The Role of Material Properties in Adhesion

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THE ROLE OF MATERIAL PROPERTIES IN ADHESION

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ABSTRACT

When two solid surfaces are brought into contact strong adhesive bond forces can develop between the materials. The magnitude of the forces will depend upon the state of the surfaces, cleanliness and the fundamental properties of the two solids, both surface and bulk. Adhesion between solids is addressed from a theoretical consideration of the electronic nature of the surfaces and experimentally relating bond forces to the nature of the interface resulting from solid state contact. Surface properties correlated with adhesion include, atomic or molecular orientation, reconstruction and segregation as well as the chemistry of the surface species. Where dissimilar solids are in contact the contribution of each is considered as is the role of their interactive chemistry on bond strength. Bulk properties examined include elastic and plastic behavior in the surficial regions, cohesive binding energies, crystal structure, crystallographic orientation and state. Materials examined with respect to interfacial adhesive interactions include metals, alloys, ceramics, polymers and diamond. They are reviewed both in single and polycrystalline form. The surfaces of the contacting solids are studied both in the atomic or molecularly clean state and in the presence of selected surface contaminants.

INTRODUCTION

When two surfaces in the atomically clean state are brought into solid-state contact, strong adhesive bonds develop at the interface and some force is required to separate the solids. The interfacial bond strength between the solids is, with a few exceptions, stronger than the cohesive bonds in the cohesively weaker of the two solids and fracture does not occur at the interface but rather in the cohesively weaker of the two materials. Thus, strong adhesion will occur with simple atomic cleaning of the surfaces.

The presence of films on the surfaces of the solids influences adhesion, and very small amounts, even fractions of monolayers of surface contamination will appreciably reduce adhesive bond strengths (Refs. 1 and 2).

In the clean state, however, there are a host of material properties of solids which will determine adhesion forces. These properties are both bulk and surface. This observation is true for different classes of materials including metals, alloys, polymers and ceramics.

The objective of this paper is to review those properties of solids which influence measured adhesion forces both surface and bulk. The materials to be reviewed include metals, alloys, semiconductors, ceramics and polymers in single and polycrystalline form. Material properties to be examined include cohesive energy, surface energy, crystallographic orientation, crystal structure, alloying, solubility and irradiation with polymer adhesion.
When a solid surface is examined either microscopically with a 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 depiction of a surface displaying these irregularities, or asperities as they are commonly called, is presented in Fig. 1(a).

Nearly all real surfaces contain the asperities except brittle, single-crystal materials that have been cleaved along natural cleavage planes and metallic pin tips that have been field evaporated in the field ion microscope. Even with brittle materials, the cleavage process results in the generation of surfaces that contain cleavage steps, and it is only the terraces between these steps that are atomically smooth.

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 Williamson (Ref. 3).

The surfaces of the asperities are not atomically clean but contain surface films (Fig. 1(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 other adsorbates. All of the reacted and adsorbed film materials can exert a strong effect on the mechanical and metallurgical behavior of the solids to which they adhere, as indicated by the collection of papers appearing in Westwood and Stoloff (Ref. 4).

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 textured regions. These surficial layers develop when any type of finishing or polishing of the surface is done, particularly when that surface is a metal. These layers can also be a region rich in bulk impurities (Ref. 5). In amorphous solids these layers may contain voids and microcracks.

When two solids are brought into solid state contact, the real area of contact is represented by those points at which the asperities of the two surfaces engage across the interface. This is depicted schematically in Fig. 1(c).

The application of a load to the solids in contact causes initially elastic deformation of the asperities in contact in Fig. 1(c) and when the load is sufficiently high with the exceeding of the material's elastic limit, plastic deformation will occur. This is seen in the deformed surface asperities of Fig. 2.

The real area of contact between two solids is represented by the flattened areas of Fig. 2 on the tips of the asperities. It is at these locations between solids in contact that adhesion between two solids takes place.

PROPERTIES EFFECTING ADHESION

Cohesive Energy

At the atomic level the strength of solids are reflected in their cohesive energies or the strength of the interatomic bonds. The loss of material from solid surfaces by such processes as erosion will be directly
related to the cohesive binding energy of the solid. This is demonstrated in the data of Fig. 3 where the wear volume or material loss is plotted as a function of the cohesive binding energy for a number of metals.

