NASA TECHNICAL NOTE

NASA TN D-4694

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NASA TN D-4694

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1968

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SUMMARY

An investigation was conducted to determine the effect of various adsorbed gaseous species on the adhesion and friction of tungsten. Experiments were conducted in a vacuum of 10^{-10} torr (1.33×10^{-8} N/m^2) with a hemispherical rider specimen ((100) tungsten) contacting a flat. The atomic planes of tungsten examined on the flat included the (100), (110), and the (210). The gases adsorbed to these tungsten surfaces included hydrogen, oxygen, carbon dioxide, hydrogen sulfide, and a homologous series of hydrocarbons (methane through decane), as well as ethylene and acetylene.

The results of the study indicate that the presence of any gas, even hydrogen, on the tungsten surface will reduce adhesion and friction. Less than a monolayer of oxygen adsorbed on tungsten is sufficient to reduce appreciably the friction of tungsten crystals. For hydrocarbons, an increase in chain length (methane through decane) resulted in a progressive decrease in friction. Furthermore, with ethane, ethylene, and acetylene, friction decreased with increasing bond saturation.

INTRODUCTION

Recent studies with surfaces in vacuum indicate the influence of the normally present surface films on adhesion, friction, and wear. Most clean metals exhibit high adhesion and friction coefficients and weld readily. However, small amounts of contaminants are sufficient to reduce adhesion and friction characteristics markedly.

The presence of surface contaminants is known to prevent seizure of metallic components in contact. However, little is known about the specific, quantitative effects of surface films on adhesion and friction. For example, copper self-welds very readily in a vacuum, and its friction coefficient prior to complete seizure is in excess of 40; in laboratory air, copper has little tendency to self-weld, and its friction coefficient is reduced to a value of 1.2. Laboratory air normally contains a number of gases and vapors, such as hydrocarbons and water. The effects of specific gases or vapors on clean metal surfaces have not been studied in detail. Some experiments have been conducted qualitatively with gases such as oxygen adsorbed on clean metals (refs. 1 to 3). The interest in the effects of specific adsorbates on such properties as friction dates back to the work of Hardy (ref. 4). These studies, however, were not conducted with clean surfaces, and adsorption took place on oxides which are normally present.

Initial studies of the influence of specific adsorbed species on adhesion or friction are simplified if they are conducted with single crystal surfaces. Adsorption and chemical reactivity on metals are orientation dependent. In addition to a variation in crystal faces exposed in polycrystalline metals, the grain boundaries act as sites for high chemical activity. Thus, a comparison of the influence of various adsorbed species on friction and/or adhesion can best be made if the surface on which reaction is taking place is kept constant with respect to atomic arrangement and density.

The objectives of this investigation were to determine, with the use of clean tungsten single crystal surfaces in vacuum, (1) the effect of the adsorption of various gaseous species on adhesion and friction, (2) the influence of atomic planes on the ability of adsorbed species to reduce adhesion and friction, and (3) the desorbed species, by means of a mass spectrometer. Experiments were conducted with a hemispherical rider sliding on a flat. The tungsten planes examined were the (100), (210), and (110). Friction determinations were made on clean surfaces and with various adsorbed species present. The gases adsorbed were hydrogen, oxygen, carbon dioxide, hydrogen sulfide, methane, ethane, propane, butane, hexane, octane, decane, ethlylene, and acetylene. Tungsten was selected as the metal surface because (1) there is more literature dealing with the adsorption mechanisms of various gases on tungsten than on any other metal, (2) tungsten, because of its high modulus of elasticity and brittleness, is the only cubic metal which does not readily cold weld when clean in vacuum, and (3) the hardness of tungsten minimizes plastic deformation which could result in the penetration of adsorbed monolayers.

ADSORPTION

The study of the adsorption of various gases on clean metal surfaces requires a consideration of the adsorption mechanisms. For gases admitted to a clean surface, the Langmuir adsorption isotherm (or variations thereof) deals with the relative rates of molecules striking a surface, condensation, and evaporation from the surface.

Once a molecule is in contact with a surface, both physical adsorption and chemisorption must be considered. Physical adsorption deals simply with forces of physical attraction. The forces involved are similar to those causing the deviations of real gases from the ideal gas laws and the condensation of a vapor on the surface of its own liquid. Physical, or van der Waals, adsorption results in the formation of mobile surface films. This type of adsorption is described in detail in references 5 to 8.

When a metal surface has free valences and a nearby phase reacts with this surface to form chemical bonds, the process is called chemisorption. The principal difference between physical and chemical adsorption is that electron transfers take place in chemical but not in physical adsorption. The following are some other characteristic differences between the two types of adsorption: (1) Chemisorption involves markedly higher heats of adsorption; (2) chemisorption occurs over a broader temperature range; (3) chemical adsorption, because it is a chemical reaction, involves high activation energies while physical adsorption does not; (4) chemisorption exhibits a certain specificity; (5) chemisorption ceases when the gases can no longer make direct surface contact and is, therefore, a single-layer process, while physical adsorption can involve many layers; and (6) physical adsorption is reversible, whereas chemical adsorption is irreversible. The most distinguishing characteristic difference between physical and chemical adsorption is the magnitude of the heat of adsorption. Table I lists the differences for some of the gases used in this study when adsorbed on a tungsten surface.

All of the gases used in this investigation will chemisorb to clean tungsten (refs. 6 to 9). Since physically adsorbed films cannot be maintained at the pressure and temper-

TABLE I. - HEATS OF ADSORPTION FOR VARIOUS GASES ON POLYCRYSTALLINE TUNGSTEN

Gas	Maximum heat of physical adsorption		Heat of chemisorption	
	kcal/mole (a)	kJ/mole	kcal/mole	kJ/mole
H_2	2.0	8.4	[b]45.0	188.3
O_2	5.0	20.9	[b]194.0	811.7
CO_2	9.0	37.7	[a]109.0	456.1
N_2	1.34	5.61	[b]95.0	397.5
CH_4	5.0	20.9	(a)	-----
C_2H_4	8.0	33.5	[a]102.0	426.8
C_2H_2	9.0	37.7	(a)	-----
H_2O	14.0	58.6	(a)	-----

[a] Data from ref. 6.
[b] Data from refs. 6 and 8.

atures used in this study (ref. 8), monolayers of chemisorbed gases will be of chief concern.

The adsorption behavior of tungsten varies with the crystallographic plane exposed. In general, the highest atomic density planes have the strongest interaction energy. Consequently, the higher the atomic density of a crystallographic plane, the more pronounced is the adsorption.

It should be noted that chemisorption and chemical compound formation are not the same. With chemisorption, the heats of adsorption are generally higher than those associated with compound or phase formation (refs. 6 and 8). Furthermore, compounds have their own distinctive properties such as structure and melting point, whereas metals with chemisorbed films maintain many of their distinctive properties.

