

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

**NASA TECHNICAL
MEMORANDUM**

NASA TM-73896

NASA TM -73896

(NASA-TM-73896) TRIBOLOGICAL PROPERTIES OF
SURFACES (NASA) 25 p HC A02/MF A01 CSCI 20K

N78-20511

G3/37 Unclass
 C9482

TRIBOLOGICAL PROPERTIES OF SURFACES

by Donald H. Buckley
Lewis Research Center
Cleveland, Ohio 44135

TECHNICAL PAPER to be presented at the
International Conference on Metallurgical Coatings
sponsored by the American Vacuum Society
San Francisco, California, April 3-7, 1978



TRIBOLOGICAL PROPERTIES OF SURFACES

by Donald H. Buckley

Lewis Research Center

ABSTRACT

The real area of contact between two solid surfaces is only a small portion of the apparent area. Deformation of these areas can result in solid state contact through surface films. For clean solid to solid contact strong adhesive bonding occurs across the interface. Under these conditions many properties of the solid such as the metallurgical and chemical nature of metals can influence adhesion, friction, and wear behavior. The presence of gases, liquids, and solid films on the surface of solids alter markedly tribological characteristics. These surface films can also considerably change the mechanical effects of solid state contact on bulk material behavior.

TRIBOLOGICAL PROPERTIES OF SURFACES

by Donald H. Buckley

Lewis Research Center

INTRODUCTION

Tribology involves the adhesion, friction, wear, and lubrication of solids in contact. The adhesion, friction, wear, and lubrication of solids is extremely dependent upon the physical, chemical, mechanical, and metallurgical properties of the surface. For example, even fractions of a monolayer of an adsorbed gas can have a marked effect upon the tribological behavior of materials.¹⁻³

The introduction in recent years of a host of analytical surface tools for the structural, elemental, and chemical identification of surfaces and surface films has contributed considerably to the understanding of the surface properties and films important to tribology. The use of these surface tools in tribology is discussed in Refs. 4 and 5.

The objective of this paper is to review those properties of solid surfaces which influence tribology and more specifically, adhesion, friction, wear, and lubrication. Basic properties of solid surfaces in the absence of films including metallurgical and chemical will be included. The effects then of the presence of films on the solid surface will be addressed.

NATURE OF SOLID SURFACES

When a solid surface is examined either microscopically with the scanning electron microscope or mechanically with a surface profilometer it is found to contain irregularities; that is, the surface is not flat and smooth. A typical surface displaying these irregularities or asper-

ities as they are commonly called is presented schematically in Fig. 1(a).

Nearly all real surfaces contain the asperities indicated in Fig. 1(a) except brittle materials, when cleaved along natural cleavage planes of single crystals and metallic pin tips the surface of which have been field evaporated in the field ion microscope. Even with brittle materials the cleavage process results in the generation of surfaces which contain cleavage steps. It is only the terraces between steps that have an atomically smooth nature.

The actual shape and distribution of surface asperities has been the object of considerable research. An excellent review of the subject can be found in Ref. 6.

The surface of the asperities are not atomically clean but contain surface films as indicated in Fig. 2(b). For metals and alloys these films generally consist of oxides and adsorbed gases usually water vapor, carbon monoxide, and carbon dioxide. With many nonmetals the surface films may simply consist of adsorbates. All of the reacted and adsorbed film materials can exert a strong effect upon the mechanical and metallurgical behavior of the solids to which they are attached as indicated in the collection of paper appearing in Ref. 7.

In addition to the films present on the surface of a solid the surficial (near surface) layers of the solid itself may vary considerably in structure from the bulk of the solid. With crystalline solids these layers may consist of recrystallized material, strain hardened regions, and/or texturing. The aforementioned which may develop when any type of finishing or polishing of the surface is attempted and particularly when

that surface is a metal. It can also be a region rich in bulk impurities.⁸ In amorphous solids these layers may contain voids and microcracks.

When two solid surfaces are brought together as indicated in Fig. 1(c) contact occurs at the asperity tips. Either under the weight of the solids, or when a load is applied, depending upon the materials, first elastic and then plastic deformation will occur in the asperities. Deformation will continue until the real asperity contact area is sufficient to support the load and then at that point deformation will cease with the resultant real area of contact being a small percentage of the apparent area of contact.

At sufficiently light loads and again depending upon the materials the surface films indicated in Fig. 1(b) may not be disrupted by the deformation process. With most materials, however, disruption of these films will occur with the result that nascent solid surface contact will take place. The extent of that contact will depend upon the properties of the solid as well as that of the film.

CLEAN SURFACES

Adhesion and Friction

The removal of adsorbed films and oxide layers from surfaces such as those of metals results in very strong interfacial adhesion when two such solids are brought into contact. This fact has been known for metals in contact with metals for some time.⁹ It also occurs with metals contacting nonmetals. When, for example, a clean gold surface is brought into contact with a clean semiconductor surface such as silicon, the adhesive bonds formed at the solid to solid interface are sufficiently strong so

as to result in fracture of cohesive bonds in the gold and transfer of gold to the silicon surface. This is indicated in the photomicrograph and x-ray map presented in Fig. 2.

In general when two solid surfaces are brought into contact and adhesion occurs the interfacial bond is stronger than the cohesive bond in the cohesively weaker of the two materials.¹⁰ This results, upon separation of the two solids in the transfer of the cohesively weaker material to the cohesively stronger. Thus, in Fig. 2 gold transfers to the cohesively stronger silicon.

