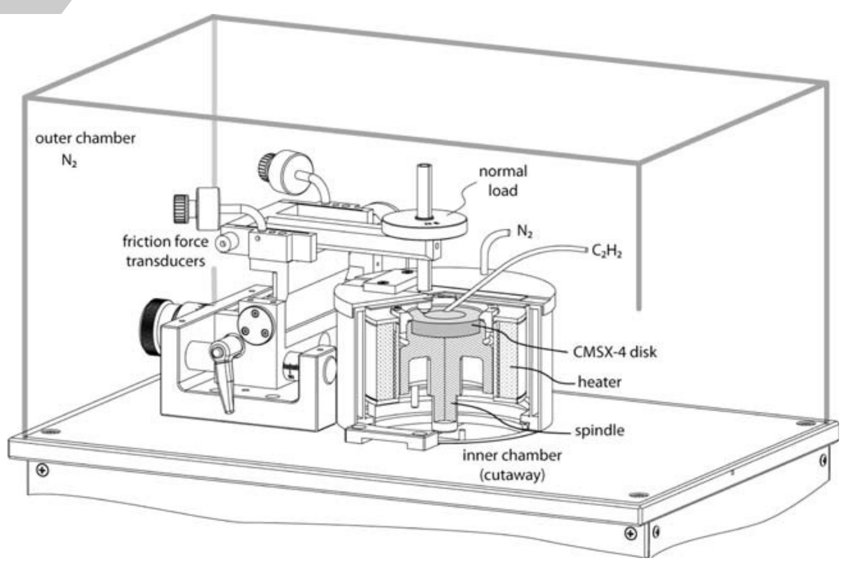

Fig. 2 A schematic of the high-temperature tribometer used for this study. The double chamber design described by Lauer and Blanchet was implemented in this study, and was able to provide inert environments that could safely promote in situ continuous lubrication with acetylene feed gas at sample temperatures of 650 °C

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2.2 Samples, Preparation, and Experimental Procedure

The pin was a 6.35-mm diameter silicon nitride sphere. The disk was a high strength and high-temperature superalloy of predominately Nickel and Aluminum (CMSX-4) that is intended for use in turbine engines. The disks were Electro Discharge Machined to have 55 mm diameters and thicknesses of 10 mm. The disk samples were carefully polished using standard metallographic techniques and had initial RMS roughness values of better than $R_q = 20$ nm.

The outer chamber was purged using N_2 to provide an O_2 concentration of less than 100 ppm before commencing heating. The temperature of the disk reached 650 °C before the pin was actuated into contact and sliding commenced. A sliding speed of 50 mm/s and normal force of 2 N were used for all tests. All tests were allowed to run to a total sliding distance of 500 m. The sliding direction was reversed thrice during the test in order to accurately compute friction coefficients [12, 13]. The pin was actuated out of contact upon completion of sliding and the disk and spindle were allowed to cool to below 100 °C before shutting off the nitrogen cover gas flow and opening the chamber to remove the pin and disk. The pin and disk were then placed in a sealed plastic container for transfer to the various characterization equipment.

3 Tribological Results

Results from three experiments are shown in Fig. 3. At the top of Fig. 3a, the friction coefficient for the silicon nitride versus CMSX-4 in a nitrogen environment at 650 °C is shown over 500 m of sliding. This combination had high friction coefficients, which near the end of the test approach unity. Over the entire duration of the experiment, the friction coefficient had an average value of $\mu = 0.77$ with a standard deviation of $\sigma = 0.07$. In stark contrast, the friction coefficient for two repeat experiments run with acetylene admixtures (with a flow rate of ~ 0.003 L/s) had average friction coefficients of $\mu = 0.03$ and $\mu = 0.02$ with standard deviations of less than $\sigma < 0.01$. Figure 3b shows the traction coefficients for the two experiments run with acetylene admixtures, where the positive and negative signs are for forward and reverse sliding directions, respectively. The friction coefficient remained very steady and low for the duration of these acetylene admixture experiments, and it was clear that the continuous supply of acetylene was sufficient to provide continuous low friction.

