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WEAR AND INTERFACIAL TRANSPORT OF MATERIAL

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ABSTRACT

Bonding across the interface for two solids in contact and the subsequent transfer of material from one surface to another is a direct result of the interfacial bonds being stronger than the cohesive bonds in either of the two solids. Surface tools such as LEED, Auger emission spectroscopy, field ion microscopy and the atom probe are used to examine adhesive contacts and to determine the direction, nature, quantity of material transfer and properties of the solids which effect transfer and wear. The electronic nature, cohesive binding energies, surface structure, lattice disregistry and distribution of species in surface layers are all found to effect adhesion and transfer or transport for clean surfaces in solid state contact. The influence of adsorbed and reacted surface films from fractions of a monolayer to multilayer reactive films are considered. It is shown that even fractions of a monolayer of surface active species such as oxygen and sulfur can markedly inhibit adhesion and transport.
INTRODUCTION

Where two solid surfaces are brought into contact and relative motion occurs between those surfaces due to sliding, rolling or rubbing wear of one or both surfaces can result. If a load or force is applied to the solids normal to the interface between the solids wear will nearly always occur. The quantity of material transferred or transported across the interface from one solid to another will depend upon on how effectively the solid surfaces are shielded from atomically intimate solid state contact by surface oxides, adsorbed species and lubricating films.

Nature has provided metal and alloy surfaces with natural lubricating films. Atomically clean metals will, when brought into contact, exhibit friction coefficients frequently in excess of 100 with gross interfacial seizure. Yet, with the normal naturally developed oxides on these surfaces friction coefficients for many of the same metals will range from 0.5 to about 1.5 with adhesion and seizure occurring only where the surface oxides have been penetrated by surface asperities or irregularities. Even with some of the better lubricating oils' friction coefficients will reach values typically of about 0.1. Thus, oxides provide approximately one hundred fold reduction in friction while lubricating oils effectively reduce it from 5 to 15 times.

Where two solid surfaces are completely separated from contact by a liquid lubricant film, hydrodynamic lubrication, friction coefficients will range from 0.002 to 0.005 and these values represent the force necessary to shear the lubricant. When that same liquid
lubricant is present as a boundary layer the friction coefficient increases to 0.1, reflecting the effects of solid state contact. In the former case ideally wear to the solids should not occur while in the latter it does.

The objective of the present paper is to review adhesion or bonding across an interface between two solids in contact, transfer or transport to one or both surfaces, wear with tangential motion and the effect of surface films on adhesion, transfer and wear. There are many forms of wear but this paper shall address itself to only adhesive wear which deals with the interfacial transport of material from one surface to another.

NATURE OF SOLID SURFACES

Topography

Most real surfaces encountered, no matter how carefully and smoothly polished, are not atomically flat and smooth but contain surface irregularities called asperities. On a microscale looking at the cross section of a real surface is much like looking at a series of foot hills, the shapes of which are in the range of 5 to 10 degrees with some being as steep as 25 degrees.\(^1\)

Atomically flat surfaces can be achieved by cleaving such materials as mica\(^2\), inorganic crystals\(^3\), and to a limited extent a few metals.\(^4\) Generally, however, such surfaces contain cleavage steps. Another technique for metals employs the use of the field ion microscope\(^5\) and field evaporation for the removal of asperities.

Thus, with the exception of the aforementioned special cases most surfaces contain asperities. When two such surfaces are placed into
contact the interface is developed at those points where the asperities of the surfaces touch one another. As a result the real area or actual area of solid state interfacial contact is usually some small percentage of the apparent area of the solids in contact. 6 With the application of a load or force normal to the interface first elastic and at sufficiently high loads or forces plastic deformation of the asperities will occur. With increasing load or force the real area of contact or this interfacial area for bonding will increase.

Surface Films

Nearly all solid surfaces in a normal laboratory environment contain on their surfaces adsorbed films, at least physically adsorbed layers and very frequently chemisorbed species. In addition thereto metal and alloy surfaces contain surface oxides. Lubricated surfaces may contain films of oil, fatty acid, ester or sulfur, phosphorus or chlorine compounds from extreme pressure additives.

Where two solids are placed into contact and surface films are present solid to solid interfacial contact strong adhesion, material transport and wear should not occur. Generally, however, depending on the lubricant ranging degrees of solid state contact is made through these films with deformation under load or applied forces either normal or tangential.