Silicon and germanium are both semiconductors having many very similar properties. One property in which they differ, however, is cohesive binding energy, germanium being much weaker than silicon and having a cohesive binding energy comparable to that of gold.¹¹ If the adhesion experiment of Fig. 2 is then repeated with germanium substituted for the silicon the results presented in Fig. 3 are obtained.

The photomicrographs of Fig. 3 indicate the contact region between the gold and germanium surface. Instead of gold transferring to the germanium, fracture occurred in the germanium with transfer of germanium to the gold taking place. The higher magnification photomicrograph of Fig. 3 indicates chevron shaped fracture cracks that have developed in the (111) crystal surface of the germanium. Thus, metal to nonmetallic contacts behavior in a manner similar to that observed for metal to metal contacts in Ref. 10.

Iron is cohesively much stronger than germanium and gold. When a similar adhesion experiment is conducted with iron in place of gold, germanium, as would be predicted, transfers to the iron. Further, if tan-

gential force is applied to the iron-germanium contact, the resistance to that tangential motion (friction force) reflects the fracture behavior.

Figure 4 presents the friction force recorded with time for the iron sliding (tangentially) along the germanium surface. The trace has a "saw-tooth" appearance reflecting what is commonly referred to as stick-slip behavior.¹² The stick portion is the adhesion of the solid surfaces at the interface which accounts for the gradually rising value in friction force of Fig. 4. At the point where the tangential force applied exceeds the adhesive bond strength or the cohesive strength of the cohesively weaker of the two materials, as in this case, fracture occurs in the germanium and sliding commences. The slip portion reflects this and is indicated in Fig. 4 by the periodic sharp drop in the friction force.

The adhesive bonding force measured for two solids in contact is, as already discussed, a function of the cohesive binding energy of the cohesively weaker of the two materials. It is also a function of the real area of contact. The greater the load, the greater the plastic and elastic deformation and the larger will be the real area of contact (see Fig. 1(c)). The adhesion data for nickel in contact with gold in Fig. 5 indicates that the adhesive force increases with increasing load.

When tangential motion or sliding is initiated between two clean surfaces in contact, the resultant applied forces in the materials can produce material changes other than those associated with adhesion and principally tensile fracture. For example, prolific cracking can occur in a relatively brittle material such as silicon. Such fracture cracking can be seen in the photomicrographs of Fig. 6 for a single crystal silicon (111) surface after an iron single crystal (110) slid across the surface.

Metallurgical Effects

With metals in solid state contact many of the basic metallurgical properties exert an influence on observed adhesion, friction, and wear behavior. Crystal structure, orientation, texturing, order-disorder, surface segregation, alloying, and ductile-brittle transitions all have an effect.¹³ The friction behavior of an iron single crystal in sliding contact with a tin single crystal at various temperatures reflects the effect of one of these properties, namely crystal structure. Below 13° C tin has a diamond type structure while above that temperature its structure is body-centered tetragonal.

The data of Fig. 7 indicate that the diamond crystallographic form of the tin exhibits higher friction than the tetragonal form. Other polymorphic metals also manifest a change in friction and also wear behavior with crystal transformation.

Small amounts of alloying element can produce very noticeable changes in both friction and wear characteristics. This subject is reviewed in Ref. 14 and shall be discussed later in reference to solid surface films.

Chemical Effects

In the 1940's Pauling recognized differences in the amount of d bond character associated with the transition metals.¹⁵ These differences can be related to the chemical affinity of surfaces for other materials. The greater the amount or percent d bond character of a metal the less active should be its surface. It might therefore be reasonably anticipated that the adhesive interaction between two metals would be related to the chemical activity of the metal surfaces. The data of Fig. 8 indicate the

relationship between the d bond character of some of the transition elements and friction coefficient, which of course reflects adhesive behavior.

Titanium, which is chemically very active, exhibits in contact with itself a very strong interfacial adhesive bonding to itself as indicated by the friction coefficient reported in Fig. 8. In contrast, rhodium and ruthenium which have a very high percent d bond character have relatively low friction coefficients.

Very frequently metals are not contacted by metals, or themselves but rather by nonmetallic substances already discussed. As indicated earlier for metals in contact with other metals as well as nonmetals fracture will occur in the cohesively weaker of the two materials and this effects adhesion, friction, and wear. What properties of metals will effect these latter tribological characteristics where the nonmetallic material is of such a cohesive strength that fracture always occurs in the metal?

The d valence bond character of the metal influences the friction coefficient for metals in contact with nonmetals just as it does for metals in contact with themselves. This is indicated in the data of Fig. 9 for various metals in contact with manganese-zinc ferrite.¹⁶ All of the metals indicated in Fig. 9 are observed to transfer to manganese-zinc ferrite. These data indicate the same kind of relationship observed for the metals in contact with themselves in Fig. 8, that is friction coefficient decreases with the increasing percent of d bond character of the metal. Thus, the chemical nature of the metal surface plays a role in observed tribological behavior.

It is apparent from the foregoing data that material properties of the solid surfaces in contact exert an influence on adhesion, friction, and wear. Even bulk structure or composition can with mechanical activity at the surface have notable effects in tribology. For example, alloying elements in metallic materials have many ways of influencing surface activity. They reduce surface energy¹⁷ and in some cases can even provide a solid film lubricant at the surface.

A typical and somewhat classic example of alloy constituent acting as solid film lubricants is the mechanism involved in the low friction and wear characteristics of gray cast iron, a traditionally good tribological material. Friction and wear data for gray cast iron as a function of carbon content are presented in Fig. 10. The data of Fig. 10 indicate that as the carbon content increases, both friction and wear decrease. The mechanism underlying this behavior is revealed in the photomicrograph of Fig. 11.