4 Discussion and Analysis of the Carbonaceous Films

The ability to provide adequate lubrication continuously using a vapor phase delivery of a solid lubricant requires that the deposition rate of the solid lubricant at least balances the removal rate. In the case of vapor phase lubrication with carbonaceous gases, the elevated temperature makes in situ studies of the competitive rates of formation and removal challenging. In competitive rates modeling efforts, Blanchet et al. [4] first treated the process as a thin film growth and removal process where the net rate of

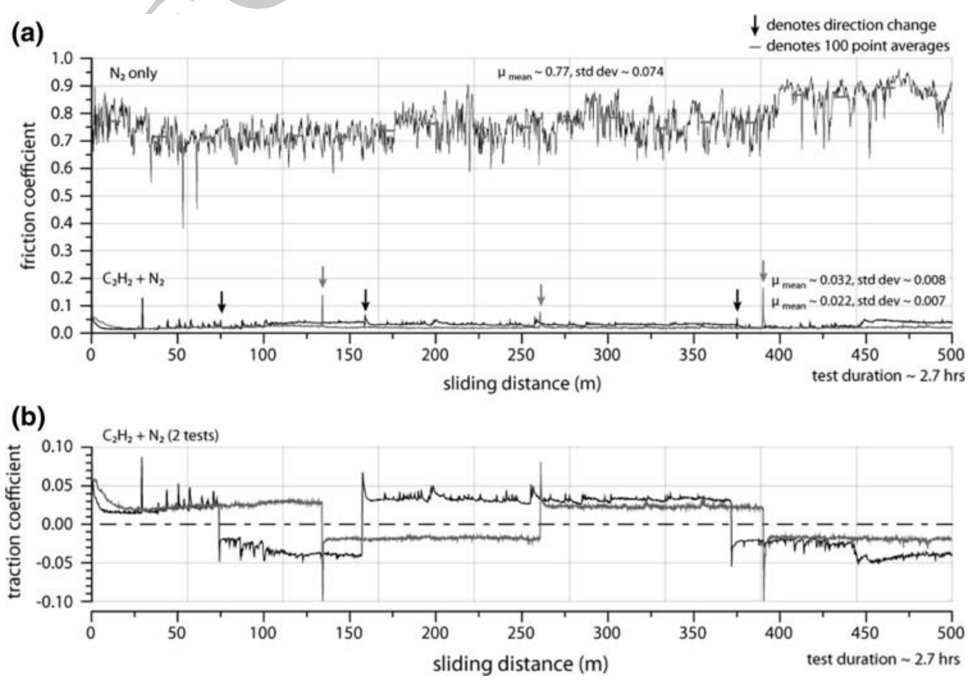

Fig. 3 Results from tribological experiments conducted at 650 °C under 2 N normal load and 50 mm/s sliding speed. **a** The friction coefficient for the silicon nitride versus CMSX-4 in a nitrogen environment is shown over 500 m of sliding ($\mu = 0.77$) and two repeat experiments run with acetylene admixtures ($\mu = 0.03$ and $\mu = 0.02$). **b** The traction coefficients for the two experiments run with acetylene admixtures, where the positive and negative signs are for forward and reverse sliding directions, respectively

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carbon solid lubricant accumulation on the surface could be described by Eq. 1.

