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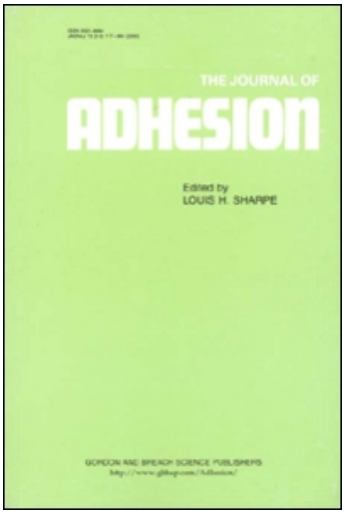

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Effect of Various Properties of FCC Metals on Their Adhesion as Studied with LEED

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Effect of Various Properties of FCC Metals on Their Adhesion as Studied with LEED

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ABSTRACT

The forces of adhesion for various face-centered-cubic metals after surface contact were measured. Surfaces were examined with LEED before and after contact to determine nature of surface changes resulting from adhesive contact. The results of the study indicate that elastic properties of metals can be related to cohesion, adhesion and the character of surface transfer with adhesion. LEED indicated that, for some material pairs studied, epitaxial transfer may occur. It was also found that the addition of a small concentration of alloying element (aluminum to copper in this study) markedly increased adhesion. Surface orientation was observed to have substantial influence on adhesive force. With gold contacting copper, the force of adhesion to the (100) surface of gold was in the following order for the various copper orientations: (110) > (100) > (111). The amount of metal transferred from one surface to another was found to be related to applied force of adhesion.

1. INTRODUCTION

THE ADHESION BEHAVIOR of metals in contact is extremely important to the fields of lubrication and electrical contacts. Friction coefficients, for example, of metals are to a large part governed by the adhesion properties of the metals in contact. Further, one of the most significant types of wear to mechanical devices is adhesive wear.

The results of many studies have shown that when clean metal surfaces are brought into contact, very strong bonding will occur [1-8]. Studies on the cohesion of metals have revealed that many properties may be related to the ability of metals to cohere [9-10]. Very little has been done, to gain a fundamental understanding of adhesion, that is, where dissimilar metals make contact. Some adhesion measurements have, however, been made on the surfaces studied with LEED for nickel [11], and rhenium [12] in contact with various materials.

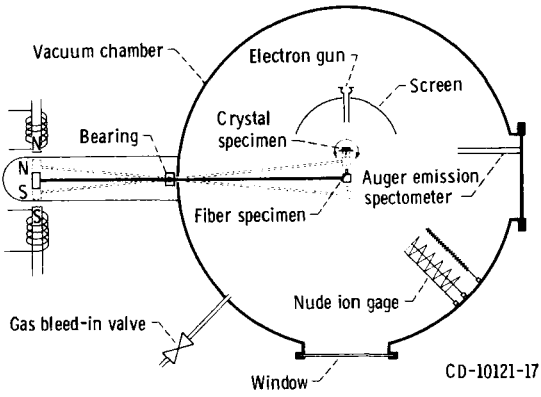

Figure 1. Low energy electron diffraction (LEED) adhesion apparatus.

The objective of this paper was to explore the influence of various properties of face-centered-cubic metals on their ability to adhere. Some of the properties examined included: (1) influence of orientation, (2) alloying, and (3) those properties which are related to cohesion of metals, namely, melting points, heats of sublimation, and elastic moduli. LEED was used to aid in the study of solid metal surface interactions. Metal surfaces were examined with LEED before and after adhesive contact. Experiments were conducted with crystals of gold, copper, nickel, silver, aluminum and copper-aluminum alloys. The adhesion experiments were conducted in the LEED apparatus after the metal surfaces had been cleaned at ambient pressures of 1.0×10^{-11} to 1.0×10^{-10} torr. In the experiments, a 1-mm diameter flat-ended cylinder contacted a larger crystal flat under various forces from 20 to 300 dynes. Contact times varied from 1 to 6000 seconds.

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2. MATERIALS

The crystals used in this investigation were grown from triple zone refined metals. The specimens were cut from single crystal rods. The specimens examined by LEED were approximately 8.0-mm diameter rods and were cut to a thickness of 6.0 mm. The flats were polished on abrasive papers (to 600 grit) and then electropolished in orthophosphoric acid to remove the worked layer. The gold crystals were electropolished in an aqueous solution of nitric and hydrofluoric acids. X-ray Laue technique was used to check orientations. The 1-mm diameter flat-ended cylindrical crystals which contacted the crystal surface examined by LEED were processed in essentially the same manner.

3. APPARATUS

The apparatus used in these studies is shown schematically in Figure 1.

The single crystal surface mounted in the center of the chamber could be rotated 360 degrees. This rotatability allowed for the making of adhesion measurements on the crystal surface shown in Figure 1, then rotating the crystal 180 degrees and obtaining a LEED pattern from the crystal surface in the adhesion contact area. The crystal could also be moved in the lateral and vertical directions.

An Auger Electron Spectrometer was located in the apparatus as shown in Figure 1. It is used to monitor the presence of transferred material as well as for determination of surface contaminants. Crystal surfaces can be examined before and after adhesive contact with Auger as well as LEED analysis of the surface.

The crystal specimen was supported in the chamber by means of two metal rods (insulated) which were used to resistance heat the crystal. A 100-ampere A.C. power supply was used for resistance heating.

The 1-mm diameter flat-ended fiber, which contacted the single crystal metal surface was mounted in a stainless steel holder which was in turn, mounted to a 1.5-mm diameter stainless-steel beam. The beam was mounted in a bearing containing yoke. At the end of the beam beyond the pivot point, and opposite the fiber specimen was a small permanent magnet. Outside the chamber wall were two electromagnets. The permanent magnet and electromagnets were positioned in such a manner as to have like poles facing each other. A variation in the current applied to the magnets could be used to move the beam.

