Lifetimes of Multiply Alkylated Cyclopentane Oil in Contact With Various Metals, Evaluated With Vacuum Spiral Orbit Tribometer

Stephen V. Pepper
Glenn Research Center, Cleveland, Ohio

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Stephen V. Pepper
Glenn Research Center, Cleveland, Ohio

National Aeronautics and
Space Administration

Glenn Research Center
Cleveland, Ohio 44135

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Summary

The dependence of the lifetimes of small quantities of a multiply alkylated cyclopentane (MAC) lubricant oil, Pennzane® 2001A (Nye Lubricants, Inc.), in rolling and sliding contact with different metals was evaluated with a vacuum spiral orbit tribometer. The metals were the bearing alloys 52100 steel, 440C steel, 17-4 PH steel, and Nitinol 60 and the elements chromium, vanadium, and titanium. The lifetimes of the lubricant oil on different metals fell into distinct groups with $52100 > 440C \approx$ Nitinol $60 > 17$-4 PH for the order of the lifetimes of the steels and chromium $>$ vanadium $>$ titanium for the order of the lifetimes for the elements. The limited life of the small quantities of oil is assumed to be due to its consumption by the tribochemical reaction of the oil with the different metal bearing materials. The lifetimes are then inversely related to the reaction rates of the oil molecules with the various metals: the longest life of 52100 steel having the lowest reaction rate and the shortest life of titanium having the highest reaction rate. Mechanisms for the tribochemical reactions are discussed.

Introduction

Tribochemistry, sometimes called mechanochemistry, is an area that receives much attention. Among the topics focused on liquid lubricants are the development of tribologically beneficial films that may form on materials in sliding contact as well as the beneficial or detrimental chemical changes in the lubricants by chemically interacting with the surface. Most of the attention on the chemically active role of the lubricated material in such studies has been given to steels. Pepper and Kingsbury (Ref. 1) have reported the limited lifetime of tribological tests when the system is lubricated with small quantities of liquid lubricants. They interpreted the limited lifetime as due to the destruction of the lubricant into nonlubricating moieties by chemical reaction of the lubricant molecules with the bearing material in tribological contact. Such limited lifetimes with small quantities of lubricant have subsequently been reported by Masuko et al. (Ref. 2). Fragments of lubricant molecules liberated into the vacuum ambient have been observed by residual gas analyzers (RGAs), confirming tribochemical reaction of the lubricant with the bearing material (Refs. 3 and 4). More reactive bearing materials should lead to shorter lubricant lifetimes. Each lubricant/bearing material combination would have its own tribochemical reaction rate. Such tribochemical reactions are then expected to depend on the chemical reactivity, or in this case, tribochemical reactivity, of the bearing material. However, such a dependence has not been systematically studied.

In this report the effect of different bearing materials on the lifetime of a lubricant is explored by using a limited amount of lubricant in a vacuum tribometer. The basic assumption in these tests is that the limited lifetime is due to the consumption of the lubricant by chemical (tribochemical) reaction of the limited number of lubricant molecules with the substrate bearing material. The different limited lifetimes then provide rankings of tribochemical reactivity of the bearing materials. The bearing materials tested here are three commonly used bearing alloys: 52100 steel, 440C steel, and 17-4 PH steel; the new bearing material Nitinol 60 (Refs. 5 and 6); and the elements chromium, vanadium, and titanium in the form of thin films on 440C steel substrates. The liquid lubricant, a multiply alkylated cyclopentane (MAC), known commercially as Pennzane® 2001A (Nye Lubricants, Inc., Ref. 7), is used as a test lubricant in order to rank the reactivity of the metals. It is often used as a lubricant on mechanical systems in vacuum,

typically on spacecraft. The results have relevance to both understanding tribochemistry and to the selection of materials for tribological service.

The tribometer, the specimens, and the procedure will be described in the Experimental section. The tribological results will be presented in the Results section. The Discussion will first treat the mechanical aspects of the tribological results and their relationship to engineering practice. This section then describes different approaches to understand surface chemical reactivity. The Conclusion section offers ideas to more conclusively establish the order of triboreactivity by experiment and to understand these results on a quantum theoretical basis.

Experimental

This section first explains the tribometer that measures friction and lifetime of lubricants. The metal specimens that form the tribological contact are then listed, together with some of their material properties, followed by the procedure for cleaning and lubricating these metal specimens for a life test. The experimental lifetime results are then presented in the Results section.

Tribometer

The components of the spiral orbit tribometer (SOT) are depicted in Figure 1. It has been described before (Ref. 8). It is basically a thrust bearing with one ball and flat races (plates). The top plate P1 is stationary while the bottom plate P2 rotates, driving the ball B in the direction of rotation of P2. The ball performs a near circular orbit that is actually an opening spiral. It may be regarded as a simplified version of the usual angular contact ball bearing. The ball contacts a "guide plate" at the end of each orbit, which forces the ball back into its initial orbital radius. The ball then exhibits, for a given coefficient of friction (CoF), a stable orbit, repeatedly over-rolling the track on both large plates and guide plate. The spiral's pitch and the length of the contact on the guide plate increase with the increase of the CoF. A piezoelectric force transducer supporting the guide plate senses the friction force developed on the ball as it slides on the rotating plate during the contact of the ball with the guide plate. During this contact, the CoF is obtained from this force (Ref. 8). An advantage of this configuration is that all surfaces of the ball, and thus all lubricant on the ball, are brought into the tribological contact (Ref. 8). In the tests reported here, only the ball is lubricated with a small amount of lubricant, and the plates and guide plate are initially clean. The tribometer is housed in a stainless steel chamber that is evacuated by a turbomolecular pump. All tests reported here were done at a vacuum $\leq 2 \times 10^{-8}$ torr. A quadrupole RGA was installed on the chamber to determine the residual gas species in the chamber as well as to detect fragments released from the lubricant under tribochemical stress.
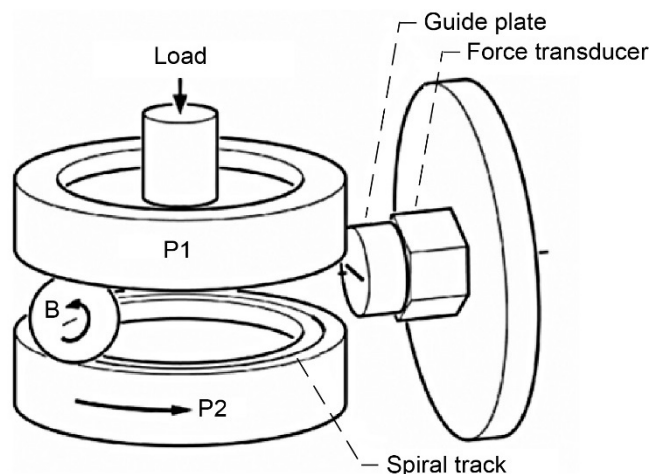

Figure 1.—Components of the spiral orbit tribometer.