$$\frac{dC}{dt} = ave^{(-E_a/RT)} - bF_n, \quad (1)$$

where a and b are constants for the deposition rate and removal rate terms, respectively. The deposition rate is assumed to follow an Arrhenius dependence, with an activation energy E_a, gas constant R, and T is the absolute temperature. The flowrate v of the carbonaceous feed gas was assumed to be responsible for setting the local concentration and thus directly influence the film growth rate. The removal rate is essentially Archard like (i.e., having a linear dependence on normal load F_n), and the details of the contact area, wear rate, and sliding speed are lumped into b. The only reason that sliding speed did not appear in [4] was that the original study was conducted at constant sliding speed. The authors successfully mapped out regimes of adequate (low friction) and inadequate (high friction) lubrication. However, the model predicted either complete coverage or zero coverage, and such a process should show a binary trend in friction coefficient. In practice, the friction coefficient could vary smoothly between the two extremes. This finding of intermediate values in friction coefficient then led to the development of a series of fractional coverage models for vapor phase lubrication [7, 8] and even a model for the removal of a fractional solid lubricant film [14].

During these modeling activities, a number of persistent questions emerged. What is the lubricating film? How thick is? Is it fractional? Some of these questions can be answered with the surface analytical instrumentation available today. Therefore, in an attempt to preserve the solid lubricant film and enable characterization the experimental approach followed here included flooding the contact with dry nitrogen during the cool down period of the experiments.

Using a focused ion beam scanning electron microscope (FIB/SEM) samples of the disk run with and without the acetylene atmosphere were imaged. The FIB instrument was used to produce site-specific thin transmission electron microscopy (TEM) samples. Figure 4a shows a solid lubricant film that has developed in the wear scar, it is clear from this image that the film is fractional. At higher magnification, Fig. 4b, there is evidence of delamination of the carbonaceous film, and film chips as seen in the center of the micrograph could be readily found within the wear track and in the debris fields. Such a removal process leaves behind bare or nascent surfaces of the CMSX-4, which are clearly visible as bright areas within the wear scar. These carbonaceous films measure approximately 100–500 nm in thickness.

A sample suitable for TEM was produced by FIB milling a longitudinal section of the wear scar in the direction of sliding from the sample exposed to the acetylene atmosphere. Figure 4c shows a bright field TEM image of the lubricant film, which has a thickness of on the order of a few hundred nanometers. The lubricant film also reveals a columnar-like grain growth normal to the counterface. Figure 4d shows a high-resolution TEM (HRTEM) taken from the sample in Fig. 4c. The very fine scale (<10 nm) of the graphite grain microstructure is apparent at this magnification. The selected area diffraction (SAD) pattern in the upper corner of Fig. 4d also indicates a textured nature of the carbonaceous lubricant film with a layer spacing measuring ~0.35 nm, which is consistent with the spacing of graphite. Together the HRTEM and the SAD pattern provide consistent indication that the basal planes are parallel to the sliding surface and that the carbonaceous film is graphite. Similar orientation of other lamellar solid lubricants has recently be shown using HRTEM and FIB sectioning along the direction of sliding [15].

Figure 5a, b is ion channeling contrast secondary electron images produced on trenches that are made by FIB milling along the direction of sliding within the wear tracks. In both figures, the top most layer is an in situ Pt deposition used to protect the area of interest from the milling beam and to provide good edge retention at the top most surface. Figure 5a is from the sample that was run in nitrogen cover gas. This sample had high friction coefficient, and shows a fine-grained region of approximately 1-μm thick that experienced severe plastic deformation. Below the fine-grained area, there is a region of larger-scale deformation as indicated by bending of the deformation of grains in the sliding direction. In Fig. 5b, the dark region just below the Pt cover is the graphite solid lubricant film. The grains in the substrate in Fig. 5b below the solid lubricant film show no deformation, as the graphite film has provided a low-friction protective layer for the nickel substrate. The final 100 m of sliding was done unidirectionally, which was sufficient to cause grain orientation in the direction of sliding in the unlubricated test. It is this protection from the solid lubricant layer and the friction reduction that likely led to the 100× wear reductions commonly reported by Lauer and co-authors in their pin-on-disk studies.