MATERIALS

The tungsten disk and rider specimens used in this study were electron-beam float zone refined. They contained less than 10 ppm of interstitials (O_2, N_2, H_2, and C). The gases were all high-purity reagent grade. The fluids hexane, octane, and decane were 99.99, 99.85, and 99.49 mole percent, respectively. The commercial high-purity hydrogen gas used in this study was further purified by passing it through a liquid-nitrogen-cooled, molecular sieve.

All specimens were cleaned on abrasive paper after they had been electric discharge machined to shape. They were then electropolished in a 10-percent sodium hydroxide solution. Orientations were determined by using the Laue back-reflection technique. Orientations indicated herein are within $\pm 2^{\circ}$ of determined orientations.

APPARATUS

The apparatus used in this investigation is shown schematically in figure 1. The specimens were a 2.54-centimeter-diameter flat disk and a 0.475-centimeter hemispherically radiused rider specimen (shown in insert of fig. 1). The disk specimen was mounted on a shaft which was magnetically driven by an instrument motor and gear assembly. The linear sliding velocity employed in these experiments was 0.001 centimeter per second.

The rider specimen was mounted in an arm which was gimbal mounted and bellows sealed to the vacuum-chamber wall. The rider specimen was loaded against the disk surface with dead-weight loading. Perpendicular to the loading device was a strain gage for monitoring friction force.

Cleaning of specimen surfaces in the vacuum chamber was achieved with an electron

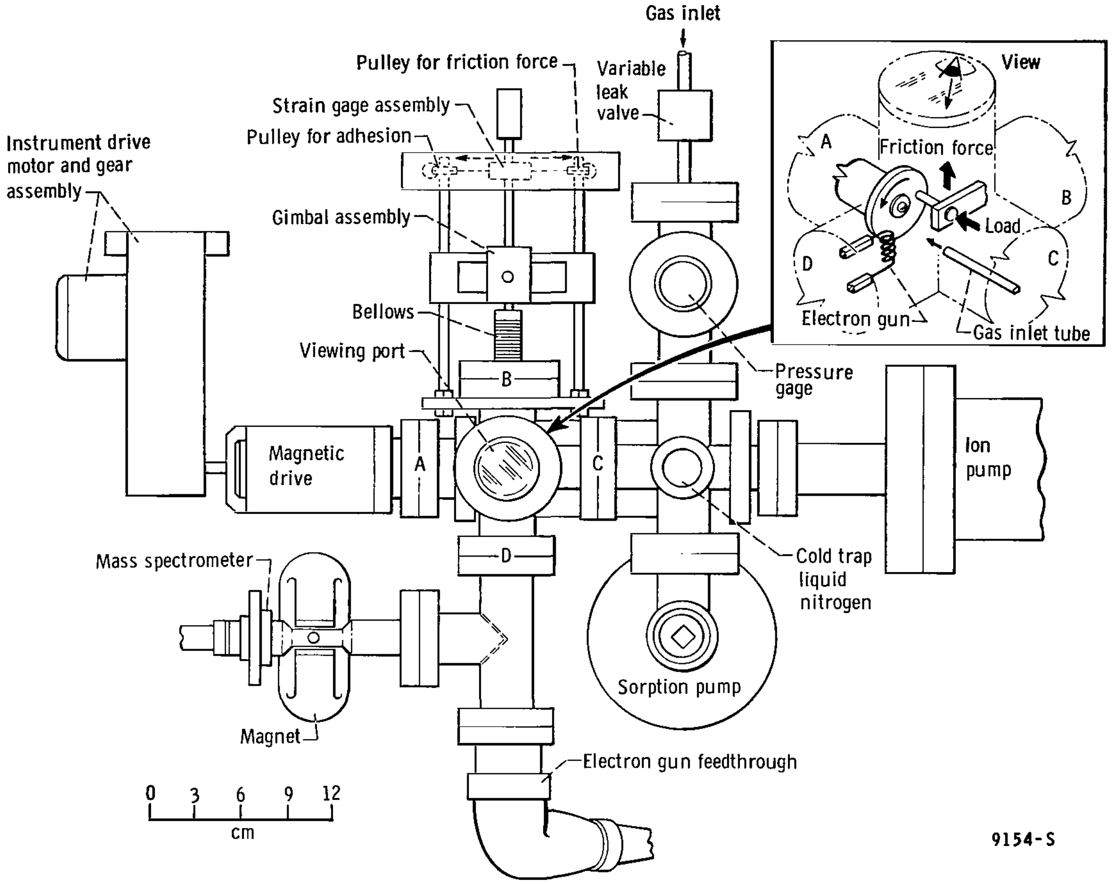


Figure 1. - Vacuum friction apparatus.

gun, and the gaseous species in the vacuum chamber were monitored with a mass spectrometer.

The vacuum system was rough pumped to 1 micron of mercury (1.33×10^{-1} N/m^2) with a sorption pump, and pressures to 10^{-10} torr (1.33×10^{-8} N/m^2) were achieved with an ion pump. A grid was provided in the pump throat to eliminate ionization in the specimen region. A liquid-nitrogen trap was used for cryopumping. Pressure was measured by a cold-cathode ionization gage, as well as by the pump current gage.

Gases were introduced into the vacuum chamber through a variable-leak valve. A separate vacuum sorption pump was used to evacuate the gas line connecting the cylinder of gas to the variable-leak valve. Both the gas line and the vacuum system were baked out with heating tapes and infrared lamps.

EXPERIMENTAL PROCEDURE

Specimen Cleaning

There are a number of techniques used to obtain clean surfaces in a vacuum. Two of the more commonly used are the ion-bombardment and the electron-beam techniques, and these are discussed briefly in this section. Based on friction results obtained, the electron-beam cleaning of surfaces was selected for use in this investigation.

A common technique used to clean specimen surfaces, particularly in low energy electron diffraction (LEED) studies, is that of argon ion bombardment followed by an anneal to remove the argon. This technique was used in the present study. While the surfaces appeared clean, the friction coefficient for the (100) plane of tungsten in sliding contact with a like plane was not nearly as high as might be expected for clean surfaces (only 0.50) during argon ion bombardment, and it rose to a value of only 0.90 after a 3-hour anneal to remove trapped argon. Since argon ion bombardment is so widely used for surface cleaning, and since apparently clean surfaces have been obtained with this technique (as determined by LEED for tungsten), it may be assumed that with an adequate anneal to remove argon a clean surface could possibly be obtained. Questions still arise, however, as to the character of the surface after such a severe treatment.