Specimens

The dependence of tribochemical reactivity on the tribomaterial is explored by changing the material of the plates P1 and P2 (and thus their triboreactivity) while maintaining the same materials for the ball, guide plate, and lubricant in all the tests. The tribochemical reactivity of materials is thus to be manifested by the different lifetimes exhibited by the chemically different plates in the tests.

Each test used a new 12.7-mm- (0.5-in.-) diameter 52100 steel ball, grade 25. This choice of material for the ball is motivated by the fact that lubricant can spread and lubricate its surface and that it is not subject to dewetting as other materials may be. It has also been found to be the least reactive material tested here so that it contributes least to the tests that rank the reactivity of the other materials.

The plate steel bearing materials 52100, 440C, 17-4 PH, and Nitinol 60 (Refs. 5 and 6) were used as solid materials. The Nitinol 60 plate material, made through vacuum casting followed by hot rolling, was obtained from Wah Chang Corporation (Ref. 9). These plates were diamond polished to surface roughness of about 3 nm, determined by interference microscopy. The 0.5-μm-thick films of pure chromium, vanadium, and titanium were sputter deposited on polished 440C plates. Although these films were used to change the chemical properties of the tribological contact, it is understood that their mechanical properties (such as roughness, hardness, elastic modulus, etc.) differ from their values in bulk form and from those of the steel substrate. It is assumed here that the small thickness of the films permits the mechanical response of the contact to be determined by the properties of the steel substrate and not those of the films. These thin-film specimens were stored in vacuum immediately after deposition until use. Each test used a new 12.7-mm-diameter 440C steel guide plate with the same roughness as the plates P1 and P2. The Pennzane® 2001A lubricant was obtained from Nye Lubricants, Inc. (Ref. 7).

Physical properties of the plates are as follows. The plates were 50.8 mm (2 in.) in diameter and were diamond polished to a roughness of $R_a < 25$ nm (1 μin.), determined by optical interferometry. The hardness of the steel plates was Rc64 for 52100 steel, Rc58 for 440C steel, and Rc45 for 17-4 PH steel. A set of 52100 steel plates was also tempered to soften them to a hardness of Rc49 and tested. These plates are designated as 52100T. The elastic modulus of all the steels was about 200 GPa. The Nitinol 60 plate material (Ref. 9) had a hardness of Rc55 and an elastic modulus of 114 GPa (Ref. 5).

The chemical composition of the plates is given in Table I.

TABLE I.—COMPOSITION OF BEARING MATERIALS TESTED

Element, wt%	Bearing steel			
	52100	440C	17-4 PH	Nitinol 60
Iron, Fe	97	80	73	
Carbon, C	1	1	0.07	
Chromium, Cr	1.45	017	17	
Nickel, Ni	0	0	4	60
Copper, Cu	0	0	4	
Manganese, Mn	0.35	1	1	
Silicon, Si	0.23	1	1	
Phosphorus, P	0	0.04	0.04	
Sulfur, S	0	0.03	0.03	
Titanium, Ti	0	0	0	40
Molybdenum, Mo	0	0.75	0	
Niobium, Nb	0	0	0.3	
Vanadium, V	0	0	0	

Procedure

The ball, guide plate, and plates P1 and P2 (without thin films) were subjected to the same cleaning procedure. A specimen was rubbed lightly with a small amount of SiC polishing powder under flowing de-ionized water; nonpowdered nitrile blue gloves were worn. After the polishing, the powder was removed as well as possible by rubbing lightly under a stream of de-ionized water, and the specimen is ultra-sonicated in de-ionized water. The specimen is then dried in a stream of nitrogen gas. The plates with thin deposited films were not subjected to this cleaning procedure; rather, they were stored in vacuum after film deposition and were installed in the tribometer chamber when needed for a test.

All metals acquire a native oxide in air, and the specimens subjected to the cleaning procedure used here were no exception. An x-ray photoelectron spectroscopy (XPS) spectrum for 440C steel that had been subjected to this procedure is shown in Figure 2.

The presence of the oxide is indicated by the oxygen peak at about 530 eV binding energy and by the peak in the Fe 2p3/2 region at a higher binding energy than the binding energy of the pure metal itself. The fact that the peak due to the pure metal is visible in the presence of the covering native oxide indicates that the oxide film itself is no more than a few nanometers thick. The escape depth of the x-ray photoelectrons is 3 to 5 nm; therefore, if the bulk metal peak is visible, then the oxide layer is thinner than that. In a sense, the pure metal can be "seen" under the native oxide. The native oxide and the role it can play in the duration of a test will be addressed in the Discussion section.

The deposition of lubricant on the ball is described as follows. The ball is weighed, then a few drops of a dilute solution of Pennzane® 2001A in hexane is dripped from a syringe onto the ball spinning on a magnetic chuck. The ball is then reweighed after the hexane had a few minutes to evaporate. The difference in weights gives the amount of lubricant on the ball. So if 20 µg of lubricant were to be deposited, the average thickness on the 12.7-mm-diameter ball is 45 nm. Lubricant weights of 10 to 20 µg were used in the tests. The coverage of the lubricant on the ball is not uniform, so this thickness is just an average. In any case, when the lubricant on the ball's surface is brought into the contact, the lubricant is squeezed out and only a few molecules of the lubricant remain in the contact. The contact will be addressed in the Discussion section.

A test is performed after cleaning the specimens, lubricating the ball, installing the specimens, and evacuating the tribometer. After an overnight evacuation, the test is started at a pressure of about 2×10^{-9} torr.
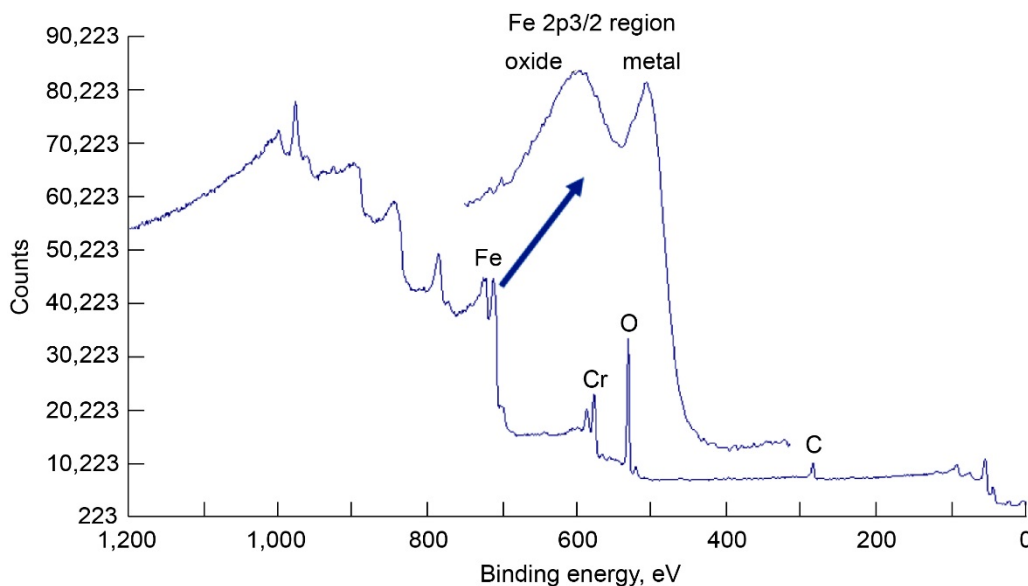

Figure 2.—X-ray photoelectron spectrum of 440C steel prepared for test.