In addition to surface films originating from the environment studies in recent years have shown that diffusion from the bulk to the surface of metals and alloys of constituents and impurities can result in surface films which effect adhesion, transfer across an
interface and wear. \textsuperscript{7-10} These diffusing species can be metallic elements such as aluminum, tin, indium, and silicon or non-metallic elements such as carbon, sulfur, and oxygen.

**ADHESION**

When two metallic surfaces are brought into close proximity and contact both long range interactions as a result of Van der Waals and electrostatic forces and short range interactions arising from chemical bonding of the two surfaces exist. These forces constitute the interfacial binding energy of the metals one to another. The amount of work necessary to overcome the interfacial bonds is then the force of adhesion or the energy of adhesion.

The jellium model has been used to consider charge densities of the metal surface in vacuum for close packed planes. This model has been recently applied to adhesion at a bimetallic interface. \textsuperscript{11} If two dissimilar metals are considered such as aluminum and zinc the electron density overlaps in the interface can be represented as indicated in figure 1.

In figure 1, \( n_1 \) and \( n_2 \) represent the vacuum-metal electron density numbers for zinc and aluminum, \( y \) is the direction normal to the interface, \( a_0 \) is the separation between the surfaces and \( n^{(1)}_+ \) and \( n^{(2)}_+ \) are the jellium positive change densities for zinc and aluminum.

In considering adhesion at a bimetallic interface all the energy sources for bonding must be taken into account. This is done for the aluminum-zinc couple in figure 2. The energy for the various bonding sources are presented as a function of separation in atomic units. The
equilibrium or minimum energy position is indicated by $a_0$.

Coupling the concept of the jellium approach to bonding with a consideration for lattice mismatch the authors of reference 11 calculated the binding energy for a number of bimetallic couples. The theoretically calculated values agreed well with experimental results.

Comparison of the calculated energies of adhesion or bimetallic binding energies with surface energies indicate that there is an overlap. Thus, the Al-Zn binding energy is lower than the Zn-Zn surface energy but larger than the Al-Al surface energy. One might therefore predict that lower surface energy metals will transfer to higher surface energy metals on solid state contact with subsequent separation of the surfaces.

When two atomically clean metals are placed into contact adhesion has been always observed to occur. Further, on separation of the surfaces the cohesively weaker metal has generally been observed to transfer to the cohesively stronger. In general, cohesive energies and surface energies correlate.

**OBSERVATION OF TRANSPORT AT THE ATOMIC LEVEL**

Conduction of adhesion experiments in the field ion microscope permit the observation of the adhesion and transfer process at the atomic level. Figure 3(a) is a field ion micrograph of a tungsten surface, asperity free, prior to contact with a gold flat. Figure 3(b) is that same surface after having been contacted by gold. Gold adheres to the tungsten surface. If the imaging voltage for the surface is increased some of the gold field evaporates from the tungsten surface revealing
clusters of gold atoms adhered to the tungsten as indicated in figure 3(c). In such clusters, there is adhesive bonding to the tungsten and cohesive bonding of the gold atoms to each other. Additional field evaporation removes all the gold and reveals the parent tungsten.

Gold and tungsten do not form compounds and gold is essentially insoluble in tungsten\(^{14}\) and yet gold bonds to the surface of tungsten. The bonding of gold to tungsten can not be mechanical in nature because the tungsten is free of asperities. It can not be electrostatic in nature because the field ionization voltages should cause a loss of the gold below the 14.5 kV required for field evaporation in figure 3(c). It must, therefore, be concluded that the gold is chemically bonded. The chemistry and physics of metallic interfaces are not dependent on the conventions of bulk metal behavior.

Gold and rhodium do not form compounds.\(^{15}\) Sliding friction experiments, however, indicate that gold will adhere to rhodium. This is indicated in the Auger emission spectrum obtained on the rhodium surface contacted by gold in figure 4. Auger peaks occur for both rhodium and gold, indicating gold transfer.

Simple adhesion experiments with gold contacting iridium in the field ion microscope revealed an ordered transfer of gold to the iridium surface. There is very limited solid solubility of gold in iridium and no compound formation.\(^{15}\) Gold decorates ledge sites and with field evaporation is removed last from the (100) plane.\(^{13}\)

The results obtained with gold contacting tungsten, rhodium and iridium indicate that bulk properties and bulk behavior may not apply
directly to surface considerations. While there is limited or no solubility of gold in tungsten, rhodium, or iridium, gold adheres and transfers to the surface of these metals.