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The current applied to the electromagnets was calibrated in terms of the force applied in the adhesion experiments. Load applied to the surfaces in contact was measured by current, as was the force required to separate the crystal surfaces.

The LEED electron optics and the vacuum system were of the standard type used by those engaged in LEED studies and is adequately described in the literature [13].

The basic LEED system was obtained commercially. The electron optics was of the Varian three grid type. The beam diameter was 0.6-mm. The vacuum system consisted of vacsorb pumps, an ion pump and a sublimation pump. The system pressure was measured with a nude ion gage and all experiments were conducted with the vacuum system in the range of pressures from 1.0×10^{-11} to 1.0×10^{-10} torr. No cryopumping was used.

4. EXPERIMENTAL PROCEDURE

The crystal specimens were mounted in the apparatus and, after pump down and bakeout, the crystals were heated to and held at 500°C for three hours to allow for thorough outgassing. The temperature was decreased to 450°C and hydrogen gas was admitted to the chamber to remove oxygen or

reduce surface oxides. With nickel, oxygen was admitted prior to hydrogen to burn carbon off the surface. Sufficient gas was admitted to raise the pressure to 10^{-6} torr. After fifteen minutes, the system was reevacuated to 10^{-10} torr. The crystal was then heated to 500°C to remove hydrogen. Pressure in the chamber after hydrogen removal and subsequent cooling of the crystal to room temperature was 1.0×10^{-11} to 1.0×10^{-10} torr. LEED patterns were then obtained from the clean surface.

The copper and copper-aluminum alloys were mounted in tantalum holders. The gold specimen was cleaned by contacting the cylindrical side of the gold cyrstal near the contacting flat with the tantalum specimen holder containing the copper alloy specimen. The crystals were heated by resistance heating of the tantalum.

The aluminum crystal surfaces were cleaned by heating the crystal to 600°C and holding it at this temperature for 72 hours to allow for the oxygen to diffuse into the metal. Cleaning by this technique has been found equally effective to ion bombardment [14]. It was used herein in preference to ion bombardment because it does not disturb the surface topography as ion bombardment is known to do.

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5. EXPERIMENTAL RESULTS

Orientation Effects:

Experiments were conducted with (100) surface of gold contacting three planes of copper, (110), (100) and (111), to determine if orientation of the copper exerted an influence on adhesive forces.

The LEED pattern for a clean (111) copper surface is shown in Figure 2(a). Figure 2(b) shows that same surface after having been contacted by the gold specimen and the surfaces separated. Examination of the LEED pattern in Figure 2(b) reveals the presence of an additional set of diffraction spots overlaying those for copper (111). These spots are believed to result from an epitaxial layer of gold on the copper (111) surface. The presence of gold was substantiated by auger analysis of the surface layer.

Table 1 presents the force required to separate gold from the (111) copper surface along with other properties of this plane as well as for the (100) and (110) planes. The force required to separate the surfaces (80 dynes) was four times the force applied (20 dynes) in making adhesive contact. It can also be seen from Table 1 that the (111) plane is atomically the most dense plane, having the highest coordination number and as might be anticipated from these other two properties, the highest elastic modulus.

When the surface shown in Figure 2(b) was heated to 500°C for 30 minutes, the pattern of Figure 2(c) was obtained. The pattern has changed sufficiently so that only two diffraction spots are readily discernible.