Tests on steel alloy plates and on film-covered 440C steel plates were conducted at a load of 43 lbf, resulting in an average Hertz pressure of 1.5 GPa and a Hertz diameter and thus a track width of 0.4 mm. Tests on Nitinol 60 plates were conducted at a load of 30 lbf, resulting in an average Hertz stress of 1.06 GPa and a Hertz diameter also of 0.4 mm (Ref. 5). The plate rotation rate was 60 rpm, leading to a ball orbit rate of 30 rpm.

Two tests were usually run on a given set of plates, with the guide plate extended after the first test so that the track of the second test lay on clean metal within the track of the first test. The ball and guide plate were changed after the first test. Since each track had a different circumference, the duration of a test is expressed in distance traveled in meters divided by the lubricant amount in micrograms to give what is designated here as a "lifetime" $\mathcal{L}$ in m/µg. This lifetime was determined when the CoF reached 0.2.

As an example of a test, the plot of CoF versus orbit number for a test of 17-4 PH is shown in Figure 3. The CoF is initially 0.08 and rises gradually to the cutoff at 6,971 orbits. In this test there was 13.4 µg of lubricant on the ball, the CoF of 0.2 was achieved at 6,617 orbits, giving a lifetime of $\mathcal{L} = 73$ m/µg. Typically, eight tests were conducted on each plate type except for the cases of Nitinol 60 and the tempered steel 52100T, for which four tests were conducted.
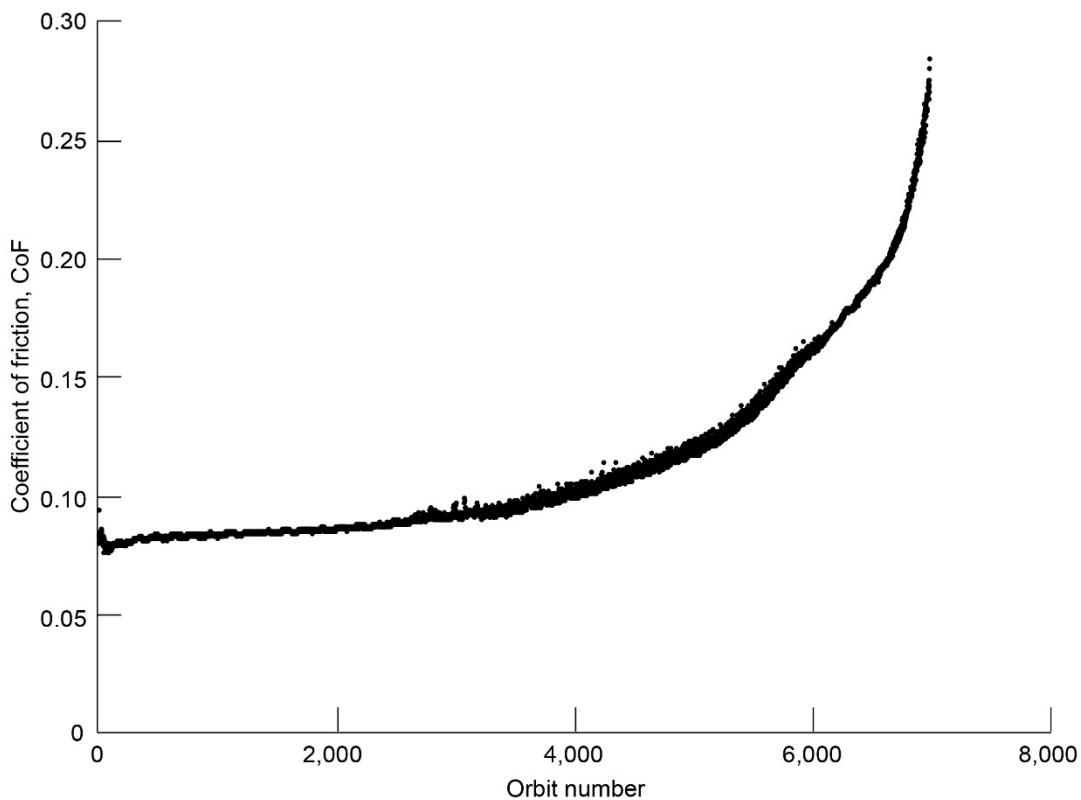
Figure 3.—Tribometer test with 17-4 PH plates.

Results

All tests reported here exhibited friction traces similar to that shown in Figure 3, even though the lifetimes varied by orders of magnitude. Examples of friction traces for the steel alloys are shown in Figure 4(a), and examples of friction traces for the elements are shown in Figure 4(b). The values for 52100 steel are displayed in duplicate and are "bookkept" as elemental iron since this alloy is 97 percent iron (Table I). The CoF in each test was initially close to 0.08, albeit with appreciable scatter in the early stages of the tests of the elements.

Figure 4.—Representative friction traces for materials studied.
(a) Bearing steels. (b) Elements.

The lifetime results are presented in Figure 5. The lifetimes were grouped into categories of elements, steel alloys and, separately, the alloy Nitinol 60. Average values of the 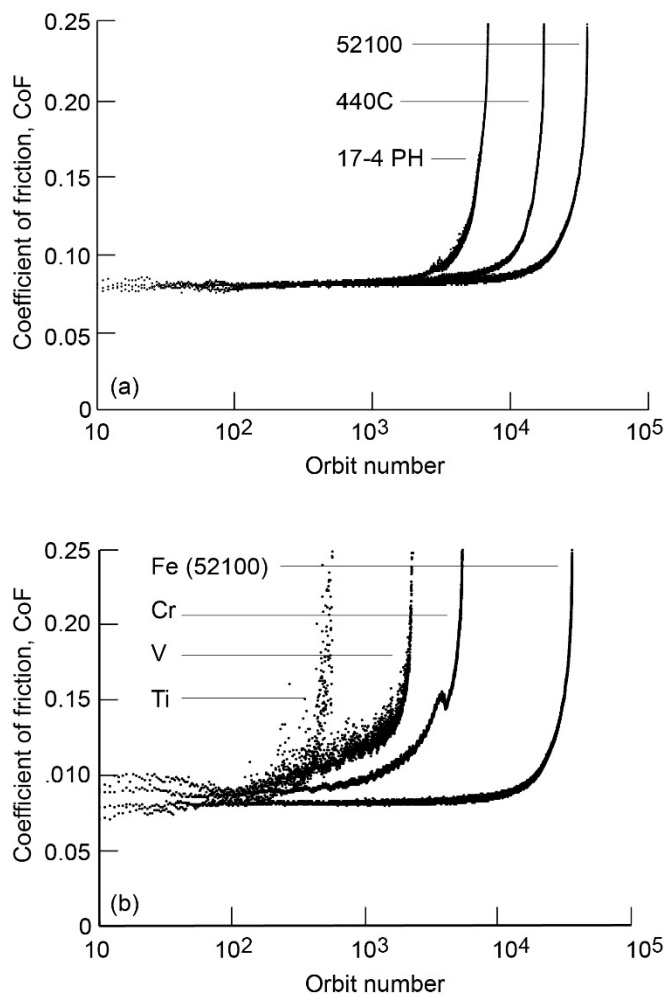tests are given in Table II. Not all test results may be visually evident since some lifetimes closely repeated, so their symbols overlap.