The sliding wear track generated on the cast iron surface is visible in the center of the photograph with virgin undisturbed cast iron and its characteristic graphite islands to either side. In the track proper the graphite islands, because of the mechanical rubbing of the steel ball, have become smeared out over the iron matrix. The smeared out graphite acts as a solid film lubricant to prevent adhesion of the iron matrix to the steel ball. The greater the graphite content, the more complete is the film and protection of the iron matrix.

SURFACE FILM EFFECTS

Gases

Most gases with the exception of the noble gases adsorb readily to clean metal surfaces and many adsorb to nonmetals as well.¹⁸ Adhesion and friction are so sensitive to the presence of these gases both qualitatively and quantitatively that even hydrogen¹ and fractions of a monolayer of other gases have an effect.³

Iron in sliding contact with silicon was examined earlier in this paper in the clean state. The effect of exposing that couple to oxygen on friction can be seen in the data of Fig. 12. In Fig. 12 the presence of oxygen on the surface reduced the coefficient of friction to half or less than observed for the clean surfaces in contact.

Liquids

Tribological surfaces are most frequently lubricated with liquids. The liquid may be a relatively simple structure such as a hydrocarbon or it may contain additives to achieve greater reduction in wear. Data are presented in Fig. 12 for the lubrication of iron sliding on silicon with mineral oil containing as an additive 0.2 percent oleic acid. The friction coefficient is extremely low and commensurate with effective boundary lubrication.

The mineral oil containing oleic acid not only reduced friction but also completely eliminated the formation of fracture cracks which were observed in Fig. 6 for this material couple in contact with their surfaces clean. The wear contact zone on the silicon surface deformed plastically with sliding, a manifestation of the Rebinder effect.¹⁹

While adhesion and friction are extremely sensitive to initial contaminant layers and fractions thereof on clean surfaces, they are less sensitive to more subtle differences in liquid structure once the initial contaminant films are already present. This is indicated in the data of Fig. 13.

In Fig. 13 friction coefficient is plotted as a function of load for gold in sliding contact with iron and lubricated with two fluids, hexane and benzene. Both hexane and benzene contain six carbon atoms but they are in a ring structure for benzene and straight chain for hexane. This structural difference in the liquid molecule is not reflected in measured friction coefficients.

Differences are observed with, however, the number of carbon atoms in a straight chain hydrocarbons.²⁰ The longer the chain length the lower is the observed friction coefficient. The addition of very active elements or functional groups in the molecular structure of a simple hydrocarbon can also effect tribological behavior.

The friction coefficients plotted in Fig. 14 for gold sliding on iron indicate the effect of adding the halogen atoms to the basic benzene molecular structure. With both fluorobenzene and chlorobenzene at loads of less than 10 grams friction coefficients are considerably higher than for bromobenzene and iodobenzene.

Auger emission spectroscopy analysis of the iron surface containing chlorobenzene is compared with a surface containing iodobenzene in Fig. 15. The surface containing chlorobenzene reveals the presence of chlorine, carbon, and iron peaks while that for iodobenzene contains only carbon. The absence of iodine on the surface indicates dissociative ad-

sorption of the iodobenzene.

Since Auger emission spectroscopy can detect elements to a depth of four to five atomic layers and iron peaks are completely absent in Fig. 15(b), the carbon has very effectively covered and protected the iron from interacting with the gold. While the chlorobenzene did not dissociate, it did not as effectively cover the iron because iron Auger peaks are present in Fig. 15(a).

Solids

There exists an ever increasing use of solids for the lubrication of tribological surfaces. Solids can be applied to the surfaces in solid state contact by a number of means. One mechanism for achieving such lubrication has already been discussed in reference to gray cast iron, namely by the incorporation of the lubricating phase directly into the material.

Another method for lubricating with solids is to apply the solid as a coating to the surface by some deposition or coating technique. Some techniques which have been employed include burnishing, electroplating, spraying with a binder in the lubricant film material, sputtering and ion-plating.

Still another method for applying solid films to surfaces is by the addition of compounds to a liquid lubricant which can decompose with the mechanical activity at contacting asperities to liberate solid films on the surface which have inherently good lubricating properties.²¹ Soft, low shear strength metals make good solid film lubricants. By adding organometallics containing these metals to oils, lubrication by such a

mechanism can be accomplished.

The Auger spectrum of Fig. 16 is for a wear surface of stainless steel which had been lubricated with dimethyl cadmium in mineral oil. A film of cadmium is detected on the surface. Lubrication by such a technique is concentration sensitive because sufficient organometallic must be present to provide for the deposition of a protective film. The data of Fig. 17 indicates the importance of concentration.

At concentrations of less than 0.5 percent in Fig. 17 the surface is not effectively being lubricated because the friction coefficient is too high. Above 0.5 percent organometallic effective lubrication has been achieved. Auger spectroscopy of the wear surfaces at less than 0.5 percent organometallic failed to reveal the presence of cadmium on the surface. Above that concentration it was detected.

CONCLUDING REMARKS

When two solid surfaces are brought into contact, strong bonding forces can develop across the interface, particularly where the surface films are penetrated by the deformation of the regions of real contact, which is only a small portion of the apparent contact area. Many metallurgical and chemical properties of metals and alloys can very markedly influence adhesion, friction, wear, and lubrication behavior. Gases, liquids, and solids which interact with either contacting solid surface can strongly influence tribological properties of surfaces. They not only reduce adhesion, friction, and wear but can alter the mechanical behavior of the solid surfaces themselves.