When the load applied to the gold in contact with the copper surface was

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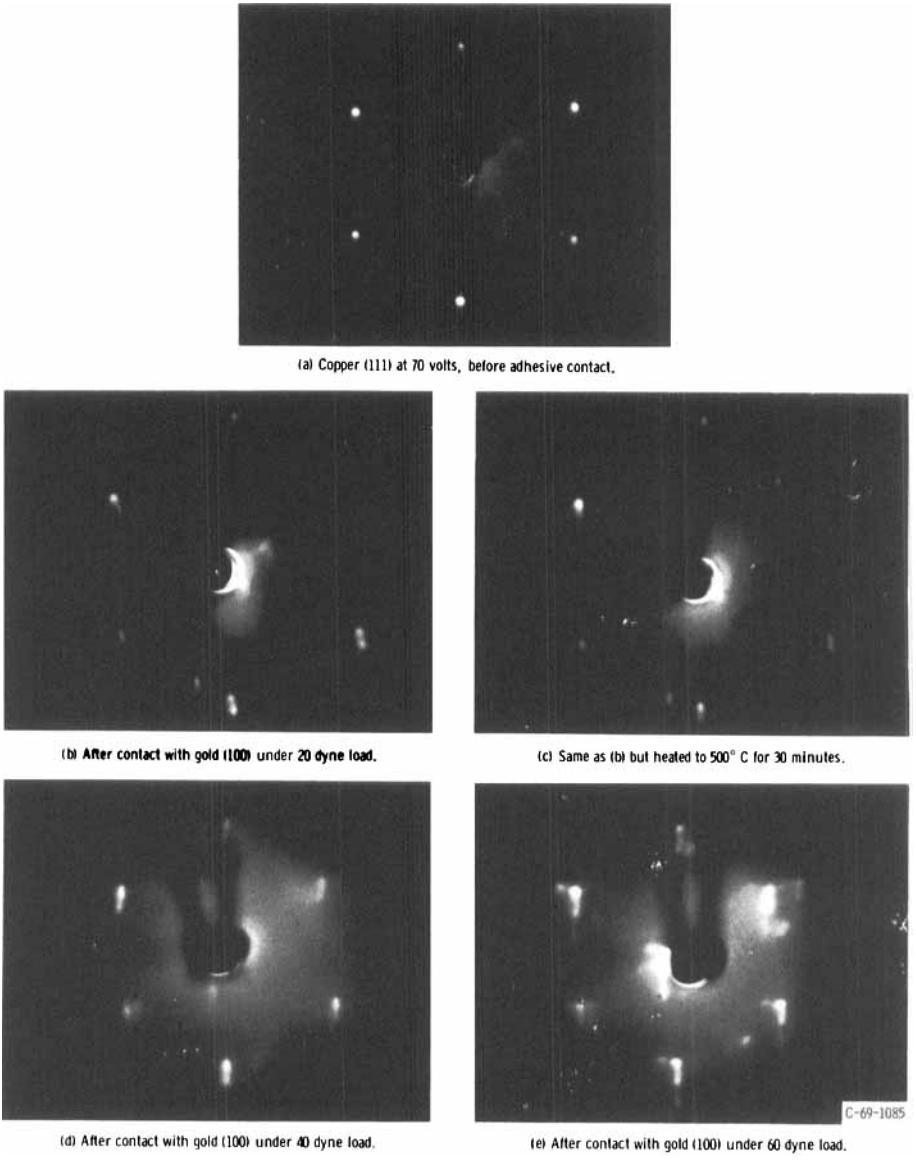
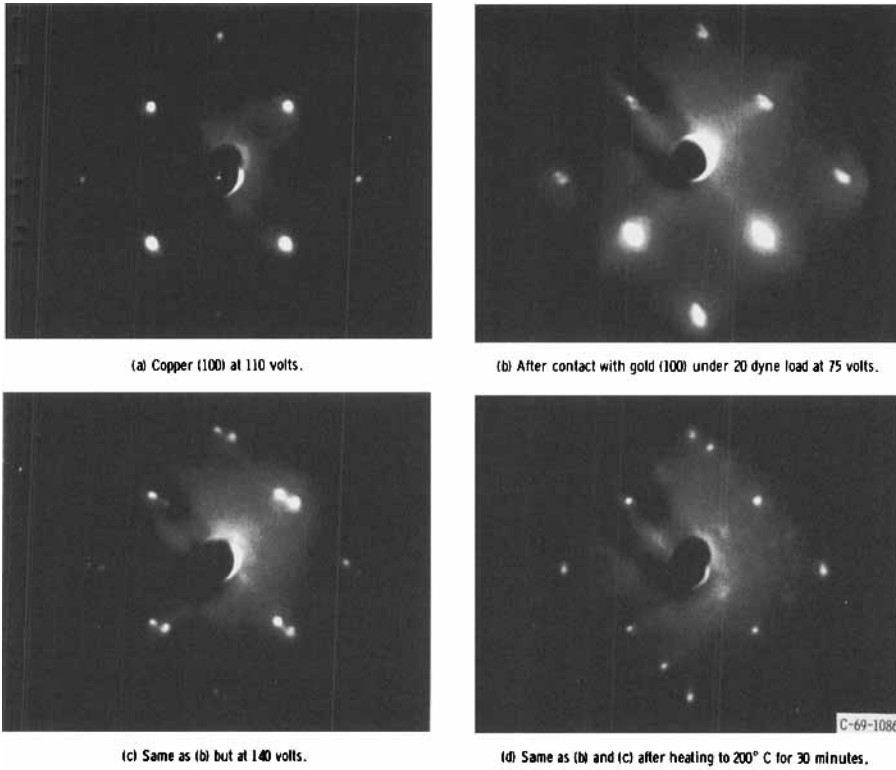


Figure 2. LEED photographs of copper (111) surface before and after adhesive contact with gold (100) surface.

increased to 40 dynes, the pattern of Figure 2(d) was obtained. A further increase in the load to 60 dynes resulted in the pattern of Figure 2(e). An increase in adhesive force required to separate the surfaces was measured and this increase in force reflects an increase in the amount of gold transferred to the copper surface. With an increase in load there is an increase in true contact area and consequently an increase in the amount of copper to



(a) Copper (100) at 110 volts.

(b) After contact with gold (100) under 20 dyne load at 75 volts.

(c) Same as (b) but at 140 volts.

(d) Same as (b) and (c) after heating to 200° C for 30 minutes.

Figure 3. LEED photographs of copper (100) surface before and after adhesive contact with gold (100) surface.

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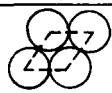
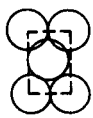
Table 1. Some Properties of Three Planes of Copper Together with Measured Adhesive Forces to Those Planes

Copper surface plane	Coordination number of surface	Atomic arrangement of surface unit mesh	Number of surface, atoms /cm^2	Elastic modulus, dynes/cm^2	Surface energy ergs/cm^2 ref. [33]	Force of adhesion to gold,[a] mg
(111)	9		1.7×10^{15}	19.4×10^{11}	$\frac{\gamma(111)}{\gamma_{max}} = 0.974$	80
(100)	8		1.5×10^{15}	6.67×10^{11}	$\frac{\gamma(100)}{\gamma_{max}} = 0.983$	185
(110)	7		1.1×10^{15}	13.1×10^{11}	$\frac{\gamma(110)}{\gamma_{max}} = 0.996$	390

[a]Applied load, 20 mg; Au (100) surface; contact time, 10 seconds.

gold bonding. Since the gold bonds are weaker than the copper to gold adhesive bonds or copper cohesive bonds more fracture occurs in the gold. While gold was found transferred to the copper surface in the adhesion experiment conducted in the apparatus shown in Figure 1 at high loads sufficient gold transferred to the copper surface to permit an independent electron microprobe analysis of the copper surface which substantiated the presence of gold on the copper surface.