Raman spectroscopy was used to examine the graphitic nature of the solid lubricant films. Raman spectral data were recorded using a confocal micro-Raman dispersive spectrometer (LabRam, Jobin Yvon) with a 632.8-nm excitation source (15 mW) and 100× objective (~5-μm focal spot). All Raman spectra were recorded using a 10-s signal integration time, averaged 25–50 times. Figure 6 shows the Raman spectra recorded within and outside of

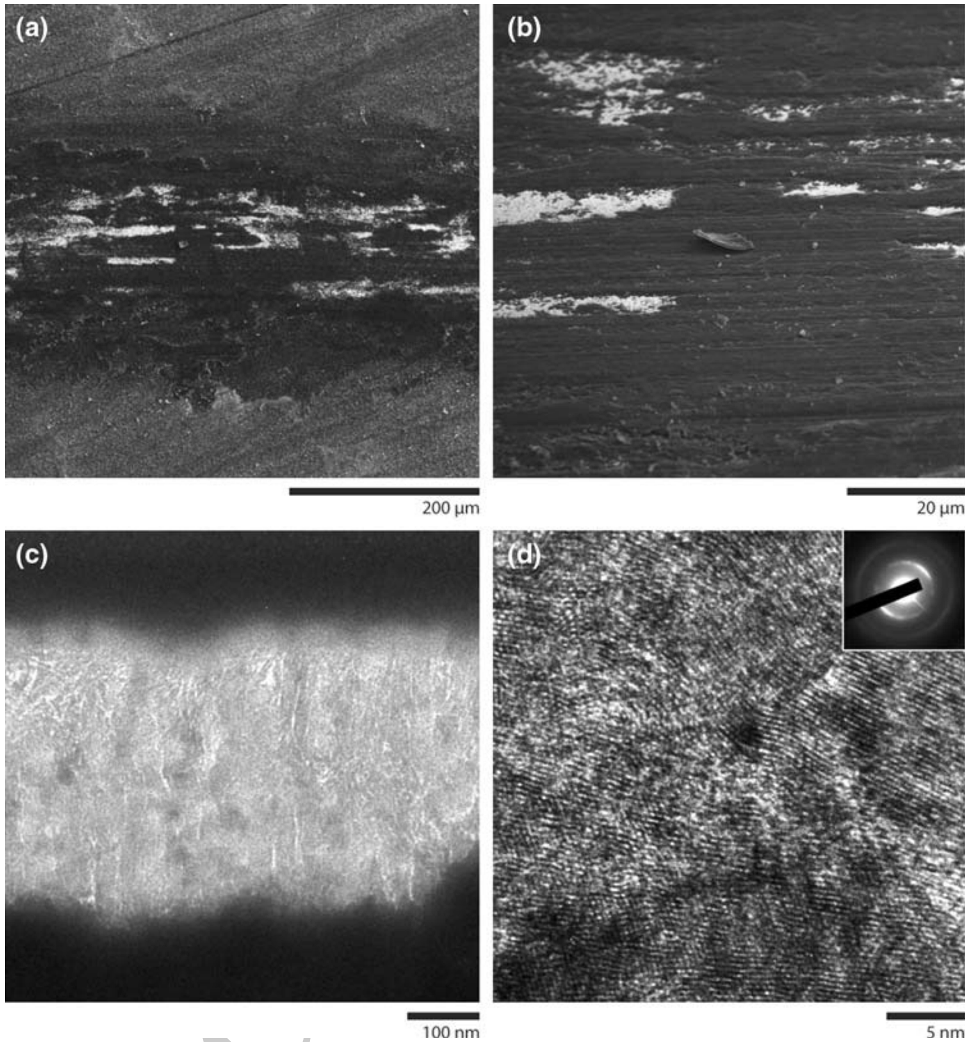

Fig. 4 **a** SEM image of wear track and solid lubricant film. **b** High-magnification SEM image showing delaminated graphite flake from the solid lubricant film. **c** TEM bright field longitudinal cross section of the graphite solid lubricant film. **d** HRTEM image from same sample as (**c**)