REFERENCES

- ¹D. H. Buckley, J. Appl. Phys. 39, 4224 (1968).
- ²D. H. Buckley, Int. J. Nondestr. Test. 2, 171-188 (1970).
- ³D. R. Wheeler, NASA TN D-7894 (1975).
- ⁴J. Ferrante, D. H. Buckley, S. R. Pepper, and W. A. Brainard, Microstructural Analysis Tools and Techniques., edited by J. L. McCall and W. Mueller (Plenum Press, New York, 93, 1973).
- ⁵D. H. Buckley, Proceedings International Conference on Wear of Materials, St. Louis, Mo. (ASME, New York, Apr. 1977).
- ⁶J. B. P. Williamson, Interdisciplinary Approach to Friction and Wear, NASA SP-181, 85 (1968).
- ⁷Environment-Sensitive Mechanical Behavior, edited by A. R. C. Westwood and N. S. Stoloff (Gordon and Breach Science Publishers, Inc., New York, 1966).
- ⁸E. K. Rideal, Surface Phase in Metals, Soc. Chem. Ind. (London) Monogr. No. 28, 3 (1968).
- ⁹F. P. Bowden and D. Tabor, The Friction and Lubrication of Solids, Pt. 1 (Oxford Univ. Press, London, 1950).
- ¹⁰D. H. Buckley, Wear, 20, 89 (1972).
- ¹¹K. A. Gschneidner, Jr., Solid State Phys., 16, 275 (1965).
- ¹²E. Rabinowicz, Friction and Wear of Materials (John Wiley & Sons, Inc., New York, 1965).
- ¹³D. H. Buckley, NASA SP-277 (1971).
- ¹⁴J. Ferrante and D. H. Buckley, ASLE Trans., 15, 18 (1972).
- ¹⁵L. Pauling, Proc. Roy. Soc., Ser. A, 196, 343 (1949).

- ¹⁶K. Miyoshi and D. H. Buckley, NASA TP-1059 (1977).
- ¹⁷E. D. Hondros and D. McLean, Surface Energies of Solid Metal Alloys, Soc. Chem. Ind. (London), Monogr. No. 28, 39 (1968).
- ¹⁸G. A. Somorjai, Principles of Surface Chemistry (Prentice-Hall, Inc., New Jersey, 1972).
- ¹⁹V. I. Likhtman, P. A. Rebinder and G. V. Karpenko, Effect of Surface-Active Media on the Deformation of Metals (Chemical Publishing Co., New York, 1960).
- ²⁰W. B. Hardy, Collected Scientific Papers (The University Press, Cambridge, Eng., 1936).
- ²¹C. N. Rowe and J. J. Dickert, Jr., ASLE Trans., 10, 85 (1967).

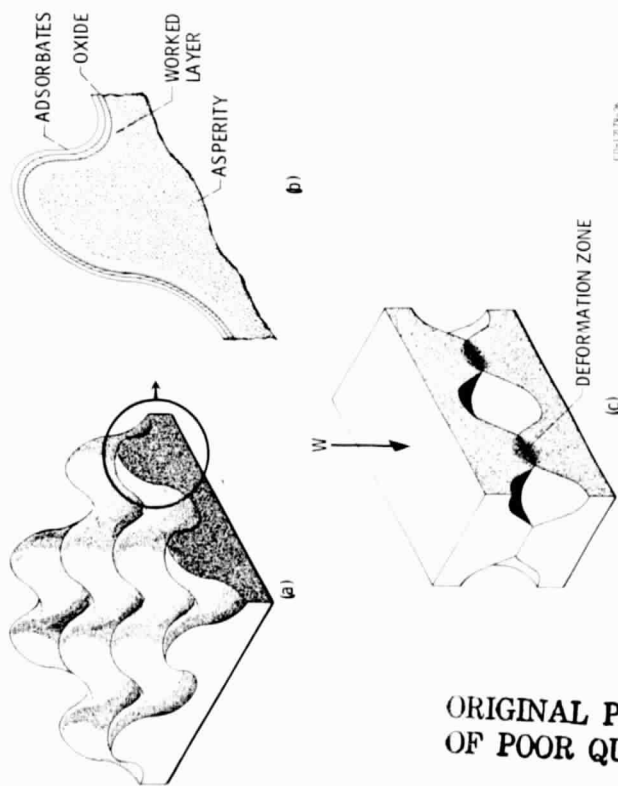


Figure 1. - Surface topography and contact.



(a) PHOTOMICROGRAPH.



(b) X-RAY MAP FOR GOLD.

Figure 2. - Photomicrograph and x-ray map for gold transferred to a silicon (111) surface after adhesive contact. Load, 30 gms; sputter cleaned surfaces; 23°C and 10^{-8} N/m^2 .