The tungsten crystal surfaces used in this study were cleaned by electron bombardment in the vacuum chamber when the pressure reached 10^{-10} torr (1.33×10^{-8} N/m^2). The crystals were heated with the electron gun to a bulk temperature of 800° C (surface temperatures were considerably higher), and hydrogen gas was admitted to the chamber to reduce surface oxides. Once the surface oxides were reduced (as determined by the mass spectrometer), the power level of the electron gun was elevated, and the crystal surface was electron bombarded for 3 hours to remove the adsorbed hydrogen. A friction coefficient of 3.0 was obtained at room temperature for the (100) plane of tungsten in sliding contact with a like plane.

Gas Admission

The specimens were cooled to room temperature after the electron bombardment, and the gas was admitted to the specimen zone through a variable-leak valve and a tube. The gases were charged from their cylinders into a line outside the vacuum chamber. Prior to the admission of gas, the line was thoroughly evacuated with a sorption pump and was baked out. The evacuated supply line was then purged three times by alternately filling and evacuating it.

Mass spectrometer traces were obtained during gas admission to the specimen surface, during the friction experiment, and following the experiment. Background data for the mass spectrometer were obtained with a saturated specimen surface at room temperature, that is, when the specimen surface was completely covered with a monolayer.

RESULTS

Clean Surfaces

The coefficient of friction was measured in vacuum for clean (100) and (110) atomic planes of tungsten in sliding contact with like planes. The results obtained are presented in table II. These results indicate that the friction coefficient for the (110) planes in sliding contact is less than that for the (100) planes. This difference in friction coefficients is predictable from the other properties of these planes presented in table II. The elastic modulus, a property important in the determination of true contact area, is the same for both planes because of the isotropic nature of the elastic properties of tungsten. The atomic density, however, is greater for the (110) plane. Furthermore, the distance between atomic planes is greater. The greater values of atomic density and the greater spacing between atomic planes imparts greater ease of shear for the (110) planes (in fact, the (110) plane is one of the preferred slip planes in tungsten). The surface energy for the (110) planes is lower than for the (100) planes (ref. 10); hence, it might be anticipated that the lower energy, more stable plane would exhibit lower friction.

TABLE II. - SOME PROPERTIES OF ATOMIC PLANES IN TUNGSTEN

Atomic plane	Elastic modulus, dynes/cm^2 (or 10^{-5} N/cm^2)	Atomic density, atoms/cm^2	Spacing between planes	Surface energy, ergs/cm^2 (or 10^{-7} J/cm^2)	Coefficient of friction (a)
(110)	38.9×10^{11}	14.1×10^{14}	2.23	3320	2.7
(100)	38.9×10^{11}	10.0×10^{14}	1.58	4680	3.0

[a] Atomic plane sliding on like plane; load, 50 g; sliding velocity, 0.001 cm/sec; temperature, 20° C; ambient pressure, 10^{-10} torr (1.33×10^{-8} N/m^2).

The sliding friction for the atomic planes of tungsten on like planes was characterized by a very pronounced type of stick-slip motion, as is indicated in the friction trace of figure 2. The figure shows that the friction level increased with sliding. This increase in friction may be attributable to a change in crystallographic direction on the

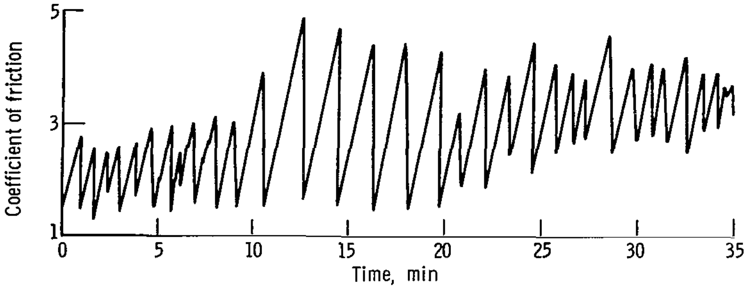


Figure 2. - Friction trace for clean (100) plane of tungsten sliding on a like plane in vacuum. Sliding velocity, 0.001 centimeter per second; load, 50 grams; temperature, 20° C; ambient pressure, 10^{-10} torr (1.33×10^{-8} N/m^2).

surface with sliding. The region of greatest amplitude in friction lies in the ⟨110⟩ direction on the tungsten disk.

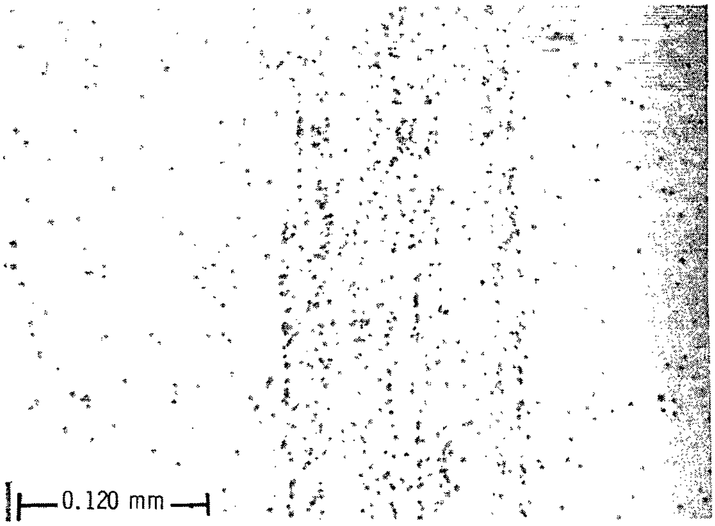
Plastic deformation to the (100) and (110) surfaces of tungsten is evident from the photomicrographs of figure 3. In figure 3(a), the wear scar was polished away and the tungsten surface was etch pitted with Millner-Saas reagent. The greater concentration of etch pits in the wear track (fig. 3(a)) attests to plastic deformation. Disk specimens were also sectioned, and figure 3(b) is the wear track of figure 3(a) shown normal to the planar sliding surface. Etch pitting again shows a very high concentration of pits and, therefore, dislocations in the sliding region. Figure 3 indicates that appreciable plastic deformation can occur to tungsten even at loads of only 50 grams.

Further evidence of the plastic deformation of tungsten crystals is presented in the photomicrographs of the unetched (110) tungsten surface in figure 4. Figure 4(a) shows the wear track on the (110) tungsten surface. On one side of the wear track the slip lines are wavy, while on the other side they are relatively straight. Figure 4(b) shows additional wavy slip lines. Wavy slip lines are common with the deformation of body-centered cubic metals.