A LEED pattern obtained for clean (100) copper surface is presented in Figure 3(a). Adhesive contact with gold resulted in the pattern of Figure 3(b). The pattern is difficult to resolve. If the voltage is increased to 140 volts on the electron gun, the pattern of Figure 3(c) was obtained. It shows, again, a doubling of spots indicative of epitaxial adhesion of gold to copper.

The diffraction patterns indicating epitaxial adhesion of gold to copper are similar to those observed in Ref. 15 with copper deposited on tungsten. Taylor in Ref. 15 interpreted the pattern as epitaxial adherence. In this investigation asterism and polygonization can be discounted as explaining the patterns because at the loads used in this investigation, with oxygen present on the surface which reduces metallic adhesion but does not alter the stress applied to the surface, double diffraction spots were not observed. Asterism or polygonization will result from the applied stress associated with the load and should occur in the presence or absence of oxygen. Faceting can be eliminated because scanning the contact zone in both the vertical and horizontal direction revealed the double set of diffraction spots to exist only in the contact zone. It appears unlikely that faceting would occur only in this area.

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When the surface of Figure 3(c) was heated for 30 minutes at 200°C, the pattern of Figure 3(d) was obtained. The pattern of Figure 3(d) indicates mobility of the gold on the copper surface appreciably greater than that seen in Figure 2(c) for the (111) plane at 500°C.

The pattern of Figure 3(d) appears to reflect a rearrangement of the copper and gold on the surface with the formation of an alloy. Palmberg and Rhodin [16] observed with vapor deposition of gold on the (100) surface of copper the formation of an ordered CuAu alloy. In the study reported herein, it appears additional energy is required to bring about surface rearrangement to the CuAu structure because of the solid state contact.

The force of adhesion of gold to the (100) surface of copper is presented in Table 1. For a 20 dyne applied force, the force required to separate the surfaces (185 dynes) was nine times that applied to the surfaces in contact. The force to separate the gold from the (100) copper surface was twice what it was to separate gold from the (111) surface. Thus, orientation appears to exhibit a marked influence on adhesion.

Adhesion experiments were also conducted with the (110) surface of copper contacting the (100) surface of gold. The results were similar to that observed with the (111) and (100) surfaces of copper contacting gold,

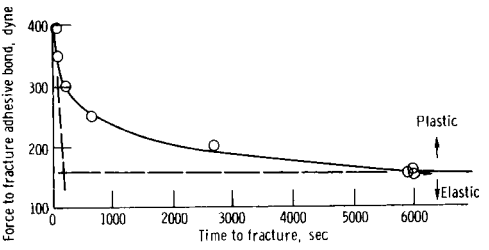

Figure 4. Time required to rupture cohesive bonds in gold. Adhesion of gold (100) to copper (110). Applied load, 20 dynes; contact time, 10 seconds; ambient pressure, 1 × 10^{-10} torr and 20°C.

namely, the gold adhered to the (110) surface of copper in an epitaxial manner. The LEED patterns obtained in this investigation are very similar to those observed by Taylor in a study of epitaxial growth of copper on tungsten [15].

The force of adhesion of gold was greatest on the (110) plane of copper as shown by the data of Table 1. On the (110) surface, a force of 390 dynes or nearly twenty times that of the applied force was measured. Table 1 indicates that the plane with the smallest coordination number and least number of surface atoms gave the highest force of adhesion. The adhesive force of gold to the least atomically dense plane of copper (110) was nearly five times that of what it was to the most atomically dense plane (111).

Some experiments were conducted to determine the time required to separate the gold from the copper surface. Since gold was identified as adhered to copper in these experiments, this consisted essentially of a tensile test on the gold. The results obtained in some of these experiments are presented in Figure 4. The force to fracture the gold is plotted as a function of time to fracture. At 390 dynes, the specimen surfaces separated very rapidly as indicated by Figure 4. As the force was decreased, the time to fracture increased. At tensile forces less than 160 dynes, no fracture of the adhered pair was obtained at times up to 6000 seconds.

At forces less than that required for fracture, the tensile stress must be below the elastic limit of the weakest region in the couple and fracture will not occur. If the stress is increased to a value where the junction area will yield plastically, fracture and separation occurs after some period of time. Figure 4 shows the intercepts of the elastic and plastic regions of the curve. From Figure 4 it can be said that, at tensile forces in excess of 160 dynes, the gold below the surface contact in the microjunctions is behaving plastically while at loads less than 160 dynes, it is elastic.

The elastic limit of gold is well known. From the intercept value of Fig. 4, it should be possible to determine real contact area. Such a determination yields a contact area 1/85th that of the apparent area. It must be stressed

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that the yielding and fracture are, in view of the LEED patterns, occurring in the outermost atomic layers and the terms as used herein are not the same as apply to bulk behavior.

Measurements of the quantity of gold on the copper surface indicated that the concentration of gold on the copper surfaces was (110) > (100) > (111). Thus, the amount of gold transferred to the copper surface was related to the adhesive forces measured on these three planes (see Table 1). It might be anticipated that the amount of gold transferred would relate directly to adhesion forces since gold cohesive bonds are being broken. The greater the degree of bonding across the interface, the higher the adhesive force or force to fracture and the greater the amount of gold left adhered to the copper.