ORIGINAL PAGE IS
OF POOR QUALITY

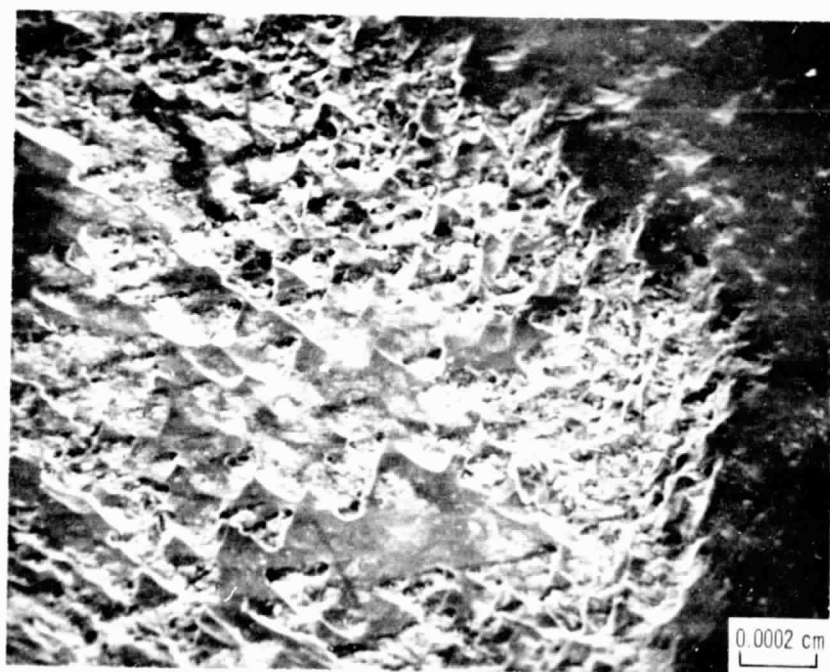
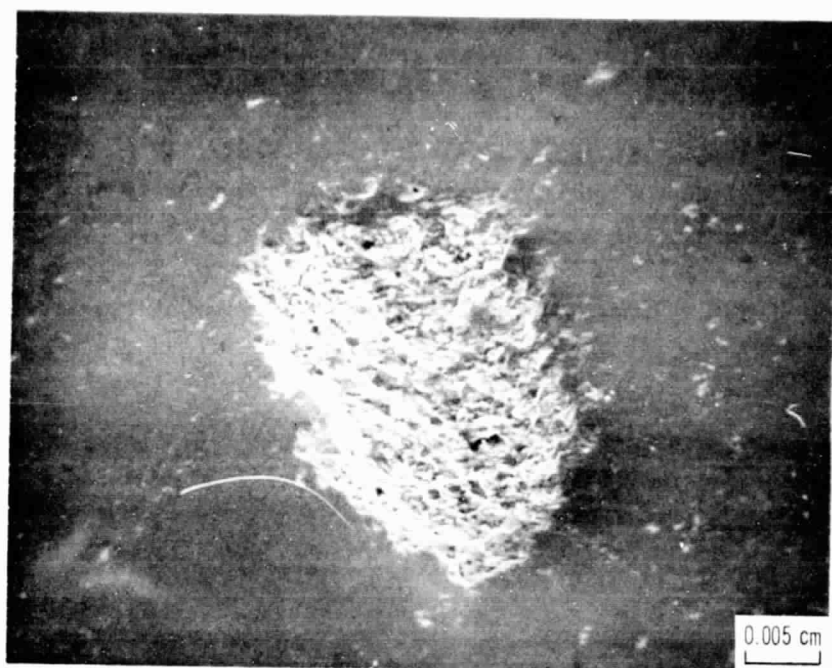


Figure 3. - Adhesion of gold (111) surface to germanium (111) surface. Load, 30 grams; temperature, 23°C; pressure, 10^{-8} N m². (Fracture occurs in germanium.)

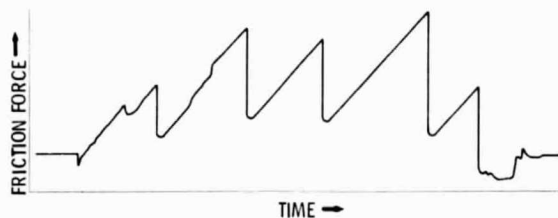


Figure 4. - Friction trace for single-crystal iron (110) sliding on a germanium (111) single-crystal surface. Sliding velocity, 0.7 mm/min; load, 30 grams; temperature, 23° C; pressure, 10^{-8} N/m².

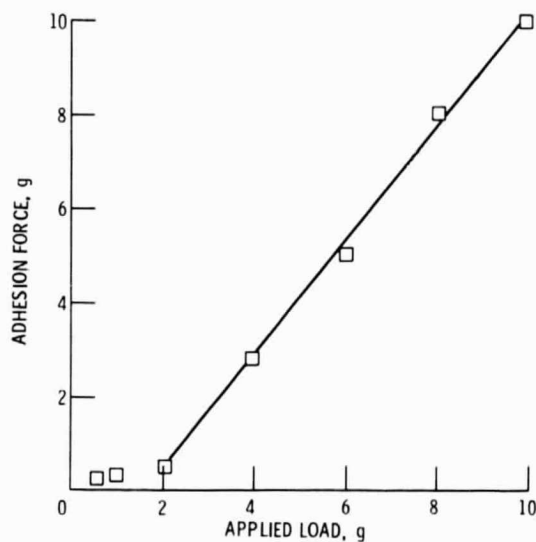


Figure 5. - Force of adhesion as function of applied load for gold (111) surface contacting clean nickel (011) surface. Ambient pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr); temperature, 23° C.