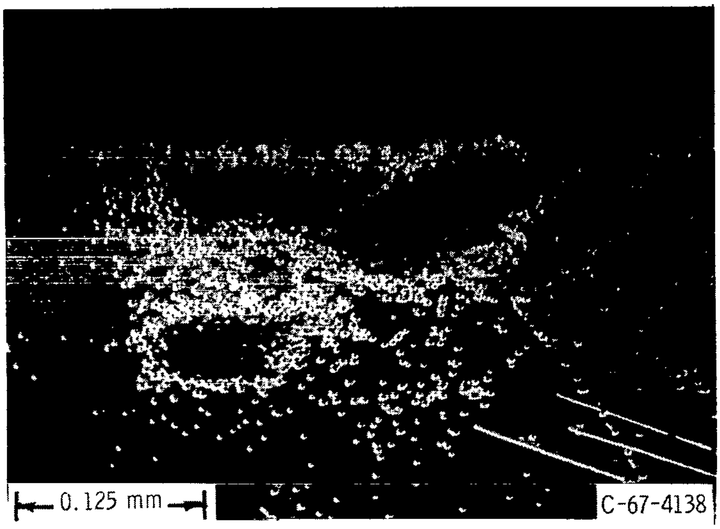
Adhesion and transfer of tungsten from one surface to another was observed. A particle of transferred tungsten is shown in figure 4(c). The transferred particle was large enough so that it was not entirely in the focus of the microscope. The microscope was focused at the disk surface in the left photograph and at the top of the transferred particle in the right photograph.

Results of adhesion experiments conducted with the (110) planes of tungsten in contact are presented in figure 5. Adhesion coefficients were measured at 20° and 800° C. For a 10-second contact time, the force required to separate the planes at 800° C was nearly twice that at 20° C.

The adhesive forces were measured at 800° C because of the marked change in the mechanical properties of tungsten with temperature increases above room temperature. The ductility of tungsten single crystals, for example, increases nearly sevenfold when

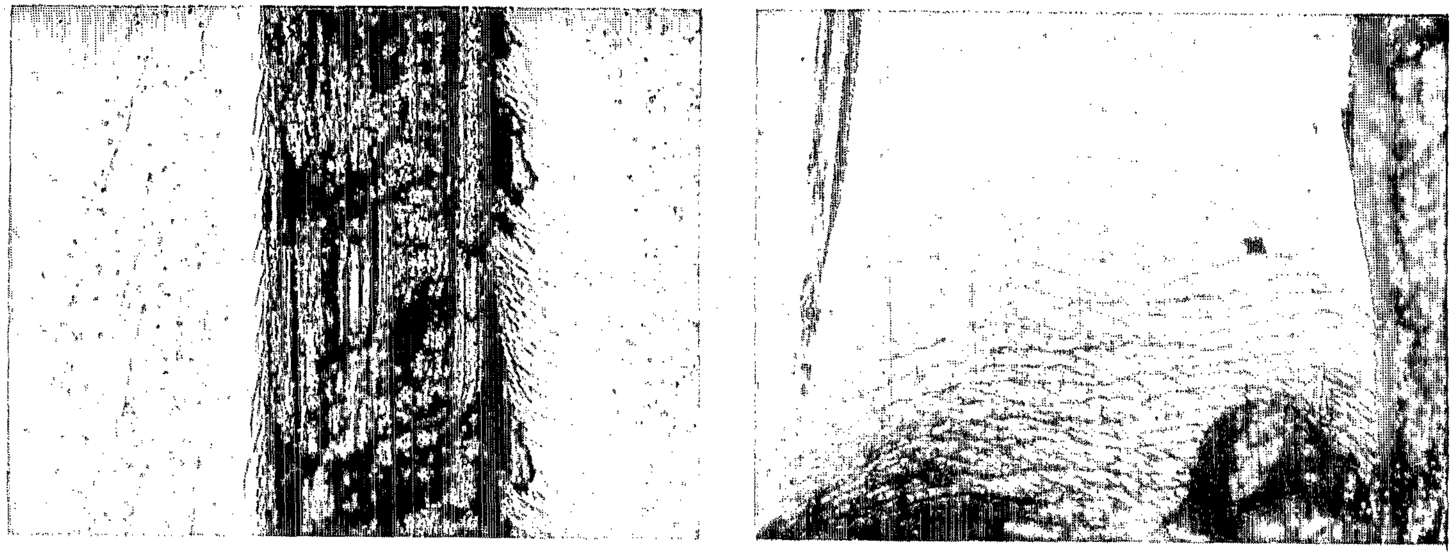


(a) Wear track etch pitted on sliding surface.



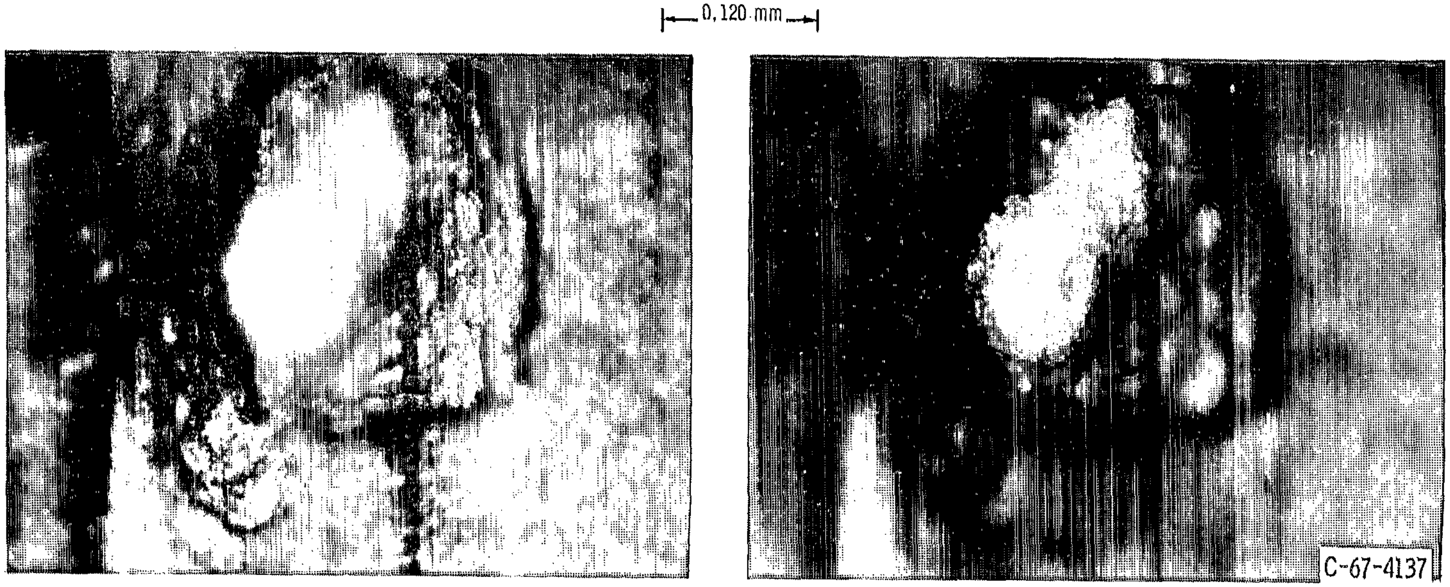
(b) Wear track etch pitted normal to sliding surface. Subsurface deformation (dark field illumination) is evident.