Transfer of gold to the surface of the tungsten, rhodium, and iridium in the surface clean state indicates that adhesion has occurred at the interface between the bimetallic couple and that the interfacial adhesive bond is stronger than the cohesive bonding in the cohesively weaker of the two metals, namely the gold. When the interfacial bonding and the adjacent surficial layers are pulled in tension fracture occurs in the gold with gold remaining adhered to the other surface. This constitutes a loss of material from the parent material and wear.

There are a number of factors which will contribute to quantity of metal which will transfer from one surface to another. First, there is the actual size of the discrete points of solid state contact which make up the real area of contact between the solids. The larger the cross sectional area of these contacts the greater the number of adhesive bonds.

Factors which shall influence the real contact area will include the applied load or force with which the surfaces are pressed into contact, the surface and bulk elastic properties of the metals, plastic behavior and to a limited extent topography. These factors are important with respect to both metals of the bimetallic couple.

If two metal single crystal of the same material have the identical surface orientation, their surfaces are atomically clean and perfect matching of planes and direction could be achieved as the surfaces
approached one another a single metal crystal free of any detectable interface would occur. As a practical matter such a condition is never achieved and the minimal interfacial defect will be a grain boundary for like materials in contact. Many of the concepts that apply to such boundaries, apply then to the interface.

The greater the degree of disregistry across the interface the greater will be the amount of lattice strain in the surficial layers of both solids and the greater will be the nature and number of interface defects including dislocations, vacancies, etc. Further, the greater the degree of interfacial mismatch the greater is the degree of boundary energy. 16

When the interfacial region of the solids adhered is pulled in tension fracture will occur in the atomically structurally weakest zone. This generally is subsurface in one of the two solids. The depth and location will be determined by the extent of lattice strain and the location of subsurface defects. With inorganic solids in sliding friction experiments, fracture was observed in the zone of the subsurface maximum shear stress where there was an intersection of slip bands and dislocation coalescence. 17

Where dissimilar solids make adhesive contact, one of the two solids may experience the greatest amount of lattice strain, presence of defect structures, etc. Generally, this occurs in the cohesively weaker of the two materials which must undergo lattice strain to accommodate itself to and to come into lattice registry with the cohesively stronger for chemical bonding.
The presence of the naturally occurring oxides on metal surfaces can inhibit strong adhesion. When, however, tangential motion is initiated, oxide layers can be penetrated and metal transport across the interface will occur. This is demonstrated in the Auger emission spectroscopy data of figure 5 where gold was observed to have transferred to a palladium surface containing an oxide. Both oxygen and gold peaks were observed in addition to palladium.

Gold does not form a stable oxide. With metals that do strong bonding of a clean metal to oxide surface can and will occur. Under such conditions the adhesion force is often a function of the force necessary to separate the metal from oxygen.  

**Sliding Friction**

The foregoing guides relative to the transport of metals in contact indicate in a fairly predictable manner, metal transfer from one surface to another in simply adhesive contact. With relative tangential motion between the surfaces as with sliding, rolling, or rubbing interfacial transport becomes more complex. Under such conditions, plastic deformation, shear and high surface temperatures due to frictional heating are but some factors which must be given attention. At relatively modest conditions of sliding, for example, surface temperatures of from 50° to 1000° C are easily achieved on metal surfaces. Such temperatures can modify or alter interfacial behavior.

In simple adhesion experiments, aluminum has been found to transfer to iron. With sliding similar results have been obtained as indicated in the wear track of figure 6 for iron. The mating surface was
an aluminum rider. The wear track is shown photographically in figure 6(a) and aluminum identified by X-ray mapping in figure 6(b) (clusters of white dots). The transfer with sliding occurs on a much more gross scale in that it can be detected with X-ray analysis.

Examination of the aluminum rider indicated considerable wear. The photomicrograph of figure 7(a) is for what was, prior to sliding, a hemispherical specimen. A flat was worn on the specimen tip. Most of the aluminum removed from the rider tip transferred to the disk surface as adhesive wear debris. The transfer of aluminum to iron is in keeping with the observation that the cohesively weaker metal transfers to the cohesively stronger.

If the end of the aluminum rider in figure 7(a) is examined with X-ray analysis for iron the map of figure 7(b) is obtained. The map shows a fairly uniform distribution of iron over the wear scan area. These results indicate that iron is present on the aluminum surface.

At about 655°C aluminum can dissolve iron in small quantities. With rapid cooling a supersaturation of iron in aluminum can be obtained. The frictional heat associated with the sliding process may result in alloying of aluminum with iron in the surficial layers of the aluminum rider. This can account for the uniform distribution of iron over the aluminum rider surface.