ORIGINAL PAGE IS
OF POOR QUALITY

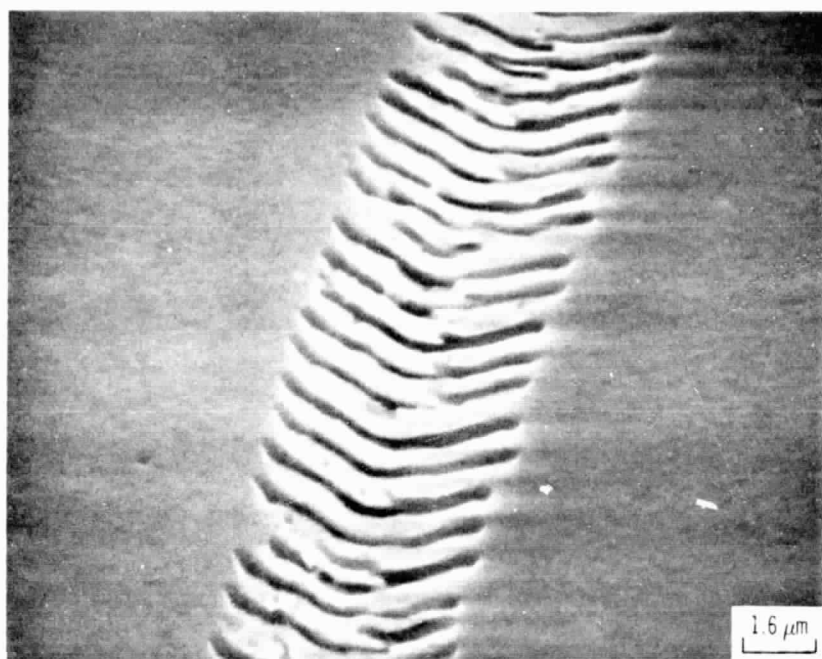


Figure 6. - Wear tracks made by single-crystal iron (110) sliding across silicon (111) surface. Sliding velocity, 0.7 mm min.; temperature, 23°C; pressure, 10^{-8} N m².

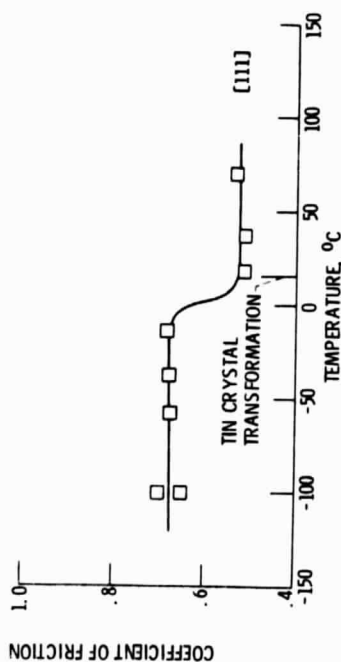


Figure 7. - Coefficient of friction for iron (110) sliding on a tin (110) single-crystal surface. Sliding velocity, 0.7 mm/min; load, 10 g; pressure, 10^{-8} N/m² (10^{-10} torr).

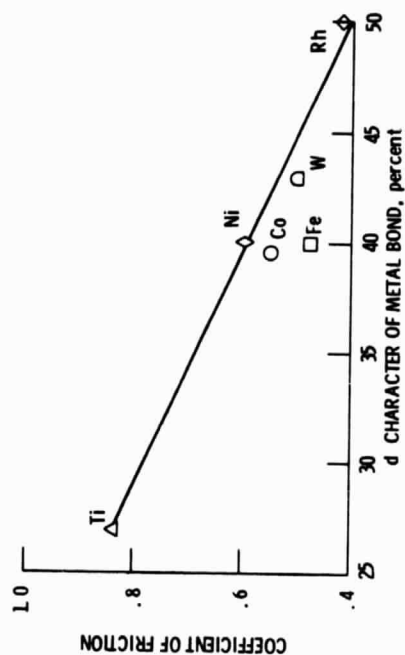


Figure 9. - Coefficient of friction as function of percent of d bond character of various metals in sliding contact with single-crystal manganese-zinc ferrite (110) surface in vacuum (10^{-8} N/m²). Single pass; sliding velocity, 3 mm/min; load, 30 grams; temperature, 25°C.

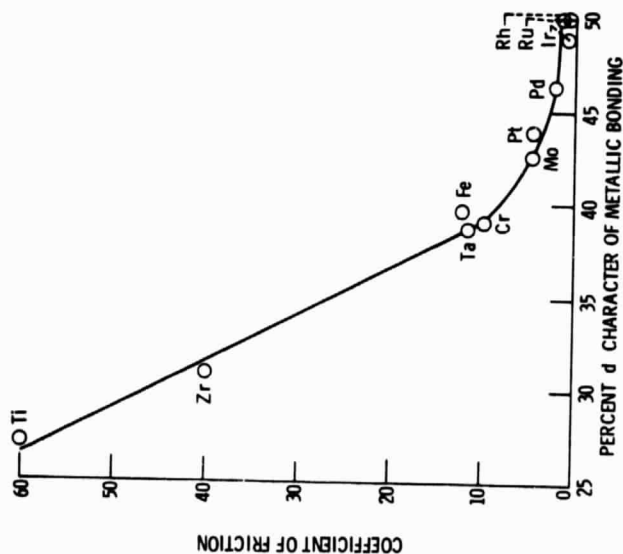


Figure 8. - Coefficient of friction as function of percent d bond character for various metals. Sliding velocity, 0.7 millimeter per minute; temperature, 25°C; pressure, 10^{-8} newton per square meter; load, 1 gram.