Figure 3. - Etch-pitted tungsten wear surface on (100) plane.



(a) Wear track on surface.

(b) Slip bands on surface adjacent to wear area.



(c) Transferred metal on surface.

Figure 4. - Wear scar and metal adhesion on surface of (110) plane of tungsten.

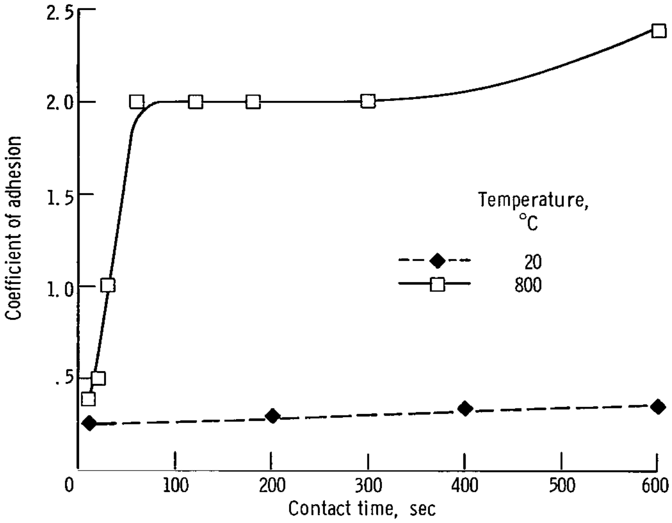


Figure 5. - Coefficient of adhesion for (110) plane of tungsten in contact with a like plane. Load, 50 grams; ambient pressure, 10^{-10} torr (1.33 N/m^2).

the temperature is increased from 20° to 800° C (ref. 11). At room temperature, the slip systems operating are the {110} ⟨111⟩ and the {112} ⟨111⟩; at temperatures above 700° C, only the {112} ⟨111⟩ system is observed. A greater degree of work hardening is therefore observed in tungsten single crystals at room temperature (ref. 12). Work hardening influences adhesion and friction (ref. 13).

Adhesion coefficients measured for various contact times under load at 20° and at 800° C are shown in figure 5. The curve obtained at 800° C differs markedly from that obtained at room temperature and from that for the face-centered cubic copper in reference 14, where a direct relation between adhesion and contact time for various atomic planes was observed. Figure 5 indicates that strong adhesive forces can be developed even for a metal that has a very high melting point and modulus of elasticity, provided the surfaces of the metal are clean. The adhesion data of figure 5 are for the (110) planes of tungsten. All other planes in contact with like planes could be expected to exhibit higher interplanar bonding forces.

The concept of elastic recovery is believed to play an important role in adhesion. In order to gain some insight into its influence on the adhesion of tungsten, an adhesion experiment was conducted. The specimens were heated to 800° C and brought into contact under a 50-gram load, and adhesion was measured. The specimens were then allowed to cool to room temperature in contact under load. When the load was removed at room temperature, the welded junctions broke. This indicates that elastic recovery has an effect on the fracture of welded junctions of tungsten. Remaking the contact at room temperature resulted in a return to the original, room-temperature adhesion.

Chemisorbed Hydrogen

It is reasonable to expect that the presence of any adsorbed gaseous film on a clean surface is going to have some effect on adhesion and friction. The influence of various gases, including hydrogen, on the adhesion of copper has been examined (ref. 15). In order to determine the influence of adsorbed hydrogen on the adhesion and friction properties of tungsten in vacuum, the gas was admitted to a clean tungsten surface. Hydrogen was adsorbed on three planes of tungsten ((110), (210), and (100)). Friction experiments were then conducted with a (100) tungsten rider in contact with the various surface planes of the disk. The friction coefficients for the clean surfaces and for the surfaces covered with the adsorbed hydrogen, as well as other properties of each of the three tungsten planes, are presented in table III.

The mechanism of hydrogen adsorption to tungsten is considered in detail in references 16 to 19. The monolayer adsorption involves one hydrogen atom for each tungsten atom (ref. 17).

Table III shows that the (110) plane has the greatest number of tungsten surface atoms and that it requires the largest time to form a monolayer of hydrogen. Also, the (110) and (210) planes have markedly lower sticking probabilities than has the (100) plane (ref. 18). The data of reference 18 indicate that it would take the longest exposure (2.43×10^{-6} torr-sec) to form a hydrogen monolayer on the (110) plane. The surface exposure employed in these experiments was 3.2×10^{-3} torr-second in order to ensure complete monolayer surface coverage for the least chemically active of the tungsten planes.

TABLE III. - INFLUENCE OF HYDROGEN AND OTHER PROPERTIES ON FRICTION OF THREE ATOMIC PLANES OF TUNGSTEN

Atomic plane of disk	Atomic density, atoms/cm^2 (a)	Surface energy, ergs/cm^2 (or 10^{-7} J/cm^2) (b)	Hydrogen sticking probability for first layer (c)	Time to form monolayer at 0.9×10^{-8} torr (1.2×10^{-6} N/m^2), sec (c)	Coefficient of friction (d)	
					Clean (e)	Hydrogen monolayer
(110)	14.1×10^{14}	3320	0.29	270	1.33	1.25
(210)	4.5×10^{14}	----	.23	111	1.90	1.33
(100)	10.0×10^{14}	4680	.66	84	3.00	1.66

[a] Calculated values.

[b] Data from ref. 10.

[c] Data from ref. 18.

[d] Rider, (100) plane of tungsten; load, 50 g; pressure, 10^{-10} torr (1.33×10^{-8} N/m^2); temperature, 20° C; sliding velocity, 0.001 cm/sec.

[e] After H_2 reduction and electron beam cleaning.

The lowest friction coefficient was obtained with the (110) plane. The greatest percent reduction in friction from a clean surface occurred with the chemically most active (100) plane. The results clearly indicate that the presence of hydrogen on the various planes of tungsten caused a reduction in friction. Adhesion measurements indicated that the planes would not stick to one another in the presence of hydrogen.

