NASA CR103450

Final Report
July, 1969

ADHESION BETWEEN ATOMICALLY PURE METALLIC SURFACES

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Prepared for

National Aeronautics and Space Administration

Office of Grants and Research Contracts, Code SC

Washington, D. C.

Grant No. ~~NsG-483~~-1 NGR-33-022-004

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Syracuse Univ.

DEPARTMENT OF CHEMICAL ENGINEERING AND METALLURGY

MET-1100-0769-F

PREFACE

The body of this report represents a complete review of the efforts of the Syracuse University research program from the early 1960's to the present on adhesion in metallic systems. This report is divided into three sections; the first and second were presented as publications(J. Adhesion,1, 142-156 (1969) and 1, 157,*1969)) during the past year and represent a consistant line of analysis of metallic adhesion data (part 1) and a refined experimental technique (part 2) which provides data in support of the analytical approach. Both of these papers have appeared previously in NASA semi-annual reports in a somewhat less refined condition.

The third section consists of a Master's thesis by M. Tsai which considers the effects of the specific contaminants hydrogen and hydrogen ions on the adhesion of ultra pure iron (8 ppm carbon). The results of this study provide strong evidence that hydrogen is adsorbed on an iron surface as a conductive film which does <u>not</u> inhibit the cold welding of iron. This is in direct contrast to the behavior of oxygen and nitrogen which do act as a barrier to adhesion. Hydrogen ions (1 Kev) also provide a significant barrier to the adhesion process. Although several other very interesting conclusions may be drawn from this particular study, the relevance of the effects of hydrogen on the adhesion of iron to the mechanisms of organic lubrication in such systems appear to be most significant. The facts to be considered are as follows:

1. The presence of an adsorbed hydrogen layer on metallic iron does <u>not</u> reduce the ability of the two surfaces to form an adhesion junction of a strength equivalent to that of atomically clean iron.

2. Oxygen adsorbed to the extent of a monolayer or more in a similar system establishes no adhesion bond of comparible strength unless severe mechanical or thermal energy is developed in the interfacial region.
3. Atomically clean iron surfaces at room temperature are capable of catalytically cracking organic molecules which provide an excess of hydrogen (organic source can provide up to 75 atomic % hydrogen). (P. G. Wright, P. 6, Ashmoreland, C. Kemball, Trans. Faraday Soc., 54, 1692 (1958).
4. Qualitative observation: metallic adhesion of ultra pure iron is not inhibited in the presence of methane to 10^{-3} Torr. (Internal).
5. Qualitative observation: mass spectrographic evidence suggests that the oxide film on an ultra pure iron surface can be removed at temperatures below 200°C with a molecular beam of methane resulting in CO and H_2O as products. (Internal).

By using these basic observations and some of the general observations regarding the chemistry of lubrication reviewed recently* by R. S. Fein** let us consider what appears to be a very important equilibrium reaction in lubricated systems:

$$H_2O \rightleftarrows H^+ + OH^-$$

or in the presence of a free iron surface

$$H_2O \rightleftarrows 2H^+ + O^=$$

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* "Chemistry in Concentrated Conjunction Lubrication" presented before the NASA Symposium "Interdisciplinary Approach to the Lubrication of Concentrated Contacts July 1969.

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Then by applying observation 1 and 2 above and the expectation that in a reducing system, i.e. and excess of hydrogen, adhesion is high which in turn will increase wear rates and friction coefficients or conversely in an oxidizing system low adhesion is expected or low friction coefficients and wear, we may examine the effect of the variation of those chemical agents which will lead to an equilibrium shift favoring oxidizing or reducing conditions. The effect of a variation of humidity, on the wear of steel exposed to cetane or cetane plus 0.43% Stearic acid (cf. Fein's report, Figure 6) serves as an excellent example. As the humidity increases in the presence of the acid additive, wear also increases which is possible due to the presence of an excess of hydrogen ions from the acid molecule. Without acid, on the other hand, the wear reduces drastically as the humidity is increased. On the basis of the equilibrium equations above the former case (with acid) shifts the water equilibrium such as to reduce the availability of oxygen (oxide ion) and the latter shifts to increase the availability of oxygen. In each case the hydrogen concentration appears to be the controlling factor.

Examine also the case of sulfur as an EP agent. Recent evidence (cf. Fein's report) shows that sulfur apparently does not act in the film as an iron sulfide to reduce wear. Again consider the water equilibrium in the light of the possibility that a free iron surface can catalytically produce H_2S which would tend to shift the H_2O equilibrium such that more oxygen atoms are available for film regeneration, e.g. lowering friction and wear. Obviously, too much water will initiate corrosion side reactions particularly in the presence of hydrogen ions.

Further support for the proposed mechanism lies in the energy levels of the following series of atomic bonds:

Bond	Bond Strength (Kcal/mole)
Fe-O	98
H-O	102
Fe-S	78
H-C	80
H-S	82
C-O	257
Fe-H	32

For example, it is evident that the competition for oxygen between iron and hydrogen is almost equally balanced unless an excess of hydrogen is present since an extra energy will be gained by (Fe-H) formation as well as (H-O) formation. The competition in an excess of sulfur will favor (Fe-O) since the excess hydrogen will be consumed in H-S formation since (Fe-S) is much smaller than (Fe-O). Obviously, carbon in the system is removed by oxygen which aids in the formation of hydrogen and the cracking of the organics. The use of single bond energies for comparison was felt to be valid on the basis that the surficial reactions involved in lubrication which are under consideration are not unlike those which are involved in the exchange chemistry of catalysis. In catalysis the overall summation of bond fractures and formations may be considered as unit processes when regarding a surface reaction rather than becoming involved with just the stability of the final products which could well involve secondary reaction steps.

Although the author does not profess to be endowed with a breadth of knowledge in lubrication chemistry, these few points and the supporting evidence:

1. The presence of oxygen extends the seizure limits when fatty acids or EP agents are involved.
2. Similar is true for most organics (within limits).
3. Organic wear products are usually saturated, hydrocarbons even though unsaturated olefinic and aromatic hydrocarbons are used as lubricants.
4. The ferrous state is a common wear product (highly reducing system).

suggest that a strong line of consistent reasoning in the chemistry of lubrication can be developed from an understanding of the static adhesion phenomena iron couples.

It is strongly recommended; therefore, that the cursory evidence from lubrication research suggested above be examined in detail to see if broad support for the proposed mechanism is developed. If this is the case, lubrication chemistry as well as additive chemistry and the relative effects on wear and friction might simply reduce to a detailed understanding and control of the reactions effecting the presence of oxygen in the interface system.

ADHESION OF METALLIC BODIES INITIATED BY PHYSICAL CONTACT

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ABSTRACT

Metallic adhesion brought about through the normal compression of two real surfaces is considered. The growth of the real area of contact caused by the impressed load results in the plastic deformation of asperities even before plastic macro-deformation is initiated. The size distribution of the asperities is Gaussian, hence some contact points supporting the load will have experienced heavy deformation while others may have only received weak elastic interactions. The rate of dispersal of the contaminant barrier which inhibits high adhesion strengths has been shown to be a function of the degree of substrate deformation irrespective of the amount or the character of the contaminating layer. The mechanism of metallic adhesion, therefore, is directly dependent on the available energy inputs to the interface, e.g., mechanical, thermal, etc., which can bring about complete dispersal of the interfacial contaminants. At normal compressive loads, when the real area of contact is small compared to the nominal area of contact, the system must be considered a multipoint contact problem with the resistance to fracture of each point contact dependent on the prior history of that point.

The extent of the open literature directed toward examining the variables of what has come to be known as metallic adhesion has reached rather significant proportions as indicated by some recent reviews on the subject (1-7). A critical examination of these presentations, however, immediately exposes an interesting situation. It appears as if each experimenter or technique, since each school seems to have an unique experimental approach, produces data and often complete interpretations which do not appear simply consistent with those conclusions of his colleagues. The situation is immediately evident if one were to examine the data and conclusions of Sikorski (4) who studied the adhesion of metals using "in air" experiments, and those of Buckley (8) who generally uses ultra high vacuum techniques. The conclusions of each, for the most part, are similar. The experimental procedures, however, are so radically different that one hesitates to establish a line of consistency between the two. The purpose of the following discussion is to examine the pertinent variables of the phenomena of metallic adhesion in a most general fashion, correlate these parameters with current investigative work and to establish a set of boundary conditions on future analyses of similar data. The experimental paper which follows provides one experimental attack which holds considerable promise in the identification of some of the variables which will be cited herein.

Two metallic surfaces brought into physical contact are usually said to experience "metallic adhesion" if an observable net tensile load is required to separate the joined system (7). The magnitude of metallic adhesion is dependent on the physical and chemical properties of the metals (9-12), the nature and extent of loading (1) and the characteristics of the contaminant layers present on all but atomically clean metal surfaces (12). Generally, the contacting process involves the elastic and plastic deformation of surface asperities, deformation of the bulk substrate, and the rupturing and dispersal of contaminant surface films (13). If the contaminant barrier can be sufficiently dispersed, the ensuing metal-metal contact along the interface results in a welded junction, the tensile strength of which may approach that of the bulk metal (7). The conclusion that similar metal couples weld under near zero normal loads providing both surfaces are atomically clean has been well accepted in adhesion literature (7,14) and would be predicted from ultra high vacuum epitaxy studies using low energy electron diffraction equipment (15), adsorption studies (16) and other investigations.

Adhesion studies which have involved deliberate gaseous contamination, e.g., cf. Gilbreath (17), from a fraction of a monolayer to ambient atmospheric conditions present an analytical problem which is most complex. Very simply, the mechanical compressive forces producing physical contact through asperity deformation with or without subsequent bulk substrate deformation can act to disperse the contaminant barrier into an ineffective state, which permits metal-metal contact regions to be established which in turn resist tensile fracture on unloading. The disruptive mechanical forces acting within the interfacial zone; or more generally, the mechanical work imparted to the interface is only one of several energy transfer mechanisms which can provide contaminant barrier dispersal. For example, increased thermal energy could cause evaporation or dissolution of the contaminant layer, or shock wave energy either from explosive impact or an ultrasonic source could also act as energy inputs which could promote contaminant dispersal along the interface. Since the contaminant layer is developed by the mechanisms of adsorption, surface creep or bulk diffusion to the surface, the energy inputs to the interface which causes dispersal may also enhance the rate of contaminant film development. In the consideration of metallic adhesion, therefore, the system must be limited to a degree of contamination which does not exceed that of a nominally clean surface exposed to ambient conditions. Specifically lubricated systems will not be considered as the analysis becomes more complex. Of the various modes of energy inputs to the interface only normal compressive loading at room temperature will be considered.

The description of metallic adhesion phenomena in real systems under bulk compressive loads corresponding to less than a 10% deformation of the massive coupled system requires a clear description of the micro-topography of each of the two free surfaces before contact. The description is necessary to provide a definition of the <u>real</u> area of contact relative to the massive system geometry. This has been presented recently by Greenwood and Williamson (13) as a distribution function, the exact form of which depended on the prior history of the surface. The macro-radii of curvature of the surfaces must also be considered. As has been suggested by many authors, cf. a recent review by Bowden and Tabor (19), a reasonable surface roughness model consists of a large diameter sphere contacting a flat or second sphere upon which are superimposed asperities the size and shape of which are dependent on the surface finishing techniques utilized before contact. For example, metallographic polishing techniques on the harder metals may result in a hill and valley contour in which the hill-valley depth is less than a micron and the peak to peak distance is in the range of 10 microns. The consequences which result when two such nominally flat surfaces are brought into physical contact under normal load have been reviewed by Greenwood and Williamson (13), Greenwood (18), and Kragelsky et al. (20). The generally accepted model for surfaces in contact under a specific load is that the highest of the asperities, which can be represented by a Gaussian distribution of heights, will yield until a sufficient number of asperities have been deformed to accept the impressed load. Due to the very small size of the asperities such deformation on a micro-scale will occur well before the onset of what is classically considered bulk plastic deformation. Since the uniqueness of the surface asperity configuration is retained until rather high compressive forces are realized (21) e.g., some (22) have suggested the range of at least 10% bulk deformation for flat surfaces, the real area of the interfacial system will consist of islands of various sizes surrounded by regions of noncontact. The real area of physical contact and the nominal area of contact are, therefore, quite different for all but the most severely loaded systems. Since surface mass transport in the form of plastic deformations must be involved during loading, the variation of real area with load time, e.g. creep, will also be involved in the expansion of the real contact area (23). The real area of contact will then be a function of the nature of the metal, impressed load, time, and temperature; this has been substantiated by hardness measurements (24) and electrical contact studies (25). Without question the most important aspect of the study of metallic adhesion is the definition of the real area of contact with respect to its magnitude and constitution since the fracture strength of this adhesion junction, the only measure of metallic adhesion stability, is dependent on the real stresses developed within this real area during the unloading process.

As is indicated in a review of the recent literature (1-7) most adhesion strength data which has been presented in the literature have involved only reference to the fracture load per unit of nominal area of contact. Let us, therefore, consider this aspect in more detail.

The process of adhesion may be considered as being comprised of two steps: two free surfaces are brought into physical contact and subjected to a compressive load; and then the applied load to the system is removed, possibly to some tensile load representing a nominal adhesion junction strength. The entire process is directly dependent on the nature and extent of the real area of contact and the fracture stresses developed therein.

Numerous suggestions based on macro-observations have been presented which relate the real area of contact (A) to the impressed load (W) (19, 22, 23). In most general form this can be given as

$$A = (k)_x W^x \tag{1}$$

where k and x are related to the particular deformation process involved in expanding the load-supporting area as the load is increased or the time is extended at a fixed load (creep). Thus, the value of <u>k</u> is directly related to <u>x</u> through the process. Under lightly loaded conditions, e.g. less than the bulk compressive yield point of the material involved in contact, such an area expansion process will involve a number of individual asperities which will have a distribution in size and position along the contacting interface as well as a relationship to massive geometrical effects such as the overall relative radii of curvature of the two macroscopic systems. Consequently as the load is impressed, the loading conditions on each individual asperity and relatively between adjacent asperities will be unique, that is, at equilibrium some asperity contact points may have been subjected to heavy plastic deformation while others may have only experienced a low level elastic contact. A more complete general expression for the real area, therefore, ought to be a summation of the contributions from each asperity in the contact system with regard to each asperity (i) in the interface system and the respective position (j) of that asperity.

$$A_{ij} = \sum_{ij}^{n} (k_{ij})_x W^{x_{ij}} \tag{2}$$

Explicit in this equation are two necessary assumptions which appear reasonable but which have not been justified experimentally. Firstly, it is assumed that each asperity deformation is a unit process, i.e. not related to the adjacent asperity and as such, and follows a simple power law of deformation similar to that observed in macro-systems. Equation (1), therefore, is representative of one unit process and not generated through an averaging process of significantly different micro-processes. The second assumption which is necessary and yet unproven, is that the representative equation is constant throughout an asperity deformation process irrespective of the percent deformation which is experienced by that unit process. Since geometrically reproducible surfaces cannot be generated in dimensions below micro-inches on real surfaces, it is unlikely that proofs will be presented in the immediate future. Consequently, we must rely on macro-scale observations to provide a possible path for interpretation. As an example of the problem facing the analyst, let us consider a simple hardness experiment in which the indenter is assumed to represent an asperity unit process. If the load (W) is sufficient to cause general plastic transport under the indenter, the projected area (A_p) has been shown (26) to be approximately

$$A_p = \frac{W^m}{3Y} \qquad (3)$$

where (m) is a material constant very nearly equal to one and (Y) the yield point of the material. The reasonably valid assumption necessary for this macro-approximation, but not necessarily valid for a similar micro-process, is that surface contaminants will not effect the plastic flow process. Such is not the case on two accounts; firstly, the apparent projected area represents only a fraction of that real area supporting the load due to the effect of asperities as pointed out by Williamson (21). Secondly, the very flow processes occurring along the interface of the indenter which are necessary to expand the area are most sensitive to the lubricative properties of the contaminants which aid or restrict the material flow along the interface. The phenomena has been clearly demonstrated during the observation of the sensitivity of hardness measurements to surface lubricants (27). Gane et al. (28) also has shown that our knowledge of the mechanical properties of metal surfaces on a micro-scale is not satisfactory.

Although the presentation of Equation (3) rests on some rather nebulous assumptions regarding the behavior of the individual asperity, it does bring forth the recognition that physical contact behavior is the result of a multitude of such interactions with plastic deformations ranging from near 100% to those near forceless contact. More specifically, the interface system has been placed in a rather complex state of stress which may per unit volume be resolved into two components: the applied stress (σ^a), and the residual stress (σ^r). As the flow stress in a unit volume of the material is exceeded that unit volume will deform plastically. In an implicit manner the model suggests that an absolute correlation of adhesion data with atomic properties, structure of the material, or defect mechanics requires a rather adventurous extrapolation, if any but the most gross generalizations are involved.

The instant that any fraction of the compressive load is removed from the system, each unit of area supporting that load will be subjected to a new stress relative to the fraction of the applied load removed from that unit area and also the availability of residual stresses adjacent to the unit area under consideration. If such a unit area is exposed to a tensile stress which exceeds some critical fracture stress (σ^c) the unit area will separate, i.e. permit crack propagation, which in turn will relieve a portion of the accumulated stresses. The condition for fracture per unit area can be presented as

$$\sigma^c < \sigma^a + \sigma^r \tag{4}$$

Under relatively light contact loads, i.e. very small bulk deformations, much of the real contact area will be subjected to rather severe stress concentrations of nearly infinite sharpness due to the presence of voids along the interface. A careful stress analysis of the system must contend with this factor (29).

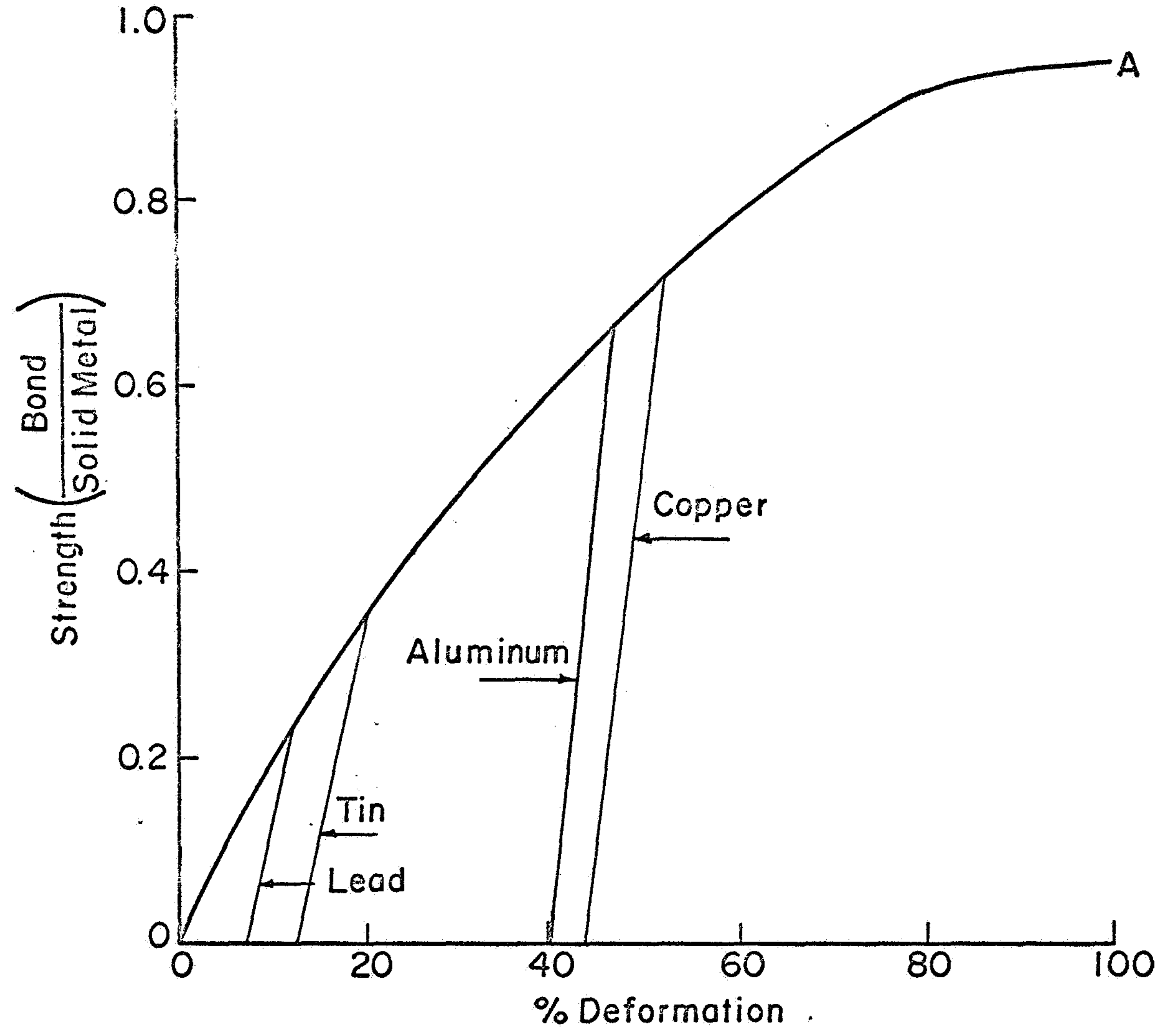
The magnitude of the critical fracture stress is related directly to the physical properties of the material through which the crack must propagate, and as a consequence is extremely sensitive to the structure and temperature of this phase as was emphasized by Gilman (30). For example, the critical fracture strength of a pure metallic junction can be compared to that of a clean grain boundary within the bulk metal while critical fracture stress of a junction completely contaminated with an organic oil ought to be compared to that of the organic material and not to that of a metal. A more extreme situation can be envisioned in the case of very lightly loaded regions along the interface between two glass plates in which the adsorbed water is not entirely dissipated in the compression process. In conclusion, the unit area resisting fracture can vary from some value approaching the bulk strength of the metal involved in the metallic couple to near zero depending on the interfacial material and the degree of its dispersion. Furthermore, fracture of a small unit area can occur even though the overall system is still in a state of compression as long as the corresponding applied load is less than the maximum load experienced by the system during the compression mode of the adhesion process. For example, the addition or deletion of applied load only effects (σ^a) in a unit asperity process, or micro-unit volume adjacent to the interface. Under certain circumstances, the residual stresses, which to a degree are independent of the applied stresses, could effect a high tensile stress in a micro-unit volume even though other regions of the contact area are bearing the compressive load. Such was clearly identified by Bowden and Tabor (1) in their discussions of "released elastic stresses" during hardness measurements.

Again, the most important parameter of the process is the definition of the unit area over which the critical fracture stress must operate and again some rather extreme simplifying assumptions in the model must be made since we must consider the real contact area of a one asperity contact to be homogeneous in σ^c even though it is clear that this need not necessarily be the case for any except the ideally clean metallic adhesion system. If we make the further simplifying assumption that the stress state is unique and homogeneous within each asperity contact region then we can represent the second half of the adhesion cycle as an equation based on $F = \sigma A$ where the force (F) on the interface of a one asperity contact is given by the nominal stress (σ) per unit real area (A) such that fracture ensues when $\sigma > \sigma^c$. In order that all of the asperities involved in one adhesion interface are considered, a summation can again be applied for the total force (F_T)

$$F_{(T)} = \sum_{ij}^{n} \sigma_i A_{ij} \qquad (5)$$