ORIGINAL PAGE IS
OF POOR QUALITY

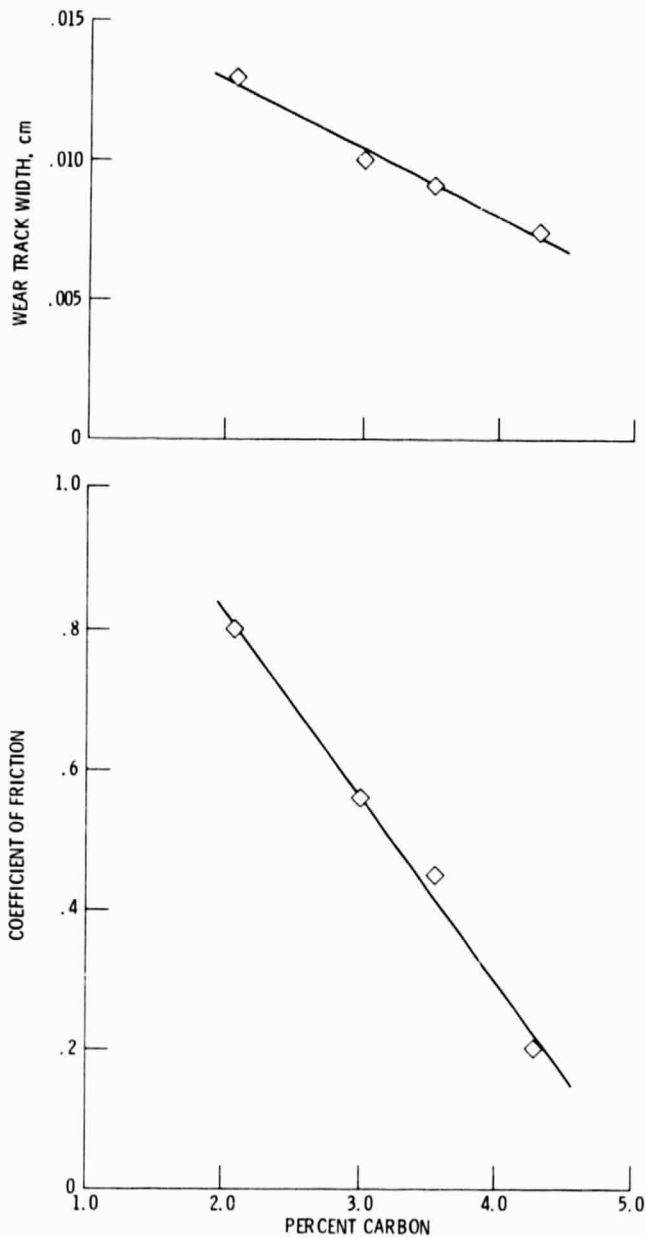


Figure 10. - Coefficient of friction and wear of gray cast iron as a function of carbon content. Mating surface steel ball, 2.5 millimeter diameter; sliding velocity, 5 centimeters per minute; load, 50 grams; argon atmosphere; temperature, 23° C; duration, 1 hour.



Figure 11. - Wear track on 3.02 percent carbon in gray cast iron after having been in sliding contact with a 52100 steel ball for 1 hour. Sliding velocity, 5 centimeters per minute; load, 50 grams; argon atmosphere; temperature, 23° C.

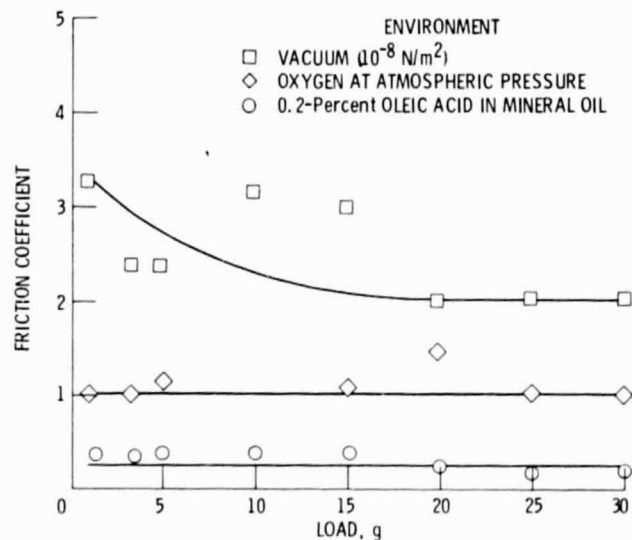


Figure 12. - Friction coefficient as function of load for single-crystal iron (110) sliding on a single-crystal silicon (111) surface in vacuum, in oxygen, and lubricated with 0.2-percent oleic acid in mineral oil. Sliding velocity, 0.7 mm/min; temperature, 23° C.

ORIGINAL PAGE IS
OF POOR QUALITY

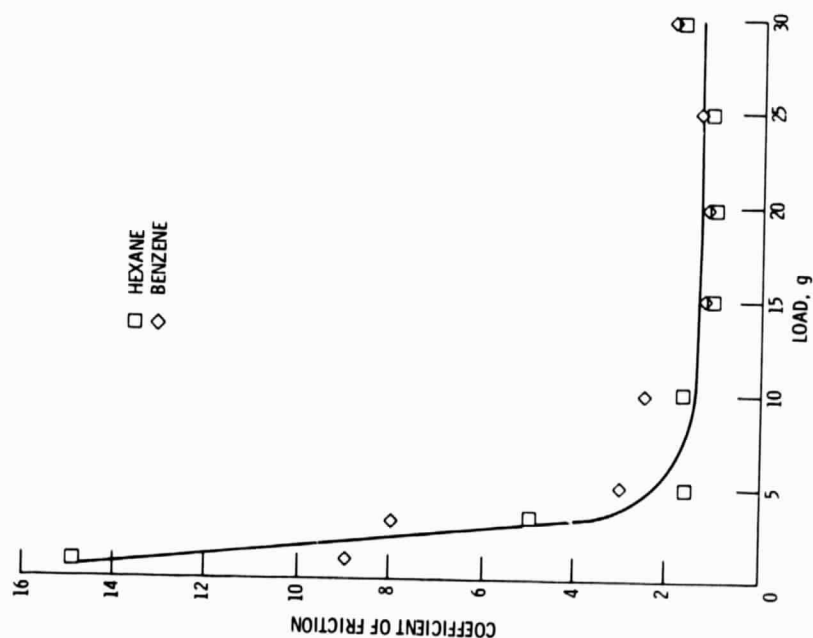


Figure 13. - Friction coefficient for gold (111) single crystal sliding on iron (011) single crystal with iron surface saturated with hexane and benzene.