In these experiments there was no evidence in the LEED patterns of lattice strain in the copper. Some experiments were conducted in which the gold (100)-copper (100) couple was reversed, that is a 1-mm diameter copper flat contacted a larger (100) gold surface. The gold surface was examined after adhesive contact with LEED. Patterns revealed considerable strain in the gold surface as a result of adhesive contact. Thus, while copper was not straining, the gold lattice was undergoing strain. This strain occurred at forces considerably below those required for strain in the bulk.

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Alloying:

LEED and other surface studies have established that small concentrations of impurities in metals can markedly alter the character of a surface. Some experiments were therefore conducted to determine the influence of an active metal, aluminum, on the adhesion behavior of copper to gold. Rather than orientation, the variable is now aluminum content in copper. In these experiments the aluminum content in the copper was varied from 0.1 to 10 atomic percent. The orientation of both the gold and copper-aluminum alloys was the same, namely, their (111) surfaces.

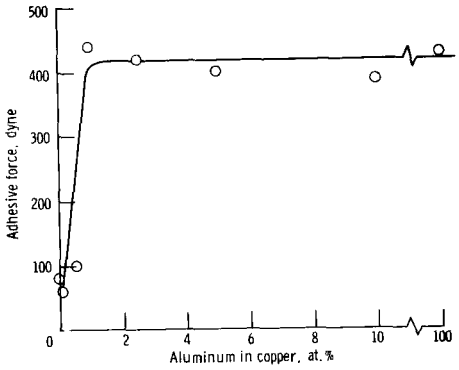

Figure 5. Adhesion force of (111) gold to the (111) surface of copper, aluminum and various aluminum in copper alloys. Initial applied load, 20 dynes; contact time, 10 seconds.

The data of Figure 5 indicate the force required to separate the gold specimen from aluminum, copper, and copper containing various atomic percent aluminum. At zero, 0.1 and 0.5 atomic percent aluminum, the force to fracture the contact was 100 dynes or less. When however, the aluminum content in the copper was increased to 1.0 atomic percent, a marked increase in adhesive force occurred.

Further increase in the aluminum content in the copper from 1.0 to 2.5,

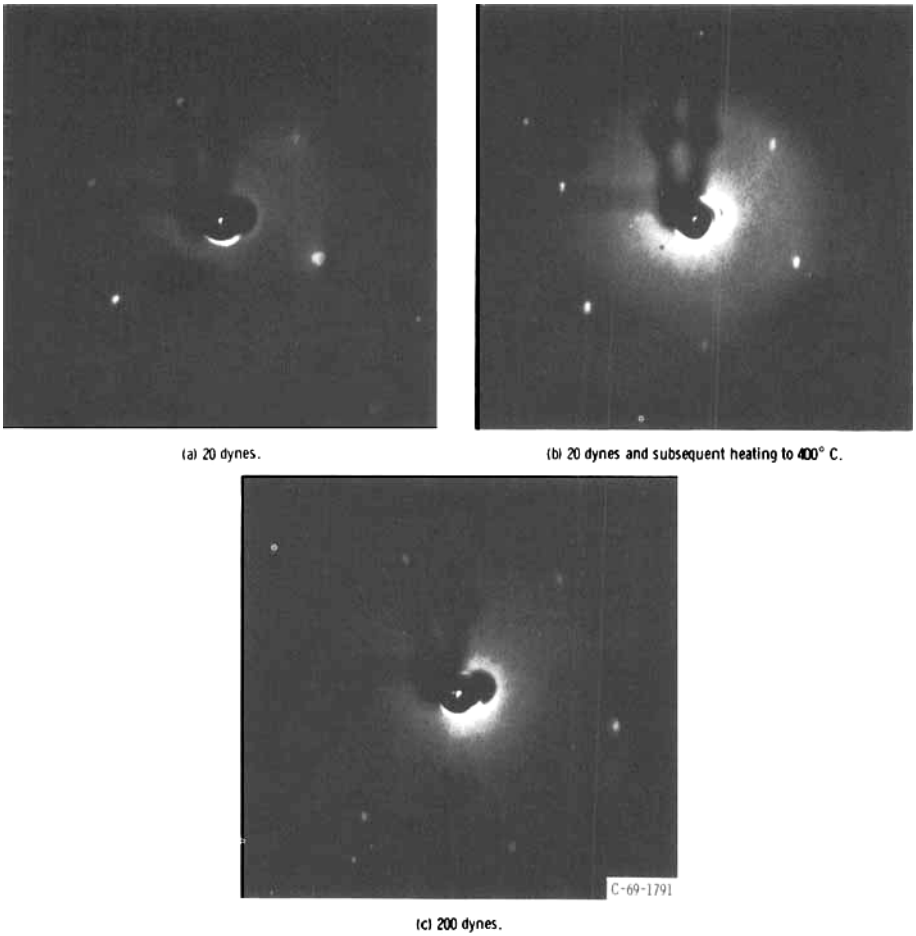

Figure 6. LEED patterns of surface of 2.5 atomic percent aluminum in copper alloy after contact with gold at two loads.

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5.0, and 10.0 percent aluminum resulted in adhesive forces comparable to that obtained with the 1.0 percent aluminum in copper alloy, Figure 5. The forces to separate the surfaces were approximately twenty times the applied load.