There is appreciable scatter in the data. However, within each category the data separate quite cleanly, without overlap of the data of one material with another. An exception is one test of titanium that is within the data set for vanadium. Another exception is the data for 52100T steel that had been softened to values of 17-4 PH steel, to be discussed below.

Within the category of elements there is a progression: the lifetime decreases from iron (52100 steel) to titanium. The interpretation of lifetimes in terms of tribological reactivity indicates that the reactivity is greatest for titanium and decreases progressively to the least reactive iron. This provides a ranking of the tribological reactivity of these elements. A similar ranking of reactivity for the steel alloys is also established, with 17-4 PH steel being the most reactive of these alloys. The reactivity of Nitinol 60 is close to that of 440C steel, at least in terms of the averages in Table II.

Fragments of the Pennzane® 2001A lubricant molecules were detected by the RGA during the tests. The mass spectra observed here were entirely similar to those reported by John, Cutler, and Sanders (Ref. 4). This observation of fragments of the lubricant molecules supports the working assumption that the finite lifetime of these tests is due to the consumption of the lubricant by tribochemical reaction of the lubricant with the bearing material.
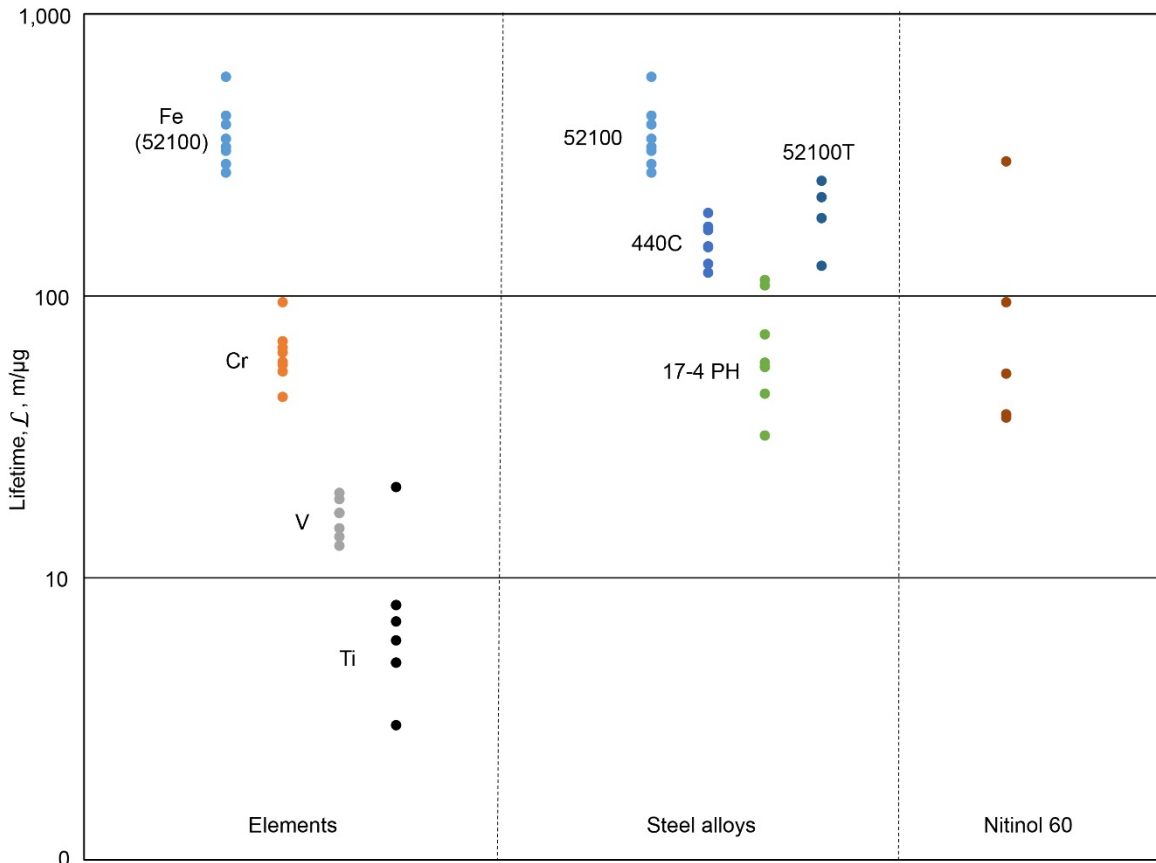

Figure 5.—Lifetimes $\mathcal{L}$ of tested materials.

TABLE II.—AVERAGE VALUES OF LIFETIMES OF TESTED MATERIALS

Tribomaterial	52100	52100T	Chromium	Vanadium	Titanium	440C	17-4 PH	Nitinol 60
Lifetime, $\mathcal{L}$, m/µg	379	199	63	16	8	156	68	158

Discussion

The discussion is divided into two parts. The first part discusses tribological factors. These include the nature of the ball and plate contact, factors that may qualify the rather clear separation of the lifetime results, the relationship to past work, and the relationship of these purely tribological results to practical lubrication. The second part considers the interpretation of the tribological results in terms of surface chemical reactivity.

The Contact

An understanding of the contact between the ball and plates is an important aspect of the interpretation of the results. Because of the restricted amount of lubricant in the system, no meniscus is formed and so the system is not in the elastohydrodynamic (EHD) regime. Rather, it is starved (Ref. 10) or what has been termed "ultrastarved" (Ref. 11). The contact is in what is known as the boundary lubrication regime, in which lubrication takes place by only monolayers of lubricant molecules in the contact (Ref. 12). The nature of the lubrication in the contact used here goes back to Hardy (Refs. 13 and 14 and see Ref. 15 for a discussion of Hardy's work), in which monolayers of lubricant molecules on the contacting surfaces slide against each other, and the resistance to this sliding of molecules is the source of the friction force. This model accounts for the independence of the CoF on the test material (Figure 4) because each test uses the same lubricant—Pennzane® 2001A. Thus, the initial CoF is the same at about 0.08 for all tests, even though the lifetimes of the tests vary by orders of magnitude.