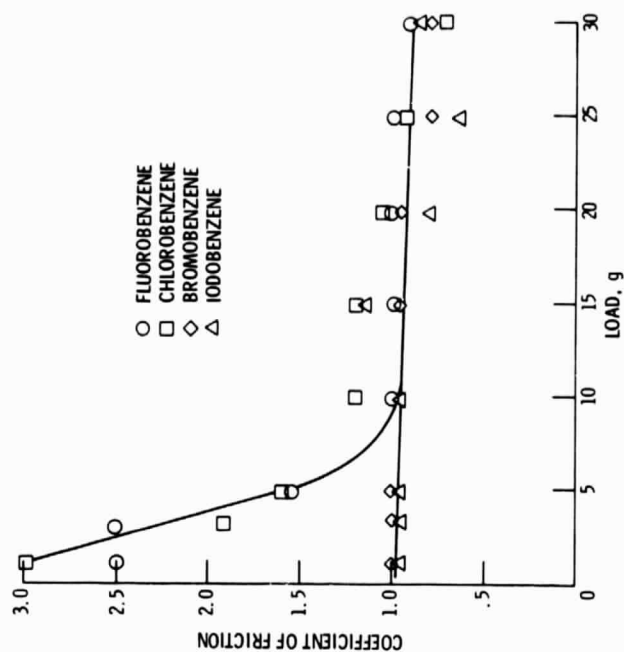


Figure 14. - Coefficient of friction for gold (111) single crystal sliding on iron (011) single crystal with iron surface saturated with halogenated benzene compounds.

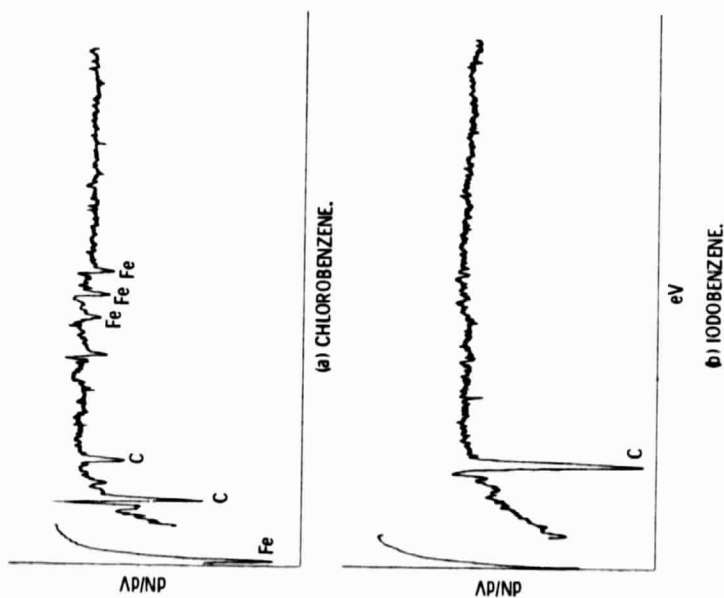


Figure 15. - Auger spectrum for iron (011) surface saturated with chlorobenzene and iodobenzene.

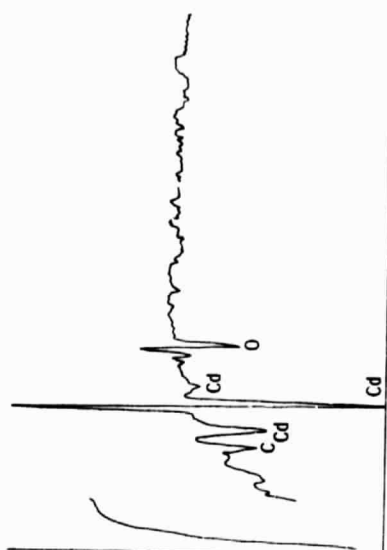


Figure 16. - Auger emission spectrum of 302 stainless steel lubricated with 1-percent dimethyl cadmium in mineral oil.

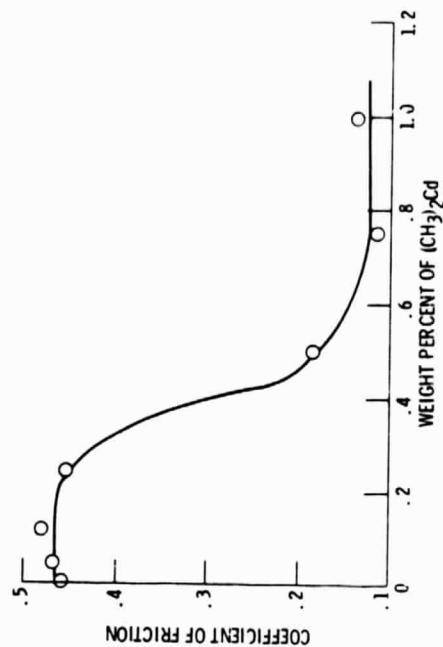


Figure 17. - Coefficient of friction for 302 stainless steel lubricated with various concentrations of dimethyl cadmium in mineral oil. Rider, 1045 steel; load, 1100 grams; sliding velocity, 150 meters per minute; temperature, 23° C.

ORIGINAL PAGE IS
OF POOR QUALITY