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EFFECT OF VARIOUS MATERIAL PROPERTIES ON
THE ADHESIVE STAGE OF FRETTING

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SUMMARY

Various properties of metals and alloys have been studied with respect to their effect on the initial stage of the fretting process, namely adhesion. Crystallographic orientation, crystal structure, interfacial binding energies of dissimiliar metal, segregation of alloy constituents and the nature and structure of surface films have all been found to influence adhesion. High atomic density, low surface energy grain orientations exhibit lower adhesion than other orientations. Hexagonal metals in general manifest less adhesive wear than cubic metal. Knowledge of interfacial surface binding energies can assist in predicting adhesive transfer and wear. Selective surface segregation of alloy constituents can accomplish both a reduction in adhesion and improved surface oxidation characteristics. Equivalent surface coverages of various adsorbed species indicate that some are markedly more effective in inhibiting adhesion than others.

INTRODUCTION

It is generally accepted that the fretting of material surfaces involves three forms of wear[1-6]. The first or initial step in the process is the development of adhesive wear particles. With metals and alloys this is followed by oxidation of the adhesive wear particles and corrosive wear can then result. The third step of the fretting process involves abrasive wear of the parent surface when the oxidized adhesive wear particles are harder than the parent surface from which they came or the mating surface.

The importance of adhesion in the fretting process was recognized thirty-five years ago. Tomlinson et al[1] in a classical paper on the subject of fretting put forth the concept that the slip in the fretting process was the result of the breaking of atomic bonds and that the attrition of surfaces was in some way caused by the severance of cohesive bonds. Through the years others have recognized the importance of adhesion in fretting[3,5,6,7,8].

It would appear to be a reasonable assumption that if in fact the adhesion of surfaces across on interface and the subsequent formation of adhesive wear particles initiate the chain of events which result in fretting or fretting corrosion then understanding and controlling this first step could do much in the mitigation of fretting. There are for example, physical, metallurgical, crystallographic and chemical properties of metals and alloys which influence adhesion, the precursor to adhesive wear.

The objective of this paper is to examine some of the basic properties of metals and alloys which exert an influence upon the adhesion and adhesive wear involved in the fretting process. The properties to be examined in relation to their effect on adhesion include, 1) orientation, 2) crystallography, 3) dissimiliar materials in contact, 4) alloying and 5) surface film effects. Only metal to metal contacts will be considered as these are the most frequently encountered in mechanical devices involving fretting.

ORIENTATION EFFECTS

Engineering surfaces are generally metals and alloys in the polycrystalline state. The surface of such materials consist of many different grains each with an orientation different from that of its nearest neighbor and separated by a grain boundary. Each orientation has its own adhesive behavior. The effect of orientation on adhesion is demonstrated for various orientation of copper in contact with itself in Table I. Friction data are also presented in Table I.

With tangential motion or rubbing the real contact area for the clean metal surfaces in increases. Thus, in Table I the adhesion coefficient before sliding is markedly less than after sliding for all these orientations.

The adhesion properties of copper as indicated in the data of Table I are very distinctly anisotropic. Similiar data have been obtained for a number of different metals. They all indicate similiar anisotropic adhesion behav-

ior[9]. Even tungsten, one of the least anisotropic metals exhibits anisotropic adhesion behavior.

In examining the literature one is led to believe that somehow the element of fretting effects the fatigue life of mechanical components and the term fretting fatigue has been applied to the process [10-12]. Fatigue as a wear mechanism required repeated stress cycles[13]. Fretting can be initiated in the adhesive phase with a single pass across a surface.

Some simple sliding friction experiments were conducted with a polycrystalline copper rider sliding across the surface of a bicrystal of copper[14]. One grain of the bicrystal was of the (111) orientation while the second was a (210) plane. With a single pass of the rider across the surface fracture cracks developed in the surface of both grains of the bicrystal. These surface cracks are shown in the scanning electron micrographs of Figure 1. The crack is much larger in size on the (210) grain than on the (111) grain indicating that surface damage in addition to adhesion is anisotropic. The fracture cracks developed at room temperature within the copper.

The surface cracks are presented for the (210) grain at a higher magnification in Figure 2. Close examination of these cracks indicates that the wall of the crack is very smooth. Further, the material at the leading edge of the crack has been curled up above the plane of the bicrystal surface. The measured angle between the crack and the orientation of the surface plane indicate that the fracture crack occurs along slip bands.

The mechanism responsible for the cracks shown in Figure 2 is presented in Figure 3. Adhesion of the rider to the bicrystal occurs. With tangential motion fracture occurs along slip bands as the tangential force parts atomic planes. At some applied tangential force, the applied force exceeds the adhesive bonding force and the rider breaks away from the bicrystal surface leaving a curl of metal projecting above the surface. A second pass shears off the curl and a wear particle has been generated. Thus, with a single stress cycle fracture occurs as may be seen with repeated cycles in fatigue and with two passes the first step in the fretting process, adhesive wear has occurred.