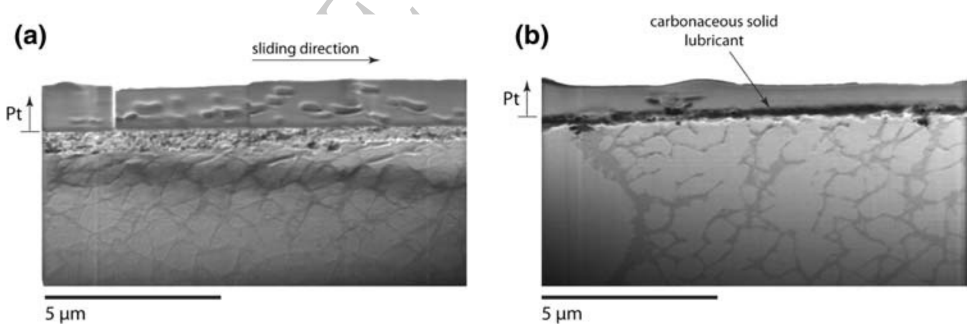

Fig. 5 Ion beam channeling contrast secondary electron image showing grain structures in longitudinal cross section orientation of **a** sample run in dry nitrogen and **b** sample run with acetylene admixture to nitrogen. The platinum layer is deposited in the microscope in order to protect the carbonaceous solid lubricant film from damage during milling

the wear track, along with the spectrum recorded for a graphite reference. Both tribological films show the D-bands and G-bands at 1315 and 1597 cm^{-1}, respectively, which are shifted and broadened with respect to the graphite reference spectrum. The G-band is attributed to the in-plane stretching of the hexagonal sheets (sp2), while the D-band is associated with increasing bond-angle disorder and decreasing micro-crystallinity [16, 17]. The spectra recorded out of the wear track were all very consistent with respect to peak location and width, whereas the spectra recorded in the wear track showed consistent peak widths and some variation in the location of the D-band

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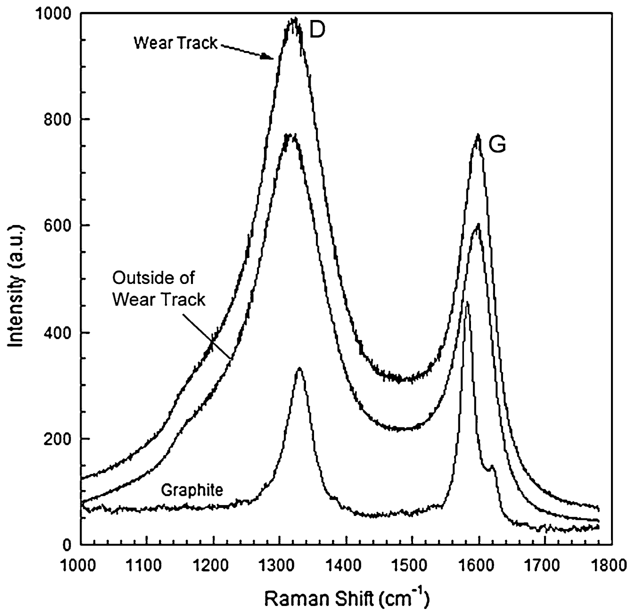

Fig. 6 Raman spectra recorded inside and outside of the wear track, along with a reference spectrum recorded for a graphite rod. The upper two spectra have the same intensity scale

peak (1315–1328 cm^{-1}) and the G-band peak (1586–1604 cm^{-1}). Overall, the Raman data suggest deposition of a microcrystalline, graphitic carbon that is not appreciably altered by the sliding motion of the pin

5 Closing Remarks

As found previously by Prof. Lauer, Prof. Blanchet, and their numerous students and colleagues, carbonaceous gases provide an effective lubrication strategy for continuous operation of high-temperature tribological contacts. This study has revealed that the solid lubricant films responsible for the friction reduction are thin (below 1 μm), fractional, and graphitic.

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