The LEED photographs of Figure 6 indicate the effect of adhesion on the surface structure of the 2.5 percent aluminum in copper. Figure 6(a) shows the pattern of the surface after adhesive contact with gold under an applied force of 20 dynes. The diffraction spots are slightly elongated. After the surface represented in Figure 6(a) was heated to 400°C for 5 minutes, the pattern of Figure 6(b) resulted. Examination of Figure 6(b) reveals the presence of a double set of diffraction spots. Figures 6(a) and (b) indicate then that while gold initially adheres epitaxially (with the gold taking on the 2.5

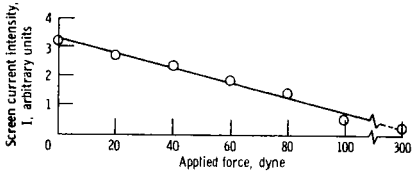

Figure 7. LEED screen current intensitv as a function of contact load for a (111) surface of gold contacting a (111) surface of a 5.0 atomic percent aluminum in copper alloy. Beam voltage, 23 volts.

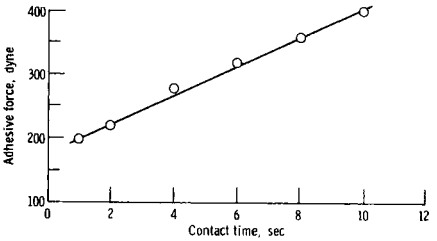

Figure 8. Effect of contact time on the adhesion of gold (111) surface to a 5.0 percent aluminum in copper alloy (111) surface. Applied load, 20 dynes.

percent aluminum in copper lattice), the addition of sufficient energy by heating will bring about rearrangement of the gold toward the development of its own lattice characteristics.

As was true with copper the presence of an adsorbed layer of oxygen on the alloy surface reduced adhesion and metal transfer but did not produce a doubling of diffraction spots. If the double diffraction spots were due to polygonization it would be anticipated that it should occur in the presence or absence of oxygen. Further, etching of the crystal surface after the experiment did not reveal the presence of any subboundaries.

The difference in lattice spacing shown in Figure 6(b) could be achieved without heating by simply increasing the contact load of gold to copper. Figure 6(c) represents the 2.5 percent aluminum in copper surface after gold had contacted under a load of 200 dynes. There were two interesting observations made from Figure 6(c); the first was that a difference in the gold and copper alloy lattice exists. This is what was essentially achieved under a 20 dyne load in Figure 6(a) only after heating (Figure 6(b)). Thus, apparently the energy associated with the higher load appears to bring about the lattice change without the necessity of heating the surface. The second observation is that, even at loads as high as 200 dynes, no noticeable strain appears to take place in the 2.5 percent aluminum in copper. This observation is in keeping with those made in earlier studies that the cohesively weaker metal, in this case gold, is straining under load.

While LEED patterns of Figure 6 indicate the presence of gold on the alloy surface, they give no indication of the quantity being transferred and its distribution. Figure 7 is a plot of the current intensity produced on the LEED screen by the diffracted electrons. With an increase in load, an inverse relation to screen current intensity is seen. This in essence indicates that as the load is increased, the amount of gold transferred to the alloy surface continues to increase. The amount of transferred gold appears to be a linear function of applied load.

The transfer of gold to the copper surface is not uniform over the copper

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surface and in various regions clusters of gold appear. As the load is increased the number of these clusters increase as well as the amount of gold in them. This gives rise to a decrease in coherent diffraction from the copper surface.

The adhesion force measured for metals in contact is frequently a function of contact time; the longer the time in contact, the greater the force required to separate the surfaces. This was demonstrated in Ref. [1] for copper crystals in contact. The adhesion force as a function of contact time was therefore measured for gold in contact with the 5.0 atomic percent aluminum in copper and the results obtained are presented in Figure 8. The results of Figure 8 indicate that, even for relatively short contact times, marked difference in adhesion forces can be measured with variations in contact time.

Variation in Metal Couple Components:

The data obtained with the adhesion of gold to copper and to copper-aluminum indicates that gold adheres to copper, not copper to gold. In order to determine if this type of behavior would occur with other dissimilar metal couples in contact, a series of experiments were conducted with various face-centered-cubic metals in contact. The results obtained are presented in Table 2. The table indicates that, in general, one metal will transfer to another when the surfaces are clean. Thus, the cohesive bonding in one of the two metals in contact is weaker than both the cohesive bonding in the other and the adhesive bonding at the interface.

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Table 2. Metal Transfer Observed in this Investigation in the Adhesion of Face-Centered-Cubic Metals

Metal couple	*Metal which transferred to the other surface*
1. Orientation effects	
(100) Au to (100) Cu	Au
(100) Au to (110) Cu	Au
(100) Au to (111) Cu	Au
2. Effect of alloy constituents	
(111) Au to (111) Cu-Al alloys (0.1 to 10 atomic % Al)	Au
3. Other dissimilar metal pairs	
(111) Au to (111) Ni	Au
(111) Ag to (111) Ni	Ag
(111) Cu to (111) Ni	Cu
(111) Al to (111) Ni	Al
(111) Au to (111) Ag	Ag
(111) Au to (111) Al	Al
(111) Pt to (111) Al	Al

6. DISCUSSION

In all the data presented herein, adhesive bonding of dissimilar metals at the interface was stronger than cohesive bonding in one of the two metals in contact and fracture of the contacting adhered pair occurred subsurface in one of the metals.

A consideration of the bond strengths, in gold, in copper, and in the gold-copper interface might provide some insight into where fracture might occur. Reference [17] give equations for such bond force calculations. The equation for cohesion is:

$$\sigma \text{ cohesion} = \frac{<C_{11}>}{\beta}$$

where:

σ cohesion = cohesive strength in dynes/cm^2
C_{11} = average elastic stiffness
β = constant

and:

$$<C_{11}> = \frac{\left(C_{44} - \frac{d}{5}\right)(2C_{12} + C_{11})}{\left(C_{44} + C_{12} - \frac{d}{5}\right)}$$

where:

$d = 2C_{44} + C_{12} - C_{11}$
C_{44}, C_{12} and C_{11} are elastic constants.