Adsorption of Oxygen, Carbon Dioxide, and Hydrogen Sulfide

Hydrogen might not be expected to afford the same surface protection from adhesion as some other gaseous species such as oxygen. In order to determine the effectiveness of other gases chemisorbed to tungsten planes in reducing adhesion and friction, oxygen, carbon dioxide, and hydrogen sulfide were adsorbed to the (110), (210), and (100) planes of tungsten and friction coefficients were obtained; the results are presented in table IV. The data for clean surfaces and for hydrogen (from table III) are included in table IV for comparative purposes.

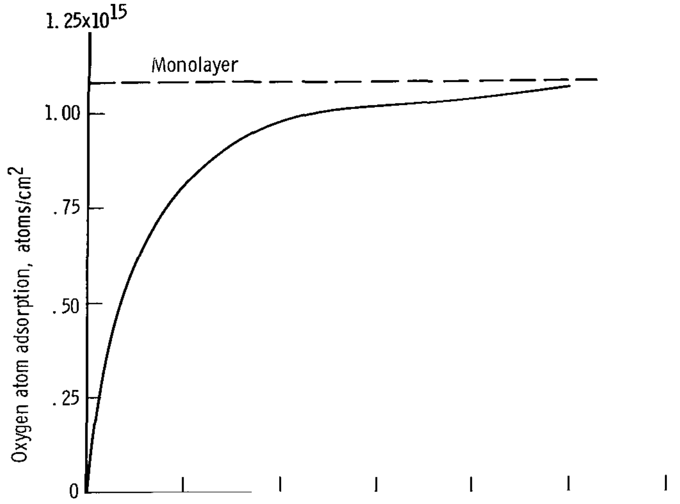
With the four chemisorbed gases listed in table IV, the lowest friction coefficients were obtained for the (110) plane. However, the greatest percent reduction in friction relative to the friction of clean surfaces occurred with the (100) plane. Oxygen provided the greatest reduction in friction for all three atomic planes. The order of these gases with respect to their ability to reduce friction on the tungsten planes (relative to the friction of clean-surfaced planes) was (1) oxygen, (2) hydrogen sulfide, (3) carbon dioxide, and (4) hydrogen.

TABLE IV. - INFLUENCE OF VARIOUS CHEMISORBED GASES ON FRICTION COEFFICIENT OF TUNGSTEN IN VACUUM

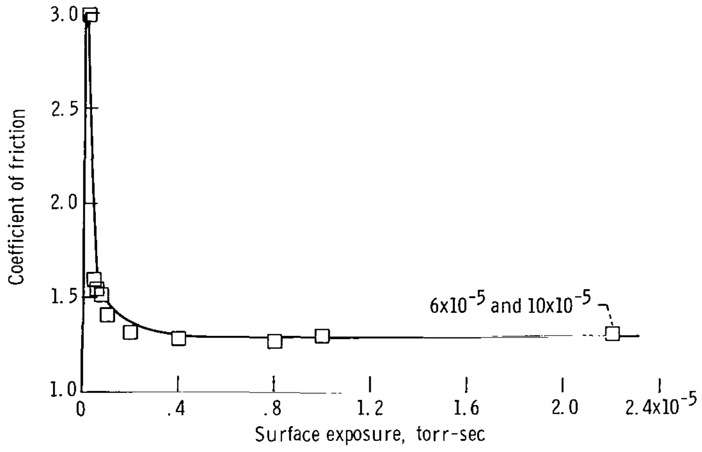
[Rider specimen, (100) atomic plane of tungsten; load, 50 g; sliding velocity, 0.001 cm/sec; temperature, 20° C; pressure, 10^{-10} torr (1.33×10^{-8} N/m^2).]

Chemisorbed gas	Coefficient of friction		
	For (110) plane	For (210) plane	For (100) plane
None	1.33	1.90	3.00
H_2	1.25	1.33	1.66
O_2	.95	1.00	1.30
CO_2	1.15	1.15	1.40
H_2S	1.00	----	1.35

The adsorption of oxygen (O) on tungsten (W) has been studied in considerable detail (refs. 20 to 36). In references 20 and 23, the adsorption of oxygen is presented as a function of oxygen exposure. The data of reference 20 have been replotted and are presented in figure 6(a). This figure indicates that with an exposure of approximately 2.0×10^{-5} torr-second, oxygen adsorption on the (100) plane of tungsten is nearing completion. Reference 23 indicates with LEED that monolayer coverage on a (110) face is complete at 3.0×10^{-4} torr-second. It has been suggested that the adsorption mechanism is $2W+O_2 \rightarrow 2WO$ (refs. 7, 23, 24, and 35). Oxygen coverage of 1.10 monolayers has



(a) Oxygen adsorption. (From ref. 20.)



(b) Friction as function of oxygen surface coverage.

Figure 6. - Oxygen adsorption and friction coefficient for (100) plane of tungsten sliding on a like plane. Sliding velocity, 0.001 centimeter per second. Load, 50 grams; temperature, 20° C; ambient pressure, 10^{-10} torr (1.33×10^{-8} N/m^2).

been reported (ref. 6). Furthermore, the data of figure 6(a) are for polycrystalline tungsten. If oxygen absorption is one atom of oxygen to one atom of tungsten (refs. 23 and 24), the denser planes of tungsten should accommodate more oxygen.

The mechanism of adsorption involves a physical adsorption of the oxygen molecule for a short time after which it may either evaporate or become chemisorbed. With chemisorption, the oxygen-to-oxygen bond is broken and replaced by the stronger oxygen-to-tungsten bond. The strength of the bond depends on the plane (ref. 24). The relation between binding energy and surface is discussed in references 8 and 36.

Friction experiments were conducted for the (100) plane of tungsten in contact with a like plane for various oxygen exposures, and the results obtained are presented in figure 6(b). With only approximately 7×10^{-8} torr-second oxygen exposure, the friction decreased to nearly half the value obtained for a clean surface. The results presented in figure 6(b) indicate that appreciably less than a complete monolayer can reduce friction markedly.

The admission of hydrogen to the heated, oxygen-covered tungsten planes resulted in liberation of oxygen, hydroxyl group, and water (M/e of 16, 17, and 18 in the mass spectrometer). This indicated that oxygen was being removed by hydrogen reduction. When oxygen removal was complete (as indicated by the absence of any detectable oxygen-containing species in the mass spectrometer), the surface was electron bombarded. After electron bombardment, the same friction value was obtained as had been achieved earlier for clean surfaces.

Mass spectrometer monitoring of the sliding friction experiment with adsorbed carbon dioxide resulted in a detection of carbon monoxide being liberated from the surface during sliding. Electron bombardment after the experiment resulted in a liberation of carbon monoxide and oxygen (M/e of 44, 28, and 16). Carbon monoxide desorption is discussed in detail in reference 37.