The concept of the loss of materials from solids and cohesive energy will become relevant later in the discussion of adhesion and interfacial bond strengths. Cohesive energy becomes important because it can be used to predict where material failure will occur with dissimilar solids in contact. Further, adhesion and transfer from the eroded surface to the erodent particle on impact cause wear loss by an adhesive transfer mechanism for certain materials (Ref. 6).

Since cohesive energy reflects the bonding of an atom in the bulk it is logical to anticipate that there be a correlation between cohesive binding and surface energy. The coordination number, that is the number of like atoms to which a atom is bound at the surface of, for example, a metal will be less than in the bulk. The atoms to which it bonds will, however, be the same. Thus, for a copper (111) surface the bond coordination number to like copper atoms will be 9 while in the bulk the copper will have a coordination number of 12.

Despite a wide variation in the experimental value found for surface energy in the literature there is a correlation with cohesive energy as indicated in the data of Fig. 4. These data are taken from Ref. 7. Surface energy can be related to the adhesive behavior of such solids as metals.

If one were to take two single crystals of the same material and match planes and crystallographic directions across an interface with the surfaces in the atomically clean state interfacial atomic bonding would occur as the two surfaces come close to each other. There would be no interface and the two crystals would become one single crystal. In practice one does not achieve such perfect registry with the experimental contact devices available. Such attempts should, however, yield the maximum in measured adhesive forces for two solid surfaces in contact.

Experiments with copper single crystals with matched planes and directions indicate that adhesion is anisotropic for the metals as indicated in Table I. The high atomic density (111) plane exhibits the lowest coefficient of adhesion (adhesion bond force divided by applied load) of the three orientations of copper examined. Because the (111) is the highest atomic density it exhibits the highest modulus of elasticity as indicated in the tables and therefore would, under a given load, offer the greatest resistance to the plastic deformation seen in Fig. 2. Accordingly the real area of contact over which adhesion occurs would also be less, than for less dense planes.

The surface energy is least one of the (111) plane and therefore the energy for interaction across an interface is less than it would be for lower atomic density crystallographic planes. Adhesion is accordingly less.

From the data of Fig. 4 and from what has been said in the previous paragraph it could be concluded that those metals with low surface energies and cohesive energies would exhibit the lowest adhesive bonding. This, however, is not the case. There are two properties which will effect adhesive bond forces, surface energy and real contact area. Under a given load a greater amount of deformation will occur on contact for the low cohesive energy metals. Upon separation of the adhesive junction bond fracture must occur over a greater area. The result is that a greater total force may be required for separation of the solids. This effect can make the differences in the surface energies of the metals when measuring adhesive forces.
Crystal structure also influences adhesive bonding. A comparison of the highest atomic density, lowest surface energy planes in the face centered cubic and close packed hexagonal systems are presented in Table II for copper and cobalt. With matched poles of the two metals, the adhesion coefficient for the hexagonal close packed surfaces is appreciably less than that for face centered cubic cobalt.

When dissimilar metals are brought into solid state contact, the adhesion forces measured are less than the matched planes of the same metal as indicated in Table III. Note that the adhesion coefficient for the copper to nickel and copper to tungsten couples are the same. The reason is that the copper in both cases is the cohesively weaker material and the real area of contact is established by the deformation of the copper. On separation copper is found transferred to both the cobalt and tungsten surfaces. Thus, the adhesive forces are determined by the fracture, cohesive strength of the copper.

ADHESIVE ENERGY

Metals and Alloys

The adhesive bond strength at the interface between two dissimilar atomically clean materials is generally stronger than the cohesive bond strength of the cohesively weaker of the two materials in contact. This was experienced in the experiments giving rise to the data of Table III where copper was observed to transfer to nickel, cobalt and tungsten.

The same general type of behavior is observed for metallic alloys when the surfaces are cleaned of adsorbates and the residual surface oxides. Figure 5 is a photomicrograph through a cross section of a transferred nickel alloy wear particle to a hardened bearing steel disk. The interfacial bond strength was stronger than the cohesive bonds in the softer, cohesively weaker nickel alloy. As a consequence of the interfacial bond strength a nickel alloy particle was plucked out of the solid alloy surface.

Metals to Semiconductors

Strong adhesive bonding also occurs for metals in contact with non-metallic materials such as semiconductors. Again, strong interfacial bonding is observed for materials in the clean state. Some simply adhesion experiments were conducted with gold contacting silicon and germanium.

With gold contacting silicon the interfacial adhesive bond strength was stronger than the cohesive bonding in the gold and with separation gold remained adhered to the silicon surface. This is indicated in the photomicrograph and X-ray map for gold found in Fig. 6. The silicon cohesive bonds were therefore stronger than those of gold with gold transfer resulting.