If the appropriate values for copper and gold are substituted into the equations, it is found that the cohesive strength for copper is 2 x 10^{11} dynes/cm^2. For gold the cohesive strength is 4.73 x 10^{10} dynes/cm^2. Thus, it should be easier to break the gold bonds. Using elastic constants for copper-gold alloy which forms at the interface, an adhesive bond force of 5.72 x 10^{10} dynes/cm^2 is obtained. From a theoretical consideration of bond forces, it might therefore be anticipated that the weakest bonding would occur in the gold. This agrees with the experimental observations reported herein.

The two basic physical properties of metals which reflect their cohesive strength are heats of sublimation and melting point. These two physical properties are related to the one single mechanical property of metals which reflects the cohesive bond strength of metal, the elastic moduli in Figure 9. All of the metals in Figure 9 are face-centered cubic. It can be seen that a relation between the physical properties, heats of sublimation and melting point, exist with the elastic modulus. From Figure 9, it might then be anticipated that, where two dissimilar face-centered-cubic metals are in contact, the metal with the lower elastic modulus would adhere to the higher elastic

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modulus material because it has the lower cohesive strength. The assumption made is that the alloy or compound formed at the interface has a higher elastic modulus than the cohesively weaker of the two parent metals. This assumption is generally valid since most compounds and alloys are most resistant to deformation than their parent metals [17].

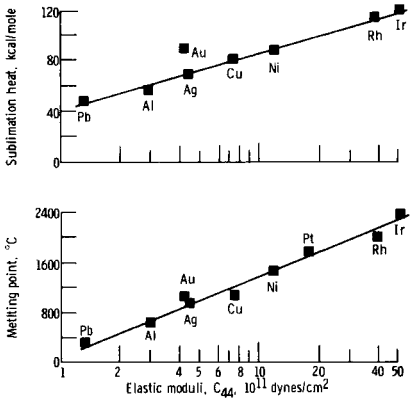

Figure 9. Heat of sublimation and melting point of various face centered cubic metals related to elastic moduli.

If Table 2 is now examined in light of Figure 9, it can be seen that for each metal couple in Table 2, the metal with the lower elastic modulus remained adhered to the metal with the higher elastic modulus. Thus, from the experimental results of Table 2, it should be possible from Figure 9 to predict which of two surfaces in contact will undergo attrition.

Another property which is related to cohesion and directly to the forces required to separate surfaces is the surface energy or the energy required to separate the face-centered-cubic lattice into two halves. In the adhesion experiments, it would be the energy required to generate the new surface in the cohesively weaker of the two metals. The surface energy for the face-centered cubic metals is related to their elastic moduli. Surface energy values in general are difficult to measure, and from representative values found in the literature the following relation for surface energy to elastic modulus was found.

$$\left.\begin{array}{l}\text{Surface energy (ergs/cm}^2\text{)} \\ \text{Elastic moduli (dynes/cm}^2\text{)}\end{array}\right\} Pt > N_i > Cu > Au > Ag > Al > Pb$$

The relative surface energy relation of the face-centered-cubic metals were obtained by examining many surface energy values in the literature. Since the character of the surface in many such studies have not been fully defined values are not referenced for the various metals. The general trend is simply presented. The absolute values are not critical to establishing the relation to elastic moduli. The latter value is accurately determinable and may be used as a guide in predicting adhesion behavior.

The photographs of LEED patterns presented in Figure 10 relate to results obtained in Table 2. While independent analysis was used to determine the presence of adhered metals, Figure 10 shows the changes that take place in the diffraction pattern of the (111) surface of nickel before and after adhesive contact with various metals. Figure 10(a) shows the nickel surface before adhesive contact. Figure 10(b) shows the same surface after contact

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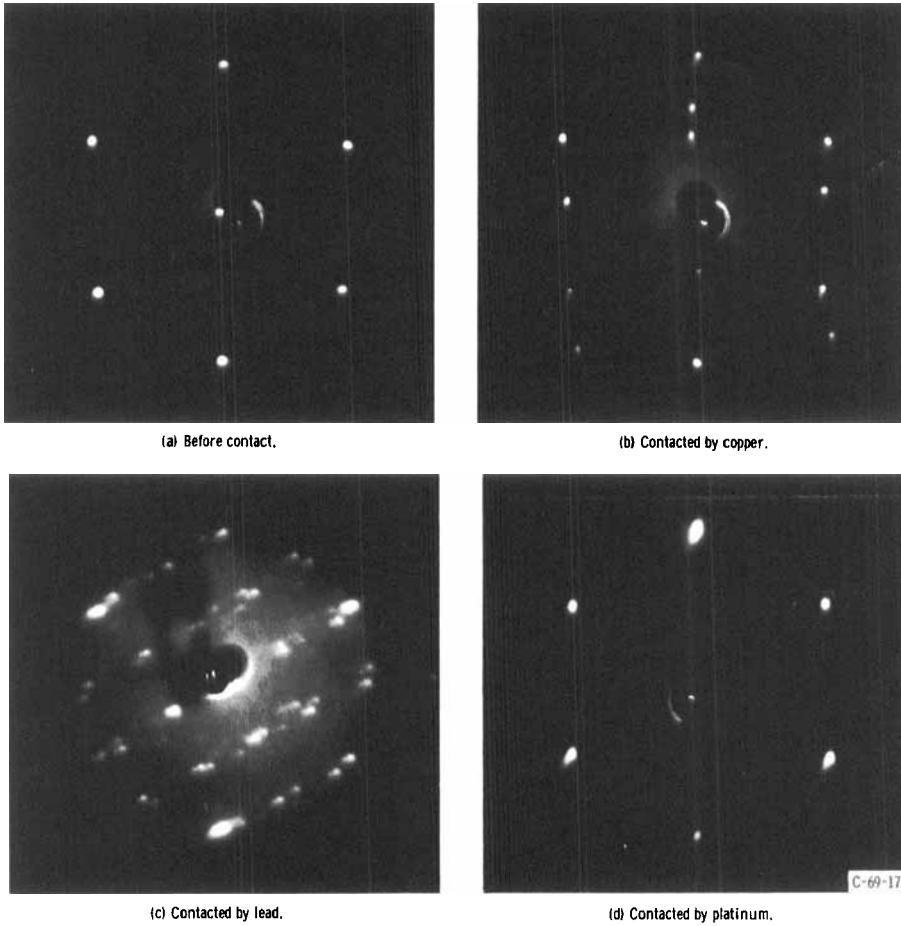