The sequence of events proposed here to account for the evolution of the contact in a test is shown in Figure 6. First, in panel **a**, some of the lubricant initially on the ball is deposited or shared with the initially clean plates. Then in panel **b**, some of the lubricant monolayer in this contact is displaced to allow lubricant to come into contact with the native oxide. This contact with the surface unprotected by lubricant is the first stage of the lubricant's chemical reaction. In panel **c**, the native oxide has been removed and lubricant comes into contact with the nascent metal. The native oxide has been removed by the shear stress of sliding, exposing nascent metal. Nascent metal is expected to be more chemically active than the oxide, so the consumption of the lubricant by chemical reaction is considered to begin with the contact of lubricant molecules with nascent metal. This scenario for the removal of the native oxide by tribological action leading to lubricant degradation has been studied by Lu et al. (Ref. 3) and Masuko et al. (Ref. 16).

Even though this scenario appears in the literature, details of the role and removal of the protective native oxide as the initial steps in the reaction of the lubricant are still a matter of conjecture, and the tests described here provide no direct evidence for this sequence of events. However, this evolution of the contact proposed here serves as a conceptual basis to initiate the discussion of the tribological results and will be brought up again below. It should be taken as a working hypothesis that aids the discussion of the results.
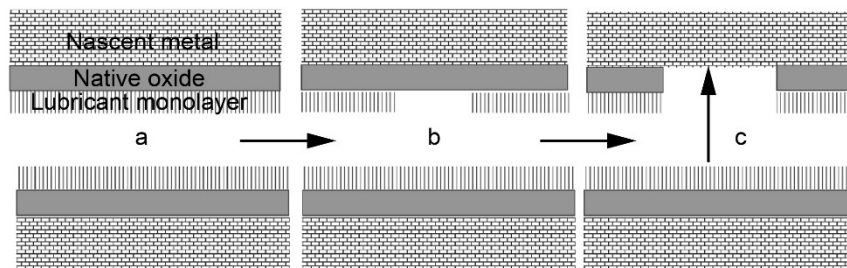

Figure 6.—Evolution leading to contact of lubricant with nascent metal during frictional contact.

Qualifying Factors

This study has focused on changing the tribological response of the lubrication system, specifically the lifetime, by changing the plate material. Although the idea behind the change has been to change its chemistry, there are other properties that change as well. Some of the factors that qualify the clear separation of the results as due only to surface chemistry are surface roughness, material elasticity and hardness, native oxide, and shedding of lubricant to the track edges. Each factor could, in principle, be important in determining the observed ordering of the lifetimes. They could also be responsible for the scatter observed within each grouping. Here we briefly discuss the factors mentioned.

Roughness

The plates without films were prepared by the same procedure, so their roughness should not differ. The plates with films, however, did have a haze that indicated a rougher surface. However, the tracks developed during the tests essentially overrode the initial roughness, so this effect is not considered important.

Elastic Modulus

Although the elastic moduli of the steel alloys are very similar, the films on them have their own different modulus. However, the films are so thin that their different moduli should not change the Hertzian pressure or diameter of the contact. This has recently been studied (Ref. 17).

Hardness

Different material hardness however, may have a significant role to play in the ordering of the lifetimes. This is brought out in the reduced lifetime of the softened 52100 steel (Rc49), 52100T, relative to the original hard 52100 steel (Rc64). Although the lifetimes of the softened material are reduced, they are not as low as the lifetimes of 17-4 PH (Rc45), which has the same hardness as the softened 52100. This is taken as an indication that the material hardness, while playing a role, does not determine the overall ordering of the lifetimes. It must also be noted that tempering a material may change its electronic structure (to be addressed below) as well as its hardness, and the electronic structure of the material may determine its tribochemical reactivity. So both the chemical reactivity of a material as well as its mechanical (tribological) response may be affected by tempering and should be taken into account in any further study. It would thus be beneficial to confirm the ordering of triboreactivity presented here using a method to assess triboreactivity that is not dependent on the lifetimes, since lifetimes may be affected by material properties such as hardness.

Native Oxide

The native oxide may play an important role in the observed lifetime. Certainly thicker oxides or oxides more resistant to displacement would take longer to displace and expose the nascent metal, thus leading to longer lifetimes (Refs. 3 and 16). In the present study, an effort was made to minimize, or at least control, oxide thickness as indicated in the Specimens section. However, each of the different types of specimen tested here may have an oxide thickness different from the others, and this may play a role in the ordering of the lifetimes observed. This is definitely a complicating factor for which there is presently no easy answer and makes the conclusions based on the ordering presented here contingent on resolving this issue. Note that the one outlying high lifetime test with titanium may be due to a thicker oxide. Also, the relatively few orbits required to end most of the titanium tests may be interpreted as simply those orbits required to expose the nascent metal and thus to allow tribochemical reaction to take place. It may be that once nascent metal is exposed, the reaction is so strong that the lubricant does not survive in the nascent titanium contact at all.

Shedding

Some of the lubricant initially only on the ball is definitely transferred to the plates and is brought into the contact on multiple orbits. However, some of the lubricant may also be shed onto the edge of the track on the plates where it is not available to the contact and thus can neither lubricate nor be subject to chemical reaction. Even though this shedding has not been observed for amounts of lubricant used here, it has been observed with larger amounts. Although it is definitely a possibility that random shedding can be responsible for the observed scatter in the lifetimes, it is not clear if it plays a role in determining the overall ordering of the lifetimes.

A change in any of the above factors can, in principle, affect the observed ordering of the lifetimes. They could also be responsible for the scatter observed within each grouping. Thus these factors introduce uncertainty in the interpretation of the observed ordering of lifetimes in terms of the tribochemical destruction of the liquid lubricant, and each factor could be the subject of a study in itself. However, in this report, the results are taken at face value as indicators of the ranking of tribochemical reactivity with the understanding that future studies may change the ordering reported here.

Prior Related Work

An early work (Ref. 18) with the SOT found that the lifetime of the fluorinated lubricant Fomblin® Z25 (Solvay Solexis, Inc.) on chromium substrates was significantly less than the lifetime on 440C steel, the same as found here for Pennzane® 2001A. This has two implications. The first is that the results found with Pennzane® 2001A are not unique to it, but are found with other lubricants. Pennzane® 2001A may then be regarded as a test lubricant to study triboreactivity in general. The second implication is that the result supports the idea that chromium really is more (tribo)reactive than steels.