Hydrocarbon Adsorption

In the field of lubrication the adsorption of hydrocarbons is of extreme interest particularly with reference to its influence on friction and wear. Experiments were therefore conducted in a vacuum of 10^{-10} torr (1.33×10^{-8} N/m^2) with various adsorbed hydrocarbons, in the homologous series methane through decane, on the (110), (210), and (100) planes of tungsten. Friction results obtained for these three planes are presented in figure 7. With all three planes of tungsten, friction decreased with increasing number of carbon atoms in the chain. A markedly greater reduction in friction occurred in going from methane to decane for the (110) and (210) planes than occurred for the (100) plane.

The hydrocarbons were monitored with the mass spectrometer while they were being

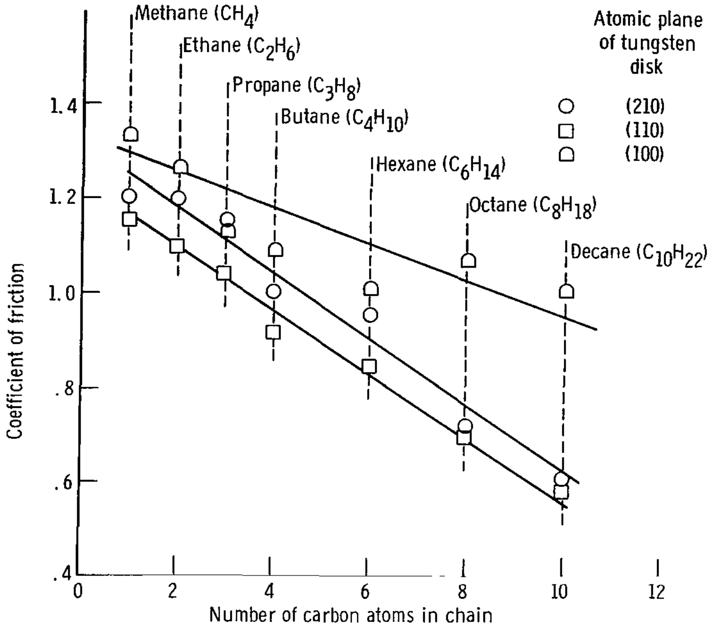


Figure 7. - Coefficient of friction for single-crystal tungsten rider (100) sliding on single-crystal disk orientations (110) and (210) with chemisorbed monolayers of hydrocarbons. Gases, homologous series methane through decane; load, 50 grams; sliding velocity 0.001 centimeter per second; temperature, 20° C; ambient pressure, 10^{-10} torr (1.33×10^{-8} N/m^2).

admitted to the surface during sliding and while they were being heated after sliding. During sliding, some low-molecular-weight species were observed to be liberated from the surface with the higher-molecular-weight hydrocarbons hexane, octane, and decane. Heating the surface after the experiment liberated a range of molecular weight fragments up to and including the specific gas adsorbed on the surface. These results indicated that the species admitted to the system had, in fact, been adsorbed as long chain hydrocarbons.

Experiments were conducted with the (110), (210), and (100) planes of tungsten and the adsorption of ethane, ethylene, and acetylene to determine the influence of the degree of saturation of the carbon-to-carbon bond on the friction of tungsten. Adsorption of these gases involves scission of carbon-to-hydrogen bonds rather than of carbon-to-carbon bonds (ref. 6). The mass spectrometer indicated that hydrogen was liberated during adsorption. The friction results obtained in these experiments are presented in table V. For all three planes, the friction decreased with an increase in the number of carbon-to-carbon bonds; that is, the greater the degree of bond saturation, the lower the friction.

Desorption of these three gases (ethane, ethylene, and acetylene) in sliding friction resulted in the liberation primarily of ethane for all three gases. For the ethane gas, about 13 percent methane was also liberated during sliding friction. These results indi-

TABLE V. - INFLUENCE OF BOND SATURATION OF CHEMISORBED GASES ON FRICTION COEFFICIENT OF TUNGSTEN IN VACUUM

[Rider specimen, (100) plane of tungsten; load, 50 g; sliding velocity, 0.001 cm/sec; temperature, 20° C; ambient pressure, 10^{-10} torr (1.33×10^{-8} N/m^2).]

Chemisorbed gas	Coefficient of friction		
	For (110) plane	For (210) plane	For (100) plane
Ethane ($H_3C\text{-}CH_3$)	1.10	1.10	1.25
Ethylene ($H_2C{=}CH_2$)	.88	.85	1.20
Acetylene ($HC{\equiv}CH$)	.70	.66	1.00

cate self-hydrogenation of the gases. Self-hydrogenation of ethylene and acetylene has been observed by other investigators (ref. 6).

Ambient Pressure Effects

At a pressure of 10^{-10} torr (1.33×10^{-8} N/m^2) with adsorbed monolayers, the friction coefficients observed for various adsorbed species were relatively high. It is of interest to know what effect multiple, physically adsorbed layers beyond the first chemisorbed monolayer have on friction properties. Experiments were therefore conducted with three gases, oxygen, hydrogen sulfide, and air, on the (100) plane of tungsten at a pressure of 760 torr (1.0×10^{5} N/m^2). These results, together with those obtained with these same three gases at 10^{-10} torr (1.33×10^{-8} N/m^2), are presented in table VI. It is evident from the data that the presence of multiple adsorbed layers beyond a simple chemisorbed monolayer produces a marked reduction in friction of tungsten. At 760 torr (1.0×10^{5} N/m^2), metal oxides and sulfides can form as a result of heat generated at the contacting surfaces. The influence of oxides and sulfides, as opposed to the influence of simple chemisorbed monolayers, is reflected not only in the friction values of the (100) plane of tungsten but also in the characteristics of the friction (see friction traces of table VI). The traces show that the sulfides at 760 torr (1.0×10^{5} N/m^2) exhibit considerably less stick-slip motion and lower friction than does the chemisorbed hydrogen sulfide at 10^{-10} torr (1.33×10^{-8} N/m^2).

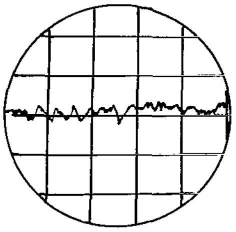
The friction results obtained for the (100) and (110) planes of tungsten in sliding contact with like planes were predictable from the results obtained with other metal crystals in sliding contact. With face-centered cubic metals and close-packed, hexagonal metals, lower friction has been observed on preferred slip planes than on other planes of the

TABLE VI. - COEFFICIENT OF FRICTION WITH VARIOUS GASES CHEMISORBED ON (100) PLANES OF TUNGSTEN IN SLIDING CONTACT

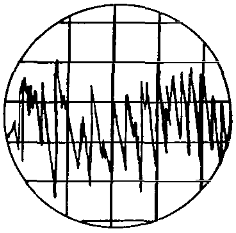
[Load, 50 g; sliding velocity, 0.001 cm/sec; temperature, 20° C.]