The aluminum transferred in globules in figure 6. The iron disk serves as an effective heat sink to adsorb frictional energy. As a consequence the iron disk does not experience the surface temperatures the aluminum rider does. The rider is in continuous contact while any
one point on the disk surface experiences only intermittent contact.

Repeated sliding over the same surface will result in continued adhesive transfer. This is demonstrated in the Auger emission spectroscopy data of figure 8 for aluminum sliding on a steel surface. Before sliding contact only iron and or carbon peaks are detected (fig. 8(a)). With a single pass of the aluminum slider aluminum has transferred appearing as a bulge in the iron peak (fig. 8(b)). After ten passes the aluminum peak becomes more fully defined (fig. 8(c)) and after twenty passes it is a distinct separate peak (fig. 8(d)). Note that with the growth of the aluminum peak the carbon peak decreases in intensity. The transferred aluminum covers the carbon making its detection more difficult. The greater the amount of aluminum transferred the smaller the carbon peak intensity.

The ratio of the aluminum to carbon Auger peak intensities are plotted as a function of the number of passes of the aluminum rider across the steel disk surface in figure 9. For the first twelve passes the transfer is relatively mild. After that, however, a marked increase in adhesive transfer is observed. This is often referred to as the transition between mild and severe adhesive wear. It is the severe adhesive wear which cause catastrophic failure of components of mechanical systems.

Adhesion and bonding not only occurs for bimetallic couples but also for metals in contact with semiconductors. Sliding friction experiments with gold in contact with germanium indicate that gold will adhere and transfer to a germanium film. Such transfer is shown in
Figure 10. Figure 10(a) is the wear track indicating that brittle fracture of the germanium has occurred. It also indicates evidence (center of track) for plastic deformation of the germanium during sliding.

Gold was observed to transfer to the germanium surface. The adhered gold of figure 10(a) is shown in more detail in figure 10(b). The gold consists of a cluster of individual crystals of gold. X-ray analysis for gold is presented in figure 10(c). Figure 10(c) indicates that the cluster of crystals is gold.

The rider specimen which slid against the germanium film was a gold single crystal. The strain and frictional heat supplied sufficient energy to induce surface recrystallization of the gold.

Surface Films

As has already been indicated, surface films can markedly inhibit strong metallic adhesion. Even fractions of monolayers are sufficient to achieve a notable effect upon adhesion and consequently material transfer. Surface active elements such as oxygen, sulfur, and chlorine are especially effective in this regard. Adhesion studies were conducted with iron single crystal surfaces exposed to varying amounts of hydrogen sulfide. Hydrogen sulfide adsorbs on a clean iron surface dissociatively leaving only sulfur on the surface. Films from fractions to a full monolayer were adsorbed. Coverage was monitored with both LEED (low energy electron diffraction) and Auger emission spectroscopy analysis.

In figure 11 the force of adhesion for iron to itself is plotted as a function of applied normal load on the surfaces. The top curve in
figure 11 having a LEED 2×4 structure, the intermediate curve a LEED 1×2 structure and the lower curve is a monolayer structure completely covering the iron with close packed sulfur. The adhesion force for clean iron was in excess of 400 dynes. With a monolayer of sulfur the force was 10 dynes.

For the two curves in figure 11 with less than monolayer coverage adhesion force increases with normal load because of increased iron to iron bonding with deformation. This does not occur for the surface fully covered by sulfur.

Static friction much like adhesion is extremely sensitive to small amounts of surface contamination. It gives an indication of the amount of interfacial bonding that has occurred. With adhesion the greater the amount of interfacial bonding the greater is the force required to separate the surfaces normal to the interface. Static friction indicates the force required to initiate tangential motion parallel to the interface. For metals then, the greater the adhesion bonding the higher the static friction.

In figure 12 the static friction coefficient is plotted as a function of the inverse of adsorbate coverage for three materials, iron copper, and a bearing steel. The adsorbates examined in reference 19 included oxygen and chlorine. For all three materials and with both adsorbates, the greater the surface coverage the lower the static friction coefficient with a direct relationship existing between the two. This, of course, reflects a reduction in interfacial bonding and adhesion and a decrease in the transport of metal or alloy from one surface to another.
There is a wide disparity in the hardness and other mechanical properties of iron and the bearing steel, yet both respond equivalently to the presence of the adsorbates. Likewise the properties of oxygen and chlorine are different yet both effect the static friction in an identical manner. It is the surface coverage which is the important factor. The more complete the surface coverage, the lower the static friction, adhesion and material transfer.