Reports in the literature using the more commonly used pin-on-disk sliding test configuration relate to the present work in many aspects, even though the relative triboreactivity of different metals has not been the point of the works. John, Cutler, and Sanders (Ref. 4) reported RGA cracking patterns of gas evolved during sliding on 440C steel lubricated with Pennzane® 2001A in vacuum and attributed the degradation of the lubricant to its reaction with nascent metal exposed by removal of the native oxide by sliding. Identical RGA cracking patterns were found in the present work. Lu et al. (Ref. 3) also reported on work similar to that of John, Cutler, and Sanders, but the sliding was on 52100 steel and the emphasis was on the effect of additives in the lubricant that affected its decomposition rate. Masuko et al. (Ref. 16) also reported on work similar to that of John, Cutler, and Sanders and Lu et al., with 440C steel substrates and with an emphasis on the effect of oxide thickness on lubricant lifetime. These studies did not compare the lifetimes of the lubricant on 440C steel with the lifetime on 52100, as done here. However these studies were complementary to the present study in many aspects and support the present work.

The reduced lifetime of Pennzane® 2001A on 17-4 PH steel relative to that of 440C steel measured by SOT testing was originally reported by Jones et al. (Ref. 19). This was followed up by Kim and Didziulis (Ref. 20) using a pin-on-disk configuration. They confirmed the observation of Jones et al. regarding the poor performance of Pennzane® 2001A on 17-4 PH steel relative to 440C steel (in accord with the present work), but concluded that tribochemical-induced degradation of the lubricant was not the cause. Although there is agreement on the general effect, the disagreement as to its cause certainly merits further study.

Nitinol 60 has been previously tested (Refs. 5 and 6) and was found to be lubricated without any problem. This capability is not so obvious since the alloy is composed of 40 wt% titanium. Since titanium has been shown here to be a material with extremely short lifetime (and will be noted below that it simply cannot be lubricated with the usual fluids), it was expected to exhibited properties close to those of titanium. That this was not found to be the case thus constitutes a challenge to any theory of surface reactivity and will be discussed in that context below.

Relationship to Lubrication Practice

All tribological "bench tests" such as the SOT are subject to the question of how well they relate to lubrication in practice. The limited life for the present tests is generally not met in practical lubrication: the supply of lubricant is usually more than enough to overcome any tribochemical consumption of the lubricant. The practical value of the present SOT tests probably lies in the extreme cases. For example, steels in general certainly can be lubricated, and the lifetimes they exhibit here are taken to be typical of that ability. At the other extreme, it is known that titanium cannot be lubricated in practice (Ref. 21), and thus the very small lifetimes found here are in accord with that aspect of practical understanding. Also, titanium is generally acknowledged to be chemically highly reactive; in fact, it is more reactive than the neighboring elements in the early 3d transition metal series. The operation of the common titanium sublimation and sputter-ion vacuum pumps are based on the extreme reactivity of titanium (Ref. 22). So it is expected that titanium is found to have the shortest lifetime, which is interpreted here as having the greatest chemical reactivity of the materials tested. In this extreme case, the lubricant in the contact is totally destroyed by the nascent titanium metal, and no lubrication is possible.

The lubrication of chromium in practice does not appear to be a problem, since "thin dense chrome" is used commercially on surfaces in tribological service. So, in practice, materials that exhibit lifetimes in SOT tests greater than—somewhat arbitrary—50 m/µg on the SOT lifetime scale, appear to be capable of lubrication without problems. However, the lifetime of 17-4 PH steel is close to this somewhat arbitrary value and the problem of its lubrication with Pennzane® 2001A has been pointed out above (Refs. 19 and 20), although this finding with a bench test has not been confirmed in lubrication of actual devices.

The rankings of lifetimes found here in SOT testing may provide a boundary on those materials that can be effectively lubricated, at least with Pennzane® 2001A. From this point of view, Nitinol 60 with its average lifetime of 158 m/µg, about the same as that for 440C steel, lies well above this boundary value; and in fact, this material has entered lubricated tribological service (Ref. 6) without apparent problem. Thus these rankings from SOT testing may be used to qualify candidate materials for tribological service.

Chemical Studies of Surface Reactivity

Before considering the study of surface reactivity, it must be emphasized that behind the interpretation of the tribological lifetime trends in terms of intrinsic chemical reactivity of the tested metals, is the assumption that the lubricant Pennzane® 2001A acts as a "neutral" test molecule to assess relative chemical reactivity. Of course it may not be so neutral. The use of other lubricant molecules may result in a different ordering of lifetimes and thus invalidate the ordering found here as indicating a true ranking of intrinsic reactivity. Two studies relate to this issue. The first study (Ref. 18), mentioned above, found that there is reduced lifetime of chromium relative to 440C steel when Fomblin® Z-25 is the lubricant. This supports the conclusion that chromium really is more chemically reactive than 440C steel and that Fomblin® Z-25 can act as a test molecule to assess the relative reactivity of metals. The works of Jones et al. (Ref. 19) and Kim and Didzuilis (Ref. 20) come to a different conclusion: although they found a reduction in lifetime with Pennzane® 2001A on 17-4 PH steel relative to 440C steel in accord with the present observation, a reduction in lifetime for Fomblin® Z-25 on 17-4 PH steel was not found. So this observation indicates that Fomblin® Z-25 may not play the role of a "neutral" molecule to assess the relative chemical reactivity of metals. This may be due to the autocatalytic degradation of fluorinated lubricants such as Fomblin® Z-25 by surface metal fluorides that has been proposed as a life-limiting mechanism (Ref. 23). Thus Fomblin® Z-25 degrades by an additional mechanism than only the direct reaction with the substrate metal as does Pennzane® 2001A, and this may be responsible for its shorter lifetime in SOT tests (Ref. 1). This is an argument against the neutrality of Fomblin® Z-25 as a test molecule. The role of Pennzane® 2001A as a neutral test molecule to interrogate the specimen plates for fundamental studies of tribochemical reactivity remains contingent and should be a topic for further study. However, for engineering tribology, the tribologist must pick a lubricant test molecule likely to be used in the intended application, especially if the rankings can be affected. The ordering of lifetimes

found here with this lubricant is taken on face value to be indicative of the ranking of fundamental chemical reactivity in the following discussions. It is also in this spirit of neutrality that 52100 steel is chosen as the ball material for all tests because it exhibits the least triboreactivity and thus permits the triboreactivity of the different plate materials to be expressed more clearly. The 52100 is also the most common and well understood of the bearing steels.

A theory of surface chemical reactivity would explain the observed rankings and provide a basis for understanding and predicting the behavior of materials not tested or used in applications. An experimental chemical method, possibly a photon or electron spectroscopy, would also provide understanding and predict the tribochemical rankings found here. It could thus screen materials before proceeding with tribological bench testing for candidate materials. From a technological point of view, the rankings of the steels and especially Nitinol 60 should be the focus of attention of both theory and experiment since the result of bench testing Nitinol 60 was unexpected because of its high content of titanium.