CRYSTALLOGRAPHIC EFFECTS

Nearly all of the metals and alloys used in engineering systems crystallize in one of three crystal forms, body centered cubic, face centered cubic or hexagonal. Crystal structure exerts an influence on adhesion.

When equivalent atomic planes of the face centered cubic metal copper and compared with planes of the hexagonal metal cobalt differences in both adhesion and friction are observed as indicated in the data of Table II. Cobalt exhibits both lower adhesive and friction forces.

The most effective demonstration of the influence of crystal structure on adhesion is to examine a single metal which is allomorphic, that is crystallizes in two different crystalline states. Cobalt is such a metal. It exists in the hexagonal state at a temperature to 417° C where it transforms to a face centered cubic structure.

Friction data for cobalt in sliding contact with itself in vacuum at various temperatures is presented in Figure 4. Since the surfaces do not oxidize in a vacuum environment the friction results of Figure 4 reflect adhesive behavior. Friction coefficient is relatively low for cobalt sliding on itself while the metal is in the hexagonal form. As the crystal transformation temperature is approached the friction coefficient begins to increase. It continues to increase through the transformation until complete seizure of the metal occurs. If the specimens were broken apart and allowed to cool to room temperature the metal reverts to the hexagonal crystal form and low friction is again obtained.

Adhesive wear increases one hundred fold with crystal transformation as indicated in the data of Figure 4. The greater the amount of adhesive wear the greater would be the fretting if the specimens were in on oxidizing environment. Thus, a one hundred fold reduction in fretting could be accomplished by the utilization of the proper crystal structure.

Hexagonal metals in general exhibit lower adhesive wear characteristics than either body or face centered cubic metals. This difference is related to the number of operable slip systems in the crystal systems. The body centered cubic metals have forty-eight possible slip modes, the face centered cubic twelve while the close packed hexagonal metals exhibit only three operable slip systems. A notable exception among the hexagonal metals is titanium.

Titanium because of its lattice spacing (c/a ratio) exhibits nine operable slip systems. The adhesion, friction and adhesive wear behavior of titanium can be altered by selective alloying to modify lattice ratio and thereby

reduce the number of slip systems to three and the mode to basal slip as in close-packed hexagonal metals. When this is accomplished marked reductions in adhesive wear for titanium result[9].

The marked effect of crystal structure on adhesive wear can be seen for the allomorphic metal lanthanum in Figure 5. In Figure 5(a) lanthanum was sliding in its cubic form on 440-C bearing steel. The white ring of material on the 440-C disk surface represents lanthanum transferred to the 440-C surface. The transfer is heavy with large globules of lanthium having transferred. When sliding is conducted with lanthanum in the hexagonal form a very thin smooth fi..u. of lanthanum transfers to the steel surface as indicated in Figure 5(b). The transfer film is Figure 5(b) has a basal texture. This provides for basal shear, minimal transfer and limited adhesive wear. Again, in air the amount of fretting would be much more severe in Figure 5(a) and 5(b).

Hardness has been mentioned as being important to the fretting process. It has been suggested that harder materials will fret less than softer ones[5]. The ulitization of the crystal structure concept indicates that this in fact may not be true, at least with respect to adhesive wear. Table III presents the wear for three materials.

In Table III, lathanum and samarium are both markedly softer than 440-C stainless steel. Both lanthanum and samarium in their hexagonal form exhibit less wear than the considerably harder 440-C stainless steel. Further, the quantitative differences for lanthanum transfer to 440-C stainless steel seen in Figure 5 is presented in Table III.

DISSIMILIAR MATERIALS

The general design engineering concept for many years has been that dissimiliar metals should be employed where two solids are in sliding or rubbing contact. Careful examination in recent years of dissimiliar metals in contact with surface tools such as LEED, Auger Spectroscopy and scanning electron microscopy has revealed that frequently one of the two metals in contact ultimately transfers to the other surface so that like material is sliding on itself.

Theoretical considerations for the binding of dissimiliar metals in contact using the electron theory of metallic binding indicate that binding energies for dissimiliar metals in contact can be greater than the binding energy for a metal to itself. This is demonstrated in the data presented in Table IV. The data of Table IV indicate that a number of the dissimiliar couples have stronger binding energies than the metals do when bonding to themselves. The exception in Table IV is aluminum. As indicated in Table IV the theoretical findings have been experimentally verified.

In the adhesive binding of dissimiliar metals in contact fracture usually occurs in the cohesively weaker of the two materials in contact. Generally the adhesive bonding at the interface is stronger than the cohesive bonding in the cohesively weaker of the two materials[15].

Many factors will influence the strength of adhesive bonding for dissimiliar metals in contact. One factor, where the metals are of the same crystal structure, to the degree of crystal lattice mismatch. The greater the degree of lattice misfit the greater is the propensity for strong adhesive bonding. This effect is indicated in Table V for various metal single crystals of the (111) orientation in contact with a (111) orientation of a gold single crystal surface.