Germanium is a semiconductor like silicon with many similar properties. It is, however, cohesively weaker than silicon and gold as well. It might therefore be anticipated that in adhesion experiments for gold in contact with germanium gold will not transfer to germanium. Further, if the interfacial bond strength between the gold and germanium is stronger than that in the germanium the germanium should transfer to gold. This is just what is observed experimentally as indicated in the photomicrographs of Fig. 7.

In Fig. 7 ceramic shaped pits are observed on the germanium (111) surface. Examination of the gold surface indicated transfer of germanium to
the gold. Thus, the interfacial adhesive bond strength was stronger than the cohesive strength in the germanium and fracture occurred in the germanium.

The data of Figs. 6 and 7 provide insight into those forces which make up the measured adhesion between the two solids. The use of cohesive binding energies such as those tabulated in Ref. 8 are extremely helpful in predicting transfer behavior.

**TYPE OF CONTACT**

**Rubbing or Sliding**

Thus far clean surfaces have been discussed where adhesion occurs on touch contact. Does adhesion between contacting solids occur in the presence of surface films. Generally, for example, when two solids are placed into contact with surface films present only very small adhesive bonding forces are measured unless the surfaces are compressed under load and asperities penetrate the contaminating films. Mechanical movement of the surfaces over one another can cause disruption of surface films and produce adhesion at relatively light loads.

When rubbing or the sliding of one surface over another takes place, frictional heating at the interface can prompt interfacial changes such as alloying. Under such conditions temperatures as high as 1500° C can be achieved (Ref. 1). Adhesive transfer can then occur via such a mechanism. Evidence for adhesive transfer by this mechanism can be seen in the micrograph and X-ray map of Fig. 8.

The micrograph and X-ray map of Fig. 8 are for an aluminum hemispherical rider specimen which was made to rub against an iron disk surface. Examination of the wear scar on the aluminum rider after rubbing revealed the presence of iron on the aluminum.

In simple adhesion experiments the cohesively weaker aluminum will transfer to iron with no evidence for the transfer of iron to aluminum. Frictional heating at the interface provides the necessary interfacial energy for alloying and the transfer observed.

**Impact**

Adhesion and adhesive transfer will also occur on simple impact between two solids even though contaminant films are present. The energy associated with the impact process can cause solid state contact, adhesive bonding and resulting transfer from one surface to another. Evidence for this type of adhesion is presented in the photomicrograph and X-ray map of Fig. 9 for a steel ball impacting a copper surface.

Figure 9(a) indicates the irregular nature of the transferred copper to the surface of the smooth steel ball. The X-ray map (Fig. 9(b)) indicates the copious amount of copper adhered to the steel surface. Again, the cohesively weaker copper is observed to transfer to the stronger steel.
Metal-Insulator Adhesion

Metal-Polymers

There is a considerable interest in the interactions of polymers with metals both from the point of view of producing adhesion in tribological applications and increasing it with polymer coatings. Just as with metals in contact with metals, strong adhesive bonds occur for polymers in contact with metals when the surfaces are clean.

Studies have been conducted in the field ion microscope containing the atom probe with polymers such as polytetrafluoroethylene (PTFE) and polyimide in contact with various metal pin specimens. Adhesive transfer of the polymer to the metal occurs with touch contact. Figure 10 is a field ion micrograph of tungsten surface after being contacted by a polyimide flat.

The rodlike structures which appear in Fig. 10 are images from polymer fragments which remain adhered to the tungsten after simple touch contact. The interfacial adhesive bonds are stronger than cohesive bonds in the polymer. With PTFE in contact with metals adhesive forces are three times the applied load. These forces reflect the polymer bond strength and that required to draw polymer fragments out of the matrix.

It might be anticipated that a correlation would exist between surface tension for polymers and their adhesive strength when in contact with metals. This is in fact observed. Recent experiments in our laboratory with polymer to metal adhesion reflect this relationship.

The data from Fig. 11 indicates the correlation between adhesive strength and surface tension for three polymers in contact with two metals, gold and nickel. First, there is an obvious relation between adhesive strength and surface tension. Secondly, adhesion strength is greater for all three polymers in contact with the higher surface energy metal, nickel. Since the polymers are deforming with applied load, the surface energy relationship would be analogous to that observed in Table I, where the higher energy metal surface exhibits the greater adhesion forces.