Three approaches to surface reactivity found in the literature are discussed here. First, the HSAB (hard and soft acids and bases) approach was pioneered by Pearson as a method to understand reactions of inorganic chemicals (Ref. 24), and then greatly extended (Ref. 25) using density functional theory. It has also been applied to surfaces by Stair (Refs. 26 and 27). Briefly, The HSAB principle is that "a hard base prefers to react with a hard acid and a soft base with a soft acid." Metals are considered soft acids. In tribological work, it has been applied to understanding reactions of additives with both nascent metal and oxidized metal surfaces (Refs. 28 and 29). Thus far, all the experimental work that invokes the HSAB principle used steels (440C or 52100) as a tribological material. No comparison of results with 440C steel and results with 52100 steel were made, and no comments on the acidic strength of either metallic elements (such as Ti, V, or Cr) or alloys were made. The experimental literature on the HSAB approach provides no insight on the rankings found here. The theoretical literature referred to above also does not provide values for the acidic strengths of the different metals or alloys used here. Thus, while the HSAB principle found in the tribological literature has proven to be useful for understanding some aspects of additive reactions, it does not appear to provide an explanation for the rankings found here for elements or guidance for predicting the tribochemical reactivity of alloys.

The next approach for reactivity, although not really a surface or even solid reactivity, derives from traditional "wet" chemistry and refers to the Pauling electronegativity scale found in elementary chemistry expositions (Ref. 30). In this approach, lower values of electronegativity correlate to greater reactivity due to the greater ease it is for the metal atom or ion to lose an electron and thus react with another moiety. Referring to Figure 7, in which the elements in the elements in the periodic table are displayed together with their Pauling electronegativity, it is seen that their decreasing value from Fe toward Ti correlates to increasing chemical reactivity, the same ordering found here for triboreactivity. No practicing chemist would be surprised at the tribochemical reactivity interpreted from the lifetime ordering found here for the elements. In a sense, this agreement of the lifetimes with traditional electronegativity concepts supports the correctness of the interpretation of tribological lifetimes of the

Elementary chemistry texts:

Pauling electronegativity

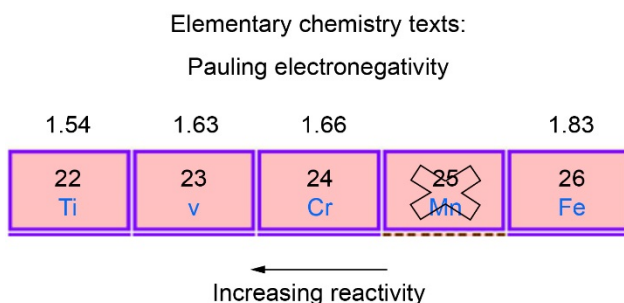| 1.54	1.63	1.66		1.83
22	23	24	25	26
Ti	v	Cr	Mn	Fe

←——— Increasing reactivity

Figure 7.—Pauling electronegativity and reactivity trend of early 3d elements.

elements tested here in terms of triboreactivity. This approach, however successful it is for the reactivity of the elements, does not address the reactivity of the alloys tested here that are important in engineering tribology. The reactivity of these alloys requires an approach that considers the reactivity of the solid surface, which is now discussed.

The current approach to metal surface reactivity goes much further than simple correlations with the Pauling electronegativity. It is through the electronic structure of the material. A motivation for this is that it is the interaction of the electrons in the material with the valence electrons of the lubricant molecules that lead to reaction and destruction. This approach focuses on the d electrons of the early 3d transition metals. Stott et al. (Refs. 31 and 32) have used density functional theory to analyze the electronic structure of Nitinol 60. Their results indicated that its reduced chemical reactivity compared to that of elemental titanium may be due to the bonding of titanium to nickel in the alloy in such a way as to render the titanium there relatively chemically unreactive compared to metallic titanium. This is definitely a step toward understanding the ability of Nitinol 60 to be lubricated.

An approach to reactivity in general notes that the 3d electrons constitute a band in the metal with a density of states has a maximum near the Fermi level, and it is the position of the center of this maximum that is considered to be the quantity that determines the reactivity of the material. Motivated by investigations into the theory of catalysis, Hammer and Nørskov formulated the "d-band center model" (Refs. 33 to 35). They proposed a concept to describe the trends in surface reactivity from one metal to another based on the position of the d-band. As the d-states shift up in energy going from right towards the left in the first transition metal row, the reactivity should increase. The general rule of the d-band center model is that the higher the d-band center is with respect to the Fermi level, the more reactive is the metal. During the last two decades, the d-band model has been widely used to understand variations in chemisorption energies of various adsorbates on transition-metal surfaces and their alloys (Refs. 36 to 38). A review may be found in the book edited by Nilsson et al., Chapters 2 and 5 (Ref. 39). This model can be applied to the trends found here for the elements Fe, Cr, V, and Ti. Figure 8 (Ref. 39, p. 268) provides values calculated by density functional theory of parameters describing the electronic structure of many elements of the periodic table. The numbers in the lower left corner of the boxes are values for the center of the d-band relative to the Fermi level. Table III gives the values of the d-band center relative to the Fermi level for the elements used here. The position of the d-band center increases going from Fe toward Ti, as does the triboreactivity of those elements, so there is accord between the d-band model calculations and the present experimental observations for these elements.
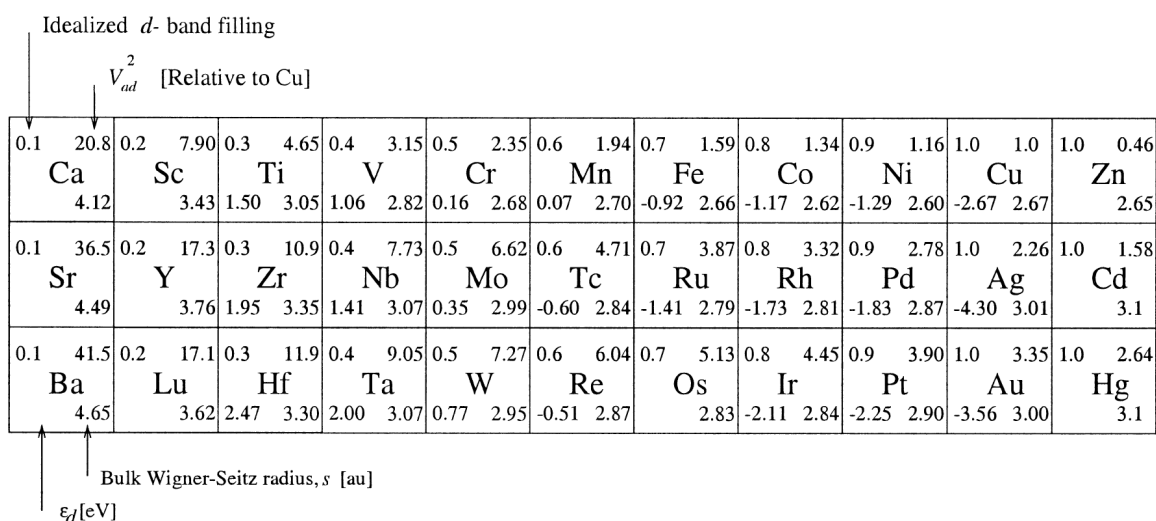
Idealized *d*- band filling