Figure 10. LEED photographs of nickel (111) surface before and after adhesive contact with various metals. Contact load, 20 dynes at 20°C; contact time, 10 seconds at 10^{-10} torr.

by copper with a force of 20 dynes. Figure 10(c) shows the surface after having been contacted by lead. Copper (Figure 10(c)) and lead (Figure 10(c)) have both adhered to the nickel (111) surface. In Figure 10(d) the nickel surface was contacted by platinum. For this material combination, nickel transferred to platinum. Note that the nickel surface has undergone strain as indicated by the elongation of the diffraction spots.

Epitaxial deposition of one metal onto another has been observed in a number of investigations [18-23]; it has been observed for inorganic crystals [23] and in oxides on the parent metal [24-25]. Thus, epitaxial adhesion in this investigation is not an unprecedented observation. The interesting observation herein is that it occurs when two solid surfaces make contact. The patterns presented herein are believed to reflect epitaxial adherence of

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gold to copper and copper-aluminum alloys. The concept of what constitutes epitaxy has been a subject of discussion by those engaged in LEED studies for some time. The interpretation presented here is essentially the same as that observed by Taylor in Ref. [15] with the deposition of copper on tungsten. There exists extremely good correlation between what was observed with gold contacting copper in this study and the characteristics of the patterns observed by Taylor for copper on (110) tungsten in Ref. [15].

It is of interest to consider what brings about such atomic registry in the two interfacial layers. Gold and copper are atomically mismatched in their lattice by about 12 percent. The mismatch can be accommodated by two processes which occur with adhesion: (1) lattice coherency strain and (2) by the generation of misfit dislocations. The subject of accommodation of lattice mismatch to achieve epitaxy has been very thoroughly examined in the literature. The work of Van der Merwe has lent considerably to the understanding of the phenomenon [26-29]; some additional work has been done by others [30-32].

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Based on the literature cited, a plausible explanation for the epitaxial attachment observed herein may be as follows. As the gold makes contact with the copper or copper-aluminum alloy surface, lattice strain takes place in the weaker of the two metals, namely the gold. As the gold makes contact with the copper or copper-aluminum alloys, the gold atoms of the outermost atomic layer are drawn to the lattice sites of the copper. This produces a strain several atomic layers deep in the gold. The depths to which gold atoms are strained will depend upon the degree of misfit [26-29]. Van der Merwe [27], in considering lattice mismatch to about 10 percent, indicates lattice strain to a depth of 10 monolayers.

The large strains produced in the lattice cannot be completely accommodated by simple atomic shift and interfacial dislocations are generated to satisfy large atomic strains. The generation of interfacial dislocations with epitaxy has been firmly established [27-29].

The presence of such misfit dislocations has been observed with electron microscopy by Matthews [20] for gold in contact with palladium, silver and platinum, the lattice mismatch for the couples being 4.4, 0.1, and 3.5 percent respectively. Since misfit dislocations are generated at these conditions of mismatch, there is little doubt that they must also exist for the gold or copper and gold to copper-aluminum alloy systems where there is an even greater lattice mismatch.

It is the presence of these dislocations which are believed to account in part for the differences obtained from junction strength determinations based upon the data of Figure 4 and cohesive energy calculations. It would be anticipated that the presence of these imperfections would decrease the force to fracture the gold surficial layers. Cohesive strength calculations based on the data of Figure 4 are less than values obtained using the cohesive strength equation indicating an effect from these imperfections.

The amount of atomic mismatch is influenced greatly by the atomic plane. Since the atomic arrangement will differ (see Table 1) it might be anticipated that the amount of gold to copper or copper-aluminum alloy bonding formed across the interface will be influenced by the orientation. Construction of models show this effect.

7. CONCLUSIONS

Based on the adhesion results obtained in this investigation with various face-centered-cubic metals in contact, the following conclusions are made:

1. From a consideration of the elastic properties of face-centered-cubic metals, adhesion behavior can be predicted. The metal with the lower elastic modulus will transfer to the other surface on fracture of the interfacial junction.

2. Epitaxial transfer was observed to occur in adhesion experiments. With gold contacting copper and copper-aluminum alloys, gold transferred epitaxially.

3. The addition of small concentrations of an alloying element can markedly alter adhesion behavior. The addition of 1.0 atomic percent aluminum to copper resulted in a five-fold increase in the force of adhesion of gold (111) to a (111) copper surface.

4. Surface orientation has a pronounced influenced on adhesion behavior. With gold (100) contacting three planes of copper, the force of adhesion was (110) > (100) > (111) where the copper orientation was varied with gold orientation held constant.

5. The amount of metal transferring from one surface to another was found to be related to applied force of adhesion (applied initial load).

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