When polymers are in contact with metals, their adhesive interfacial bond strengths can be altered with some metals by such polymer altering treatments as irradiation. This effect can be seen in the data of Fig. 12.

In Fig. 12 while irradiation does not markedly effect the adhesion of PTFE to gold it has a pronounced effect on the polymer's adhesion to nickel. Thus, this may be a technique which can be used to strengthen the polymer to metal interfacial bond.

Metal-Ceramic

Strong adhesive bonding is observed for metal to both oxide and non-oxide ceramics (Ref. 2). A correlation between adhesive bond strength and the percent d valence bond saturation for the transition metals has been found to exist. The greater the degree of d bond saturation the less is the adhesive binding force.

Silicon carbide is a material of considerable practical interest. Experiments were conducted with various transition metals in sliding contact with the (0001) surface of silicon carbide. The adhesive interaction effects of two metals rhodium and titanium are presented in the micrographs of Fig. 13. With rhodium, a metal with a high degree of d valence bond saturation, the interfacial adhesion is strong enough to cause in addition
to metal transfer to the silicon carbide, the development of fracture cracks along the (1010) planes (Fig. 13(a)). Titanium, a metal with less a percent of d valence bond saturation, bonds so strongly to the silicon carbide that not only does titanium transfer to silicon carbide but subsurface fracture along (0001) cleavage planes of the silicon carbide occurs.

Both the metals and silicon carbide of Figs. 13(a) and (b) undergo damage as a result of the adhesive interfacial bonding. It is more severe with titanium. Wear debris from both materials are found on the surface.

ADHESION TO DIAMOND

Metal to Diamond

The most resistant material to deformation is diamond. Therefore the effect of asperity deformation on interfacial adhesion should be minimal with this material. Further, diamond is generally not thought of as a reactive surface. When, however, a metal such as titanium is brought into contact with diamond strong adhesive bonding occurs between the metal and the diamond surface. The adhesive bond is sufficiently strong that when tangential motion is attempted shear occurs in the metal with metal remaining transferred to the diamond. This is demonstrated in the photomicrograph of Fig. 14 where titanium is seen to have transferred to the diamond (111) surface.

Static friction coefficient (μ) is a relatively good measure of the adhesive bond forces that develop at an interface between two solids in contact. The stronger the interfacial adhesive bonding the greater is the resistance to initiate tangential motion, or the static friction. Studies with diamond and copper contacts indicate that adhesive bonding at the interface between these two materials can be related to the metal conduction band electrons and the band gap states on the diamond surface. Surface electrical conductivity is effected as well (Ref. 9).

In the absence of annealing the diamond polished surface exhibits no measurable surface adhesion. With annealing, however, the surface exhibits both occupied and unoccupied surface states in its electronic structure. Further, the annealed surface exhibits some electrical conductivity (Ref. 9).

The data of Fig. 15 present the static friction coefficient for copper in contact with diamond at various temperatures. With increases in annealing temperature in the range of from 750 to 900° C, there is an increase in friction coefficient, reflecting an increase in adhesion, and the appearance of unoccupied surface states in the band gap. This correlation was observed both for the (111) and (110) surfaces of diamond.

Diamond's surface is normally covered with hydrogen. Therefore exposure to hydrogen in Fig. 15 in the excited state causes a decrease in interfacial bonding, adhesion and accordingly static friction.

The data of Fig. 15 can be directly correlated with band gap state of the diamond surface. This has been done in Ref. 9.

SUMMARY RESULTS

From the data presented for the adhesive behavior of materials in solid state contact some general remarks can be made. First both the physical or
topographical as well as the chemical nature of surfaces must be considered in understanding adhesion between two solids.

When dissimilar materials are in solid state contact, the adhesive bond at the interface is generally stronger than the cohesive bonds in the cohesively weaker of the two materials and fracture occurs in the weaker material on separation. This is observed for metals, alloys, semiconductors, ceramics, and polymers.

Mechanical interfacial activity such as rubbing or sliding supplies sufficient interfacial energy to produce such effects as surficial alloying which results in the transfer of both materials.

Treatments of materials such as the irradiation of polymers can increase interfacial adhesive bonding. This has been observed for such polymer as PTFE when in contact with certain metals.

With ceramics the adhesive bonds that develop at the interface with metals are sufficiently strong so as to result in subsurface fracture in the ceramic on separation of the materials. With tangential motion transfer of metal to the ceramic and fracture in the ceramic occurs. The damage to the ceramic depends upon the metal in contact with the ceramic. For the transition metals the greater the degree or percent of d valence bond saturation the less the adhesion and, accordingly, damage to the ceramic.