V_{ad}^2 [Relative to Cu]

0.1 20.8	0.2 7.90	0.3 4.65	0.4 3.15	0.5 2.35	0.6 1.94	0.7 1.59	0.8 1.34	0.9 1.16	1.0 1.0	1.0 0.46
Ca	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
4.12	3.43	1.50 3.05	1.06 2.82	0.16 2.68	0.07 2.70	-0.92 2.66	-1.17 2.62	-1.29 2.60	-2.67 2.67	2.65
0.1 36.5	0.2 17.3	0.3 10.9	0.4 7.73	0.5 6.62	0.6 4.71	0.7 3.87	0.8 3.32	0.9 2.78	1.0 2.26	1.0 1.58
Sr	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
4.49	3.76	1.95 3.35	1.41 3.07	0.35 2.99	-0.60 2.84	-1.41 2.79	-1.73 2.81	-1.83 2.87	-4.30 3.01	3.1
0.1 41.5	0.2 17.1	0.3 11.9	0.4 9.05	0.5 7.27	0.6 6.04	0.7 5.13	0.8 4.45	0.9 3.90	1.0 3.35	1.0 2.64
Ba	**Lu**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**
4.65	3.62	2.47 3.30	2.00 3.07	0.77 2.95	-0.51 2.87	2.83	-2.11 2.84	-2.25 2.90	-3.56 3.00	3.1

Bulk Wigner-Seitz radius, *s* [au]

ε_d[eV]

Figure 8.—A section of periodic table with 3d, 4d, and 5d transition metals. Value in lower left corner is the center of the d-band ε_d (eV), calculated for the most close-packed surface for each metal (Ref. 39, p. 268).

TABLE III.—VALUES OF d-BAND CENTERS
AND LIFETIMES FOR ELEMENTS TESTED

Element	Ti	V	Cr	Fe
d-band center, [a] eV	1.50	1.06	0.16	−0.92
Average lifetime, m/μg	8	16	63	379

[a]Values are from Figure 8.

Attention to the electronic structure of materials offers a way forward to understand triboreactivity. The work may progress both theoretically and experimentally. As noted, the values for the center of the d-band of elements have been calculated by density functional theory. There have been experimental attempts to use the d-band approach to reactivity with surface-sensitive photoelectron spectroscopy analysis techniques such as x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) to determine d-band centers (Ref. 40). However a vigorous debate has developed (Refs. 41 and 42), and the correspondence between theory and experiment using XPS and UPS is not settled. Current experimental work on surface reactivity applied to catalysis uses x-ray emission spectroscopy and synchrotron radiation (Refs. 43 and 44), so future experimental work will probably not include Auger electron spectroscopy (AES) or XPS, techniques within the capabilities of typical tribology research laboratories. As useful as studies have been for work in catalysis, the approach has not been applied to tribology. Future theoretical and experimental research in catalysis may also be useful in understanding the present results in triboreactivity and also in predicting the tribological behavior of materials not yet subject to tribological evaluation. However, the theoretical framework is daunting and experiments requiring synchrotron radiation remove evaluation of alloys for tribological service from the usual tribology facility. The field of triboreactivity remains quite challenging.

Conclusions

Tests of a liquid lubricant in the spiral orbit tribometer (SOT) on different metal bearing materials have found that the lifetime of a limited amount of liquid lubricant strongly depends on the chemical constitution of the bearing materials. The lifetimes of different bearing materials form groups that are separate from each other. The different lifetimes that are characteristic of the separate groupings have been interpreted as being due to different tribochemical reaction rates of the lubricant molecules with the bearing material, which consumes the limited amount of lubricant in the test. This interpretation can be made with some confidence for the elements tested because their lifetimes are in accord with the reactivity expected from simple chemical considerations as well as modern modeling of surface chemical reactivity. However, the interpretation of the lifetime of the alloys in terms of chemical reactivity cannot be made with as much confidence due to the possibility that their ordering could be affected by their different hardnesses. There is also the effect of the native oxide that must be displaced in order to allow the lubricant molecules to react with the nascent metal. The native oxides on the different alloys may have different thicknesses and other properties leading to different displacement rates and thus different lifetimes. Also, the alloys do not have the theoretical support as do the elements. These issues remain to be resolved before the lifetime groupings of the alloys can confidently be interpreted in terms of tribochemical reaction rates. Considering these aspects of uncertainty regarding the mechanism responsible for lifetimes, it would be advantageous to have a method independent of tribological lifetime to assess the tribochemical reaction rates that are a major topic of this note.

Aside from tribochemical interpretation, the lifetime trends could very well have value in themselves as indicators of relative performance in tribological practice. The extremely limited lifetime found here with titanium as a bearing material in the tribometer is already consistent with field experience of the impossibility of the lubrication of titanium with organic lubricants. Another consistency is for Nitinol 60: the lifetime of Nitinol 60 in these tests is similar to those of common bearing steels such as 440C and 52100, and so Nitinol 60 should be capable of lubrication by organic lubricants in a practical device. This is found to be the case. However, a limit to the SOT relevance to engineering practice may be found in the case of chromium. The reduction of lifetime for chromium relative to bearing steels suggests that

lubricated chromium should not perform well in applications. However, "thin dense chrome" is used commercially as a coating to reduce friction, wear, and corrosion. Perhaps an oversupply of lubricant in engineering practice masks the effect of the reduction of lifetime observed here. Although the relevance of SOT testing to engineering practice is not firmly established, the present lifetime rankings may still be found to be useful in practice. The SOT may be a means to compare lubricants and additives as well as surface coatings and alloys, with the caveat that many may well be "good enough" for practical purposes. Such caveats, of course, apply to any bench type of tribometer.

Tribochemical reactivity is a fundamental tribological phenomenon and should be understood in terms of surface chemical reactivity. Pennzane® 2001A may function as a "neutral" test fluid to assess the chemical (really tribochemical) reactivity of bearing materials. Two approaches to understand surface reactivity have been discussed: the HSAB (hard and soft acids and bases) originated by Pearson and the d-band center theory of Hammer and Nørskov, both developed for applications in catalysis. The d-band center approach has had some success in explaining the trend found here for elements, but has not been developed sufficiently either theoretically or experimentally to account for the present results for alloys. It may yet prove to be a fruitful approach to understand these results. It is, however, unfortunate that a full basic understanding of the present observations in terms of surface chemical reactivity has not been achieved for application to tribology. This is particularly so in the case of alloys such as Nitinol 60, which was not expected to permit lubrication because of its high concentration of titanium, but, in fact, has been found to be capable of normal lubrication. In the absence of either a theoretical or experimental spectroscopic approach to metal reactivity, metal alloys that are candidates for tribological service still have to be evaluated by bench-top tribometers such as the SOT employed here.

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