Material Chemistry

If surface films inhibit the formation of interfacial bonds between metal and alloy surfaces and thereby reduce adhesion, static friction, and transfer or wear then those properties of materials which effect surface film formation should have an effect on these same behavior characteristics. With metal alloys the alloying elements have different affinities for environmental constituents and such substances as lubricants. It might therefore be anticipated that alloying can effect adhesion, interfacial transport, and wear.

Gold is relatively inert chemically at best with respect to interactions with oxygen and conventional lubricants. Small additions of another noble metal, copper to gold can alter both friction and wear behavior. Copper is more reactive with lubricants and does form stable oxides. Its effect on the friction and wear of gold is indicated in the data of figure 13.

The data of figure 13 indicate that with additions of 2.5 percent copper in gold both friction and adhesive wear were markedly reduced. In this same composition range the microhardness remains unaffected.
Thus, the change in friction and wear can not be attributed to changes in mechanical properties such as hardness.

The specimen surfaces in figure were cleaned in vacuum prior to the admission of the lubricant. The stearic acid reacted chemically more readily with copper than with gold providing a protective surface film of copper stearate which is very effective in reducing interfacial bonding, adhesion, and as the data indicate friction and wear. Thus, in the formulation of alloys for practical lubrication systems, attention must be given to the effects of alloy additions on surface chemistry as well as upon mechanical properties.

CONCLUDING REMARKS

From the data presented, some general observations and remarks can be made relative to the adhesion, interfacial transport and wear for metals and alloys in contact. These are as follows:

1. Strong interfacial adhesive bonding will occur for metals in contact. This bonding will occur on contact. The resulting interfacial adhesive bond is generally stronger than the cohesive bond in the cohesively weaker of the two materials. The result is that upon separation of the surfaces transfer of the cohesively weaker material to the cohesively stronger will occur.

2. With tangential motion of two metal surfaces in contact such as is encountered with sliding, rolling, or rubbing contact the frictional energy can be dissipated in a number of ways, one of which is heat. Heating of the surfaces can produce metallurgical changes such as alloying.
3. The presence of adsorbed and reacted films on the surface of metals and alloys even in frictions of a monolayer can reduce interfacial bonding, adhesion, and transfer. Bulk alloy chemistry can effect transfer and wear as well as friction by increasing the activity of lubricating species with the alloy surfaces.

REFERENCES

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Figure 1. - Jellium charge density to scale for Al-Zn. \( n_1 \) and \( n_2 \) denote the metal-vacuum electron number densities for Zn and Al respectively (ref. 11).

Figure 2. - Energy components for the typical case of Al-Zn. \( a_0 \) is the location of the energy minimum (ref. 11).
Figure 3. Field ion micrographs of tungsten-gold contact. Image gas: helium.

(a) Tungsten prior to contact. Voltage: 15.0 kilowatts, liquid nitrogen cooling.
(b) Tungsten after gold contact at 11.0 kilovolts; liquid-nitrogen cooling.

Figure 3. Continued.
Figure 4. - Auger emission spectrum for a rhodium (111) single crystal surface after a single pass in sliding of a gold (111) crystal across the rhodium surface. Sliding velocity 0.7 mm/min, load 10 grams, 10^{-10} torr and 23°C.

Figure 5. - Auger emission spectrum for a palladium (111) surface containing oxide after a single pass sliding of a gold (111) crystal across the surface. Sliding velocity 0.7 mm/min, load 10 grams, 10^{-10} torr and 23°C.
Figure 6. - Wear track of iron disk after running with aluminum rider. X350.
Figure 7. - Rider wear scar of aluminum rider after running on iron disk. X 5.
Figure 9. Detection of aluminum adhesive transfer to steel surface during sliding friction experiment. Sliding velocity, 20 centimeters per minute; 500 grams; load, temperature, 23°C.
Figure 10. Scanning electron micrographs of wear track on germanium film on nickel (111) substrate. Rider, gold (111) single crystal.

(a) Wear track.

(b) Adhered gold.
Figure 10. - Concluded.

Figure 11. - Influence of hydrogen sulfide adsorption on adhesion of iron (011) surfaces. Diameter of contacting half 3.0 millimeters; contact time, 10 seconds.
Figure 12. - Static coefficient of friction as function of inverse of adsorbate concentration (ref. 19).

Figure 13. - Friction, deformation, and microhardness of polycrystalline gold as a function of copper content. Load, 50 grams; sliding velocity, 0.033 millimeter per second; temperature, 20° C; lubricant, 0.02 percent stearic acid in hexadecane. Specimens cleaned in vacuum prior to admission of lubricant.