Gas	Coefficient of friction at pressure, torr (N/m^2), of -	
	760 (1.0×10^5)	10^{-10} (1.33×10^{-8})
O_2	0.66	1.30
H_2S	[a].50	[b]1.35
Air	.33	1.80

[a]Friction trace:



[b]Friction trace:



crystal because the shear stress (friction force) is least when the plane is oriented for easy shear. In addition to having the greatest atomic density and spacing between planes (consequently, ease of shear), the preferred crystallographic slip planes usually afford the greatest resistance to deformation (ref. 38). Thus, for these planes under a fixed normal load the true contact area should be less than for more readily deformable planes. Since area of true contact and shear forces are the friction force determinants, the preferred slip planes in metals should exhibit the lowest friction coefficients. Furthermore, the friction coefficient should be least in the preferred slip direction on the slip plane.

For clean metal surfaces, matched atomic planes in contact should exhibit greater adhesive and friction forces than those of mismatched atomic planes. The more closely the atoms in the planes are matched, the less lattice strain is required for bonding.

However, even with matched planes, some mismatch in orientation will always occur when surfaces are brought into contact under mechanical load. Thus, the interface is analogous to a grain boundary or, at best, a twin boundary. The greater the mismatch of the planes, the lower should be the bonding force. The data of table III indicate that mismatched planes exhibit lower friction.

The work of some other investigators (particularly ref. 1) indicates that the adsorption of hydrogen on clean metal surfaces has very little, if any, effect on the adhesion and friction of clean metals. However, it is unlikely that any chemisorbed layer of gas on a metal surface does not have some effect on adhesion and friction. In this investigation, adhesion of clean tungsten planes occurred when they were brought into contact under load. The presence of a hydrogen surface film prevented this adhesion from occurring on touch contact.

The data obtained with oxygen and carbon dioxide (table IV) indicate that different friction values are obtained on various planes of tungsten with the adsorption of these gases. In these studies, only a single pass was made over the surface; that is, the rider slid over a plane with the adsorbed species just once. With carbon dioxide on the surface, carbon monoxide was liberated during sliding and was detected by the mass spectrometer. This indicated that oxygen remained adsorbed to the tungsten surface. Thus, if repeated passes had been made over the same surface, the friction values for oxygen and carbon dioxide might have become essentially the same. The decomposition and desorption of adsorbed gases during sliding friction experiments prevent the speculation that the friction data (table IV, lowest with oxygen and highest with hydrogen) are or could be related to chemical bond strengths of the adsorbed gaseous species.

The data obtained for oxygen adsorbed on tungsten indicate that less than a complete monolayer of adsorbed gas is sufficient to produce a considerable reduction of friction. This conclusion is compatible with the adhesion theory of friction. On contact, a portion of the real contact area is represented by direct tungsten-to-tungsten adhesion, while the remaining area is represented by tungsten covered with oxygen. In this oxygen-covered area, adhesion is reduced considerably. With continued adsorption and surface coverage, the true contact area of clean metal continues to diminish. Therefore, adhesion and friction continue to decrease as the surface coverage increases until a complete monolayer has formed. Reference 21 indicates that, even at a pressure as high as 1 torr (1.33×10^{2} N/m^{2}), no more than a single monolayer of oxygen can be adsorbed on the (110) plane of tungsten and that there will be as many oxygen atoms on the surface as tungsten atoms.

The adsorption of hydrocarbons on tungsten generally results in the carbon-to-hydrogen bond being broken. The mechanism for methane, for example, is

$$CH_{4(gas)} + M \rightarrow M(CH_N)_{adsorbed} + \frac{1}{2}(4 - N)H_{2(gas)}$$

The value of N varies for different metals and also varies with temperature. For tungsten, N varies from 3.15 to 2.2, depending on the surface temperature (ref. 6).

It would be extremely useful to know just how the hydrocarbons in the long chain are bonded to the tungsten surface. Most literature interpretations have a terminal carbon atom anchored to the surface with the chain extending away from, and normal to, the surface. While this interpretation could explain the results obtained in figure 7, it does not explain the results presented in table V. If the bonding mechanisms of ethane, ethylene, and acetylene are as proposed by some other investigators, the two carbon atoms bond directly to the metal surface (ref. 6). Since the carbon atoms are more closely bonded in acetylene, it may be possible to accommodate a greater carbon concentration on the tungsten surface. Furthermore, the sequence of the bond energies is acetylene > ethylene > ethane. The mass spectrometer indicated the liberation of about 13 percent methane from ethane. The fact that methane was not liberated from ethylene or acetylene may reflect the differences in bond strengths.

The friction data in table VI indicate that, at 760 torr (1.0×10^{5} N/m^2), friction for the (100) planes of tungsten in contact is highest in oxygen and lowest in air; at 10^{-10} torr (1.33×10^{-8} N/m^2), friction is lowest in oxygen and highest in air. In air, adsorbed species other than oxygen are present on the surface (e.g., hydrocarbons, water vapor, etc.) which desorb in vacuum. This may account for the higher friction in vacuum of specimens simply pumped down in air from atmospheric pressure. In contrast, with oxygen, a complete layer (monolayer) is present to provide uniform surface coverage.

SUMMARY OF RESULTS

Friction and adhesion experiments with clean, single-crystal surfaces in the presence of adsorbed monolayers in a vacuum of 10^{-10} torr (1.33×10^{-8} N/m^2) yielded the following results:

1. The friction characteristics for clean and film-covered tungsten surfaces are anisotropic.
2. Marked adhesion occurred for planes of tungsten in contact. Matched planes across an interface ((110) on (110)) had higher adhesive forces than mismatched orientations.
3. The presence of any of the adsorbates used in this investigation, including hydrogen, reduced the friction of tungsten. Each of the four gases (oxygen, hydrogen sulfide, carbon dioxide, and hydrogen) reduced friction on the clean tungsten surfaces; oxygen

provided the greatest reduction in friction, and hydrogen provided the least.

4. The friction coefficient of tungsten decreases with increasing number of carbon atoms in the homologous series of hydrocarbons methane through decane for the (110), (210), and (100) tungsten planes.

5. The number of carbon-to-carbon bonds in a hydrocarbon influences the friction for all three tungsten planes examined. With the gases ethane, ethylene, and acetylene, the order of decreasing friction was CH_3-CH_3, CH_2=CH_2, CH=CH. Desorption of gases during sliding friction or by heating after the experiments resulted in self-hydrogenation with the liberation of ethane.

6. Less than a monolayer of oxygen provided a marked reduction in friction relative to that of a clean surface.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 27, 1967,
129-03-13-02-22.

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