Metals adhere very strongly to diamond and the adhesive bond strength can be directly related to the band gap state of the diamond surface.

REFERENCES


### TABLE I. - PROPERTIES OF SINGLE AND POLYCRYSTALLINE COPPER (99.999 PERCENT)

<table>
<thead>
<tr>
<th>Copper form and orientation (matched planes and direction)</th>
<th>Young's modulus, $10^3$ dynes/cm²</th>
<th>Adhesion coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystal (100)</td>
<td>6.67</td>
<td>$&gt;130$</td>
</tr>
<tr>
<td>Single crystal (110)</td>
<td>13.1</td>
<td>50.0</td>
</tr>
<tr>
<td>Single crystal (111)</td>
<td>19.4</td>
<td>10.5</td>
</tr>
<tr>
<td>Polycrystal</td>
<td>12.0</td>
<td>100</td>
</tr>
</tbody>
</table>

### TABLE II. - COEFFICIENTS OF ADHESION COPPER AND COBALT SINGLE CRYSTALS IN VACUUM ($10^{-11}$ torr) (50 GMS)

<table>
<thead>
<tr>
<th>Metal couples, matched poles</th>
<th>Adhesion coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (111) (110)</td>
<td>10.5</td>
</tr>
<tr>
<td>Cu (111) (110)</td>
<td></td>
</tr>
<tr>
<td>Co (0001) (1120)</td>
<td>$&lt;0.05$</td>
</tr>
<tr>
<td>Co (0001) (1120)</td>
<td></td>
</tr>
</tbody>
</table>
TABLE III. - COEFFICIENT OF ADHESION FOR VARIOUS SINGLE CRYSTAL METAL COUPLES IN VACUUM (10^{-11} torr)
(50 GMS)

<table>
<thead>
<tr>
<th>Metal and couples orientations</th>
<th>Adhesion coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (111)</td>
<td>10.5</td>
</tr>
<tr>
<td>Cu (111)</td>
<td></td>
</tr>
<tr>
<td>Cu (111) [1TO]</td>
<td>2.0</td>
</tr>
<tr>
<td>Ni (111) [1TO]</td>
<td></td>
</tr>
<tr>
<td>Cu (111) [1TO]</td>
<td>0.5</td>
</tr>
<tr>
<td>Co (0001) [1120]</td>
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<tr>
<td>Cu (111) [110]</td>
<td>0.5</td>
</tr>
<tr>
<td>W (110) [111]</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. - Surface topography and contact.
Figure 2. - Deformed surface asperity as a result of loading beyond the material elastic limit.

Figure 3. - Erosive wear resistance as a function of cohesive binding energy of some elemental metals. Glass beads; impact time, 10 sec; impact pressure, 560 kPa; distance, 5 mm.
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Figure 5. - Adhesion and transfer of one alloy to another.
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(b) ACu Kα x-ray emission map of the region shown in (a).

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Figure 14. - Replication electron micrograph of wear track on \{111\} diamond surface. Single pass of titanium rider; sliding direction, <1\bar{1}0>; sliding velocity, $3 \times 10^{-3}$ m/min; load, 0.2 N; room temperature; vacuum pressure, $10^{-8}$ Pa.
Figure 15. - Copper-diamond static friction coefficient as a function of diamond annealing temperature.
The Role of Material Properties in Adhesion

When two solid surfaces are brought into contact strong adhesive bond forces can develop between the materials. The magnitude of the forces will depend upon the state of the surfaces, cleanliness and the fundamental properties of the two solids, both surface and bulk. Adhesion between solids is addressed from a theoretical consideration of the electronic nature of the surfaces and experimentally relating bond forces to the nature of the interface resulting from solid state contact. Surface properties correlated with adhesion include, atomic or molecular orientation, reconstruction and segregation as well as the chemistry of the surface specie. Where dissimilar solids are in contact the contribution of each is considered as is the role of their interactive chemistry on bond strength. Bulk properties examined include elastic and plastic behavior in the surficial regions, cohesive binding energies, crystal structure, crystallographic orientation and state. Materials examined with respect to interfacial adhesive interactions include metals, alloys, ceramics, polymers and diamond. They are reviewed both in single and polycrystalline form. The surfaces of the contacting solids are studied both in the atomic or molecularly clean state and in the presence of selected surface contaminants.