The data of Table V indicate that for gold, silver and aluminum where there is only adhesive bonding force is large. Where, however, as with copper, the lattice misfit is large the adhesion force decreases appreciably.

In the data of Table V the gold transfers to the copper surface. The presence of gold on the copper surface was verified structurally with LEED (low energy electron diffraction) and chemically with Auger emission spectroscopy analysis.

The mechanism for adhesive bonding and fracture in the copper - gold couple is demonstrated in Figure 6 schematically. The gold adheres to the copper epitaxially. In order for this to occur the lattice of the cohesively weaker of the two materials must strain with adhesive bonding of the gold to copper. Gold being the cohesively weaker of the two metals it's lattice in the surficial layers strains to match that of the copper. When the adhesive bond is pulled in tension, fracture occurs in the weakest region. The three possible sites for such fracture to occur are, 1) in the copper, 2) at the interface and 3) in the gold. Fracture occurs in the gold cohesive bonds with gold adhering to the copper surface.

ALLOY EFFECTS

The practical problems of adhesion and fretting most frequently involve alloys rather than elemental metals. Adhesion experiments were conducted with various binary copper alloys to determine the effect of the alloying elements on adhesion. The presence of small concentrations of alloying elements in metals can markedly alter their adhesion behavior. The effect of aluminum on the adhesion behavior of copper can be seen in the data of Figure 7. The addition of as little as one atomic percent aluminum in copper produces a fivefold increase in adhesive force. Further additions of aluminum do not increase the force above that measured with the one atomic percent alloy.

It should be noted in Figure 7 that the adhesion force measured for the one atomic percent alloy is the same as that measured for pure aluminum. LEED and Auger analysis of the alloy surface indicated that aluminum segregated out of the alloy and onto the surface. The manner in which the aluminum segregates in indicated in Figure 8. Since the outermost or surface layer of atoms was pure aluminum, the adhesive behavior of that surface with other surfaces is the same as aluminum. Other alloy systems have been shown to exhibit a similar behavior. Adhesion can be increased or decreased depending on the alloying element. With copper the elements tin and indium reduce adhesion and adhesive wear.

SURFACE FILMS

Nearly all materials adsorbed to or reacted with solid surfaces tend to reduce adhesion and adhesive wear. One of the most effective lubricant for solids, particularly metals and alloys are naturally occurring metal oxides. If metal surfaces are carefully outgassed in a vacuum environment and the surfaces carefully cleaned complete seizure of the metals occur when the metals are placed into contact. Adhesion with friction coefficients in excess of one hundred are readily measured. The presence of naturally occurring oxides reduces the value to 0.5 to 1.5. The use of conventional lubricating oils will reduce the value to 0.1. Thus, oxides are extremely good natural lubricants.

There are suface films that are even more effective in reducing adhesion than surface oxides. Some controlled experiments were conducted in which equivalent amounts of oxygen and sulfur were adsorbed to an iron (011) surface. The adhesion   iron to itself in the presence of the two film materials was measured at various loads. The results obtained are presented in Figure 9.

In figure 9 both LEED and Auger spectroscopy analysis were used to ensure that the surface coverages for oxygen and sulfur were equivalent. A comparison of the data indicate that the sulfur is more effective in the reduction of adhesion than is oxygen. Further, the data of figure 9 indicate that adhesion with sulfur is uneffected by load. If the sulfide film is however, exposed to oxygen the oxygen will completely displace the sulfur from the surface with only oxygen remaining [16].

Hydrocarbons, the most frequently used materials as lubricants, exhibit varying effectiveness in the reduction of metallic adhesion. This is demonstrated by the data of Table VI where the effectiveness of various hydrocarbons in the reduction of the adhesion of iron are compared. The first observation to be made from the data of Table VI is that two carbon atom ethane is more effective in reducing adhesion than is single carbon atom methane.

The second observation to be made from the data of Table VI is that adhesion is related to the degree of hydrocarbon bond saturation. A comparison of the adhesion data for ethane, ethylene and acetylene indicate that the greater the degree of bond unsaturation the lower is the adhesive binding force.

The third observation to be made from the data of Table VI is that the addition of very surface active elements such as chlorine (vinyl chloride) and oxygen(ethylene oxide) to the basic ethylene structure reduces adhesion still further. It is of interest to note that with ethylene oxide a close packed monolayer develops on the iron surface which completely shields the iron. This is the only hydrocarbon in Table VI which in monolayer form completely masks the iron. It accordingly provides the maximum surface protection from adhesive bonding of iron to itself. Thus, it represents an ideal surface structure.

DISCUSSION

Adhesion is fundamentally very important in the fretting process. It represents the initial phase in the de-

velopment of the adhesive wear particle, which when oxidized is the manifestation of fretting. If the adhesion process can be arrested, fretting can be reduced or eliminated. Various methods have been proposed to accomplish this objective. These include mechanical tightening, redesign, increasing load, surface stressing, flame spraying, material imposition and lubrication[17].

In this paper an attempt was made to show that there are many basic properties, physical, metallurgical, chemical and crystallographic of metals which can be exploited to reduce adhesion. For example, in practical devices the proper surface texture (grain orientation) in polycrystalline metals can be achieved to minimized adhesion by mechanical working. The crystal structure concept can be utilized by the selection of hexagonal base alloys. Fretting does not readily occur with metals such as beryllium and cobalt in its hexagonal form. While fretting may occur with platinium that process has not been seen to occur with the sister element to platinium in the periodic table, hexagonal osmium.

The dissimiliar material concept can be effective in reducing fretting if transfer of a thin film of the lower wearing material to opposite surface is achieved. For example, with cobalt in contact with steel a thin film of cobalt will transfer to the steel surface resulting in minimal adhesive wear.

With metal alloys the segregation of alloy constituents to the surface can achieve a reduction in adhesion such as observed with the addition of tin or indium to copper. Further, more dense, tenacious oxides can be formed on metal surface and thus more impervious to penetration of metal asperities if metals such as aluminum are alloyed with copper. Oxidation of copper alloys containing small amounts of aluminum result in the formation of aluminum oxide surface films. These are certainly more impervious to penetration by asperities than copper oxides. In addition they form thinner films so that when oxide penetration does occur and oxide debris is generated there is quantitatively less than would occur with copper oxides. Protective oxides would also kinetically form more rapidly with aluminum than with copper. This is important once nascent metal is exposed.

Surface films in equivalent surface coverages can effect adhesion of metals to varying degrees. Certain hydrocarbons are more effective than others in achieving reduction in the adhesion of metals such as iron. Thus, where the lubrication approach is used to reduce adhesion proper selection of the species to be adsorbed or reacted is important.

An interesting dichotomy exists with adhesion and its relation to fretting. Strong adhesion across an interface is desirable to minimize tangential displacements and the development of slip. It is for this reason that increased loading is effective in reducing fretting. Conversely, if relative motion cannot be prevented, as for example, in aircraft splines, then adhesion should be minimized.

Adhesive wear particles, the product of adhesion when repeated oscillatory slip does occur are particles in a highly strained state. In general strained metals are chemically much more reactive than the same metal in the annealed condition. Thus, in a vacuum environment, such as used herein these particles can adhere to one another. They also can adhere singly or in aggregates to the parent surface from which they came. Once, however, a film forming material is admitted into their environment they react very rapidly and the surface films formed (e.g. oxides) impedes the self bonding of the particles.

CONCLUSIONS

Adhesion which is the initial stage in the development of fretting is influence by many basic properties of metals and alloys in contact. Some of the properties found to influence adhesion and adhesive wear include. 1) orientation, 2) crystallography 3) interfacial bonding of dissimiliar couples, 4) alloying element and 4) the structure and nature of surface films.

In general high atomic density, low surface energy grain orientations exhibit lower adhesion and less adhesive wear than do other orientations. Hexagonal metals and alloys manifest adhesive wear which is markedly less than is observed with cubic metals. Interfacial bonding energies can assist in the prediction of metal transfer for dissimiliar metal couples. Selective alloying and surface segregation of alloying elements can reduce adhesion and provide more effectively protective surface oxides. Certain surface films are much more effective, in equivalent surface coverages, in reducing adhesion. Sulfur on iron for example is more effective than oxygen.

6

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Table I

COEFFICIENTS OF ADHESION AND FRICTION FOR VARIOUS SINGLE CRYSTAL ORIENTATIONS OF COPPER

MATCHED PLANES	ADHESION COEFFICIENT BEFORE SLIDING	COEFFICIENT OF FRICTION[a] (DURING SLIDING)	ADHESION* COEFFICIENT AFTER SLIDING
(100)/(100)	1.02	>40.0	>130
(110)/(100)	0.25	>40.0	32.5
(111)/(100)	0.20	>40.0	40.0

[a]0.001 CM/SEC; [110] DIRECTION; SLIDING DISTANCE, 0.735 CM; 10^{-11} TORR; 20^0 C; 50 GM.

CS-42785

Table II

COEFFICIENTS OF ADHESION AND FRICTION FOR COPPER AND COBALT SINGLE CRYSTALS IN VACUUM

METAL COUPLES (MATCHED POLES)	ADHESION COEFFICIENT BEFORE SLIDING	FRICTION COEFFICIENT[a] (DURING SLIDING)	ADHESION* AFTER SLIDING
$\underline{Cu(111)[110]}$ Cu(111)[1̄10]	0.30	21.0	10.5
$\underline{Co(0001)[112̄0]}$ Co(0001)[112̄0]	<0.05	0.35	<0.05

[a]0.001 CM/SEC; SLIDING DISTANCE, 0.735 CM; 10^{-11} TORR; 50 GM.

CS-42784

Table III
WEAR FOR VARIOUS RIDER MATERIALS
SLIDING AGAINST 440-C S.S.; LOAD, 1000 g (9.8 N); 10^{-9} TORR; 1 HR

RIDER MATERIAL	HARDNESS (DPH)	CRYSTAL STRUCTURE	RIDER WEAR RATE, $CM^3/$ CM SLIDING
LANTHANUM	40	HEXAGONAL FACE CENTERED CUBIC	6.08×10^{-10} 2.83×10^{-9}
SAMARIUM	45	HEXAGONAL	2.62×10^{-10}
440-C STAINLESS STEEL	600	CUBIC	2.09×10^{-9}

CS-70464

Table IV
ORDERING OF ADHESIVE BINDING ENERGIES

THEORETICAL	ORDERING BINDING ENERGY, ERGS/CM^2	EXPERIMENTAL ORDERING[1]
Al-Al	525	1
Al-Au	465	2
Al-Cu	455	3
Al-Ag	385	4
Cu-Cu	375	5
Au-Au	345	6
Cu-Ag	335	7
Ag-Ag	290	8

[1] D. H. BUCKLEY (VACUUM RESULTS).

CS-65541

Table V

EFFECT OF LATTICE MISFIT ON ADHESION OF GOLD TO VARIOUS FACE CENTERED CUBIC METALS

METAL	LATTICE PARAMETER, $\overset{\circ}{A}$ (OR 10^{-10} M)	% MISFIT WITH (111) Au	FORCE OF ADHESION OF Au (111) TO (111) METAL SURFACE, DYNE (OR 10^{-5} N)
Au	4.078	0	>400
Ag	4.086	.19	>400
Al	4.049	.71	>400
Cu	3.615	11.1	80

CS-70297

Table VI

EFFECT OF VARIOUS HYDROCARBONS ON ADHESION OF CLEAN IRON

HYDROCARBON CHEMISORBED TO IRON	ADHESIVE FORCE*, DYNES
CLEAN Fe	>400
ETHANE C_2H_6	280
ETHYLENE $H_2C = CH_2$	170
ACETYLENE $HC \equiv CH$	80
VINYL CHLORIDE $H_2C = CHCl$	30
ETHYLENE OXIDE $H_2C \overset{O}{-\!\!-} CH_2$	<10

*LOAD 20 DYNES, 10^{-10} TORR, 20^0 C, BOTH SURFACES (001) PLANES
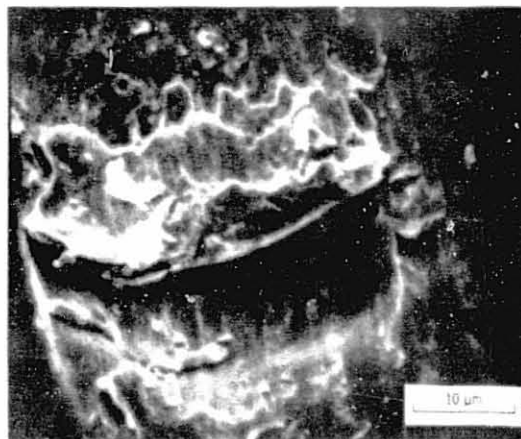
CS-54407

Figure 1

WEAR TRACKS ON BICRYSTAL GRAINS
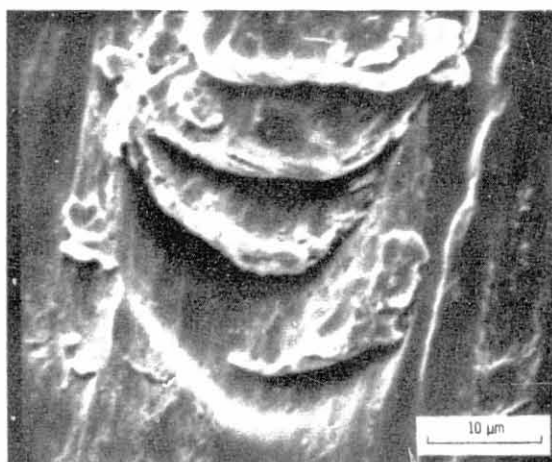### COPPER SLIDER; LOAD, 100 g; SLIDING SPEED, 1.4 MM/MIN
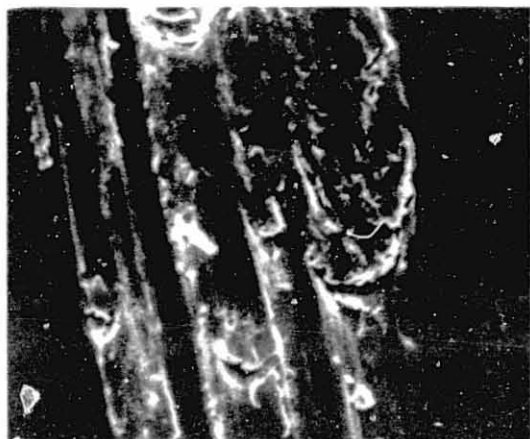
(111) GRAIN

(210) GRAIN   CS-66592

Figure 2

AREAS OF WEAR ON (2IO) COPPER GRAIN
50 g/MIN, 1.4 MM/MIN

CS-69321

Figure 3

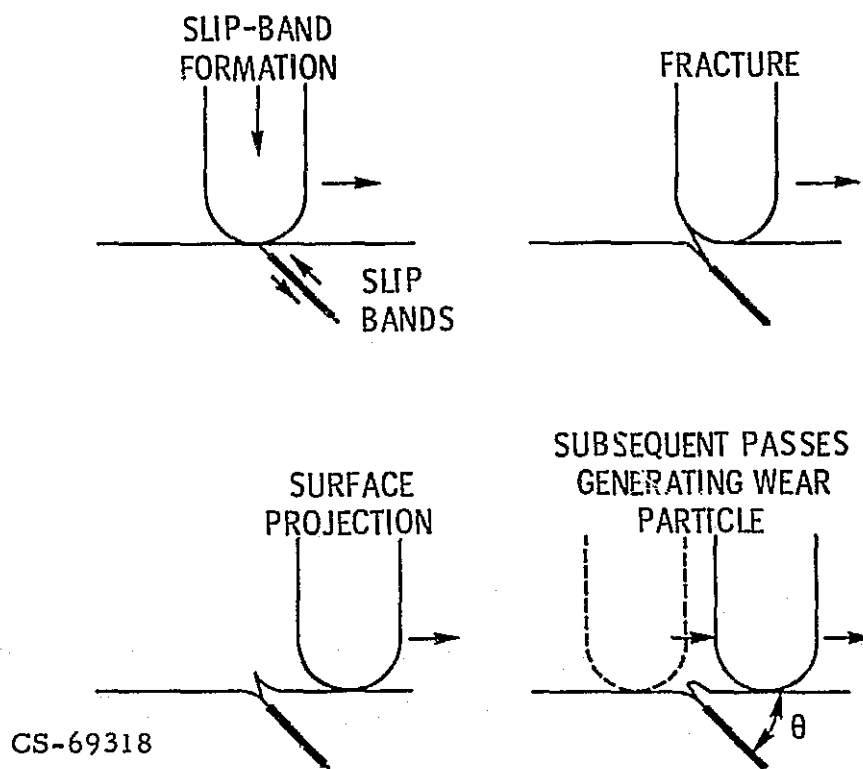# ORIGIN OF SURFACE FRACTURE AND FORMATION OF WEAR PARTICLE

SLIP-BAND
FORMATION

SLIP
BANDS

FRACTURE

SURFACE
PROJECTION

SUBSEQUENT PASSES
GENERATING WEAR
PARTICLE

θ

CS-69318

Figure 4

COEFFICIENT OF FRICTION FOR Co SLIDING ON Co IN VACUUM AT VARIOUS TEMPERATURES

10^{-9} MM Hg, 1000 GM

◆ DATA OBTAINED AFTER SPECIMEN COOLED TO 25° C

FACE CENTERED CUBIC ON FACE CENTERED CUBIC

COMPLETE WELDING

RIDER WEAR RATE, CM^3/CM OF SLIDING
3.50×10^{-9}

HEXAGONAL ON HEXAGONAL

3.78×10^{-11}

SLIDING VELOCITY, 198 CM/SEC

COEFF OF FRICTION

AMBIENT TEMP, °C

CS-33631
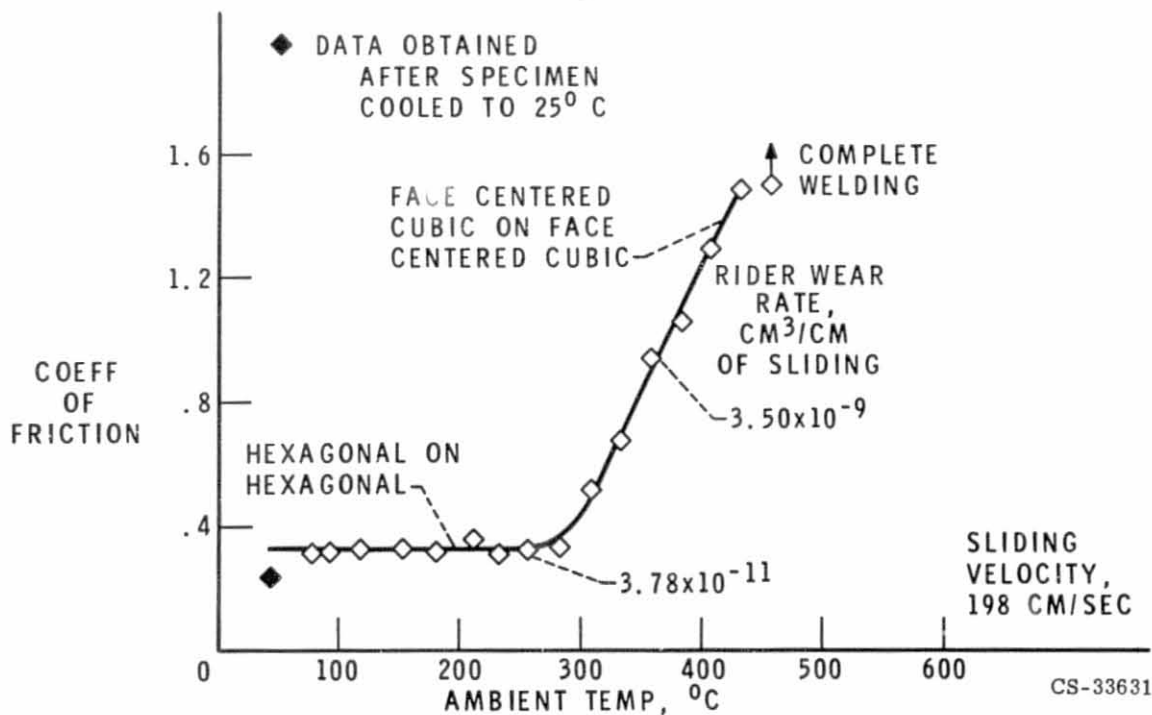
Figure 5

440−C DISK, RIDER WAS LANTHANUM LOAD, 1000 GMS; 10^{-9} MM Hg 75°F; 1 HR

SLIDING WITH CUBIC FORM   SLIDING WITH HEXAGONAL FORM   CS-33642

0 INCH 1
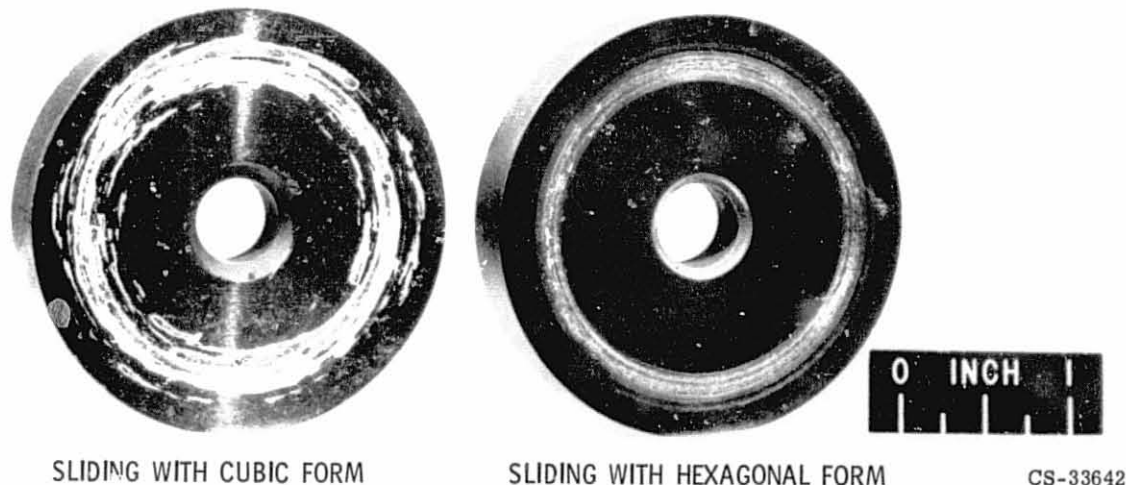
Figure 6

ATOMIC ARRANGEMENT AND LATTICE BONDING

COPPER-   ADHESION OF GOLD
GOLD ALLOY   TO COPPER
                  EPITAXIALLY
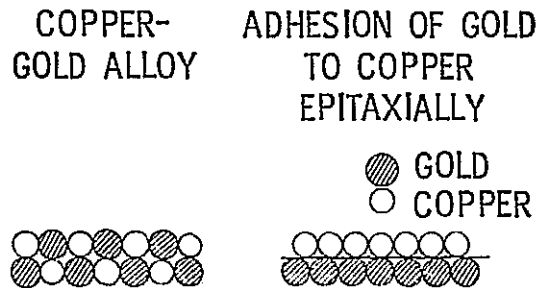
GOLD
COPPER

LATTICE STRAIN IN GOLD ON ADHESION TO COPPER

COPPER-GOLD
BONDING   INTERFACE
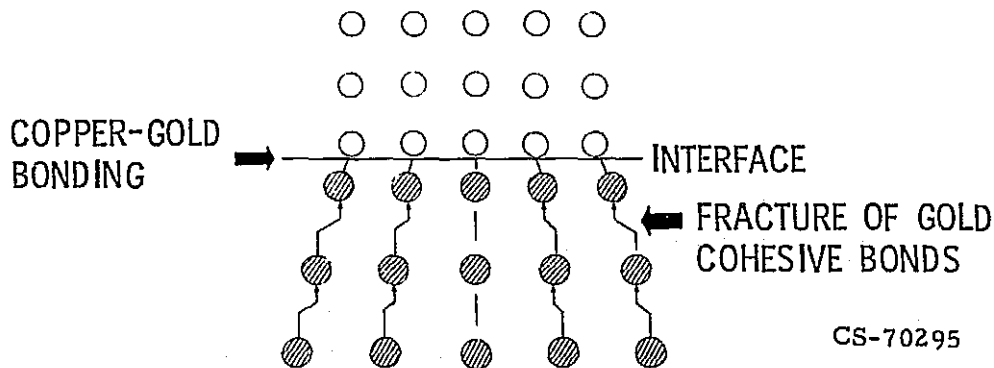
FRACTURE OF GOLD
COHESIVE BONDS

CS-70295

Figure 7

ADHESIVE FORCE OF (III) GOLD TO (III) SURFACE OF COPPER AND COPPER ALLOYS

ADHESIVE FORCE,
MG

o Cu-Al
□ Cu-Sn AFTER SPUTTERING
◇ Cu-Sn AFTER HEATING 200° C

SOLUTE IN COPPER, AT. %
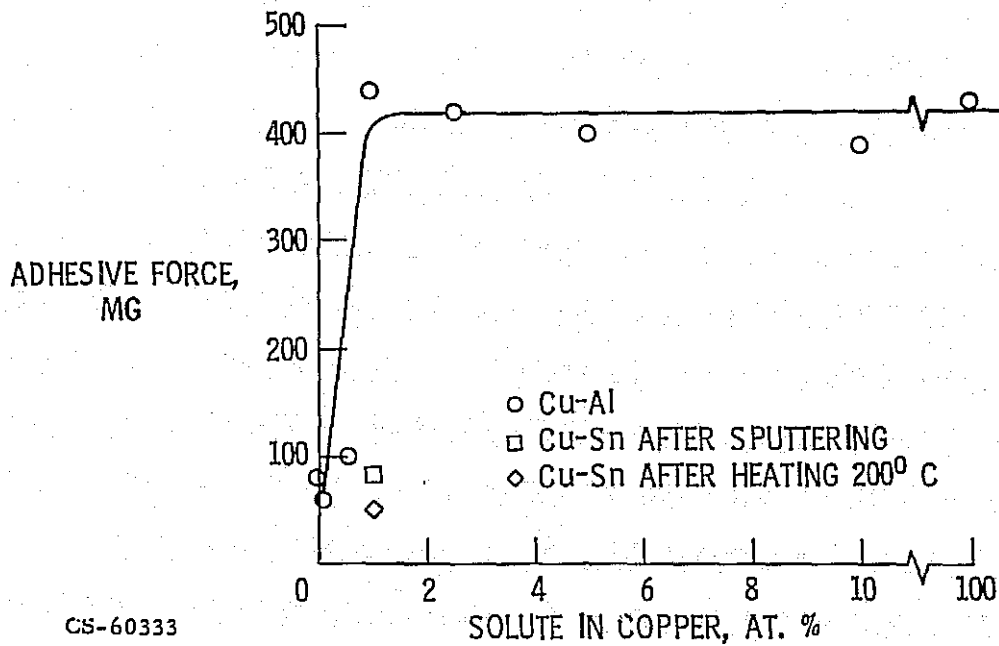
CS-60333

Figure 8

POSSIBLE DIRECT LATTICE STRUCTURE
FOR LEED PATTERN SHOWING
1/3 MONOLAYER COVERAGE

TOP VIEW

● ALUMINUM

○ SUBSTRATE

SIDE VIEW

● ● ● ● ALUMINUM
⎍⎍⎍⎍⎍⎍⎍⎍⎍⎍⎍⎍⎍⎍⎍⎍ SUBSTRATE
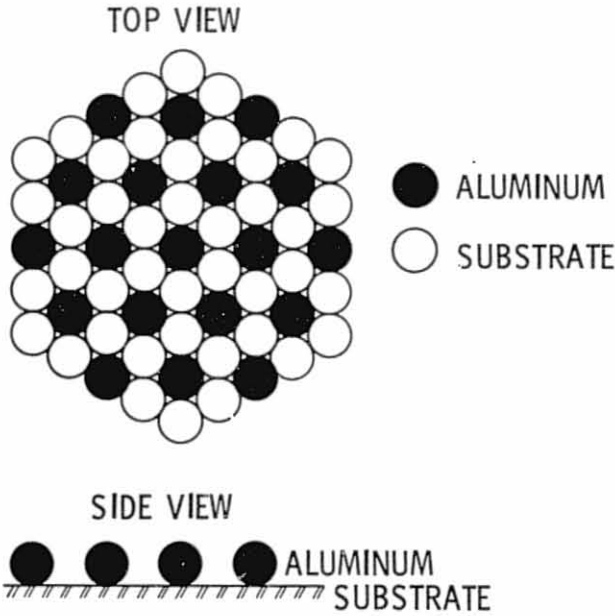
CS-60331

Figure 9

EFFECT OF OXYGEN AND SULFUR ON ADHESION
OF IRON TO ITSELF

DIAM OF CONTACTING FLAT, 3.0 MM;
CONTACT TIME, 10 SEC

Fe (011) c(2X4)-O

FORCE OF
ADHESION,
DYNES

Fe (011) c(2X4)-S

NORMAL LOAD, DYNES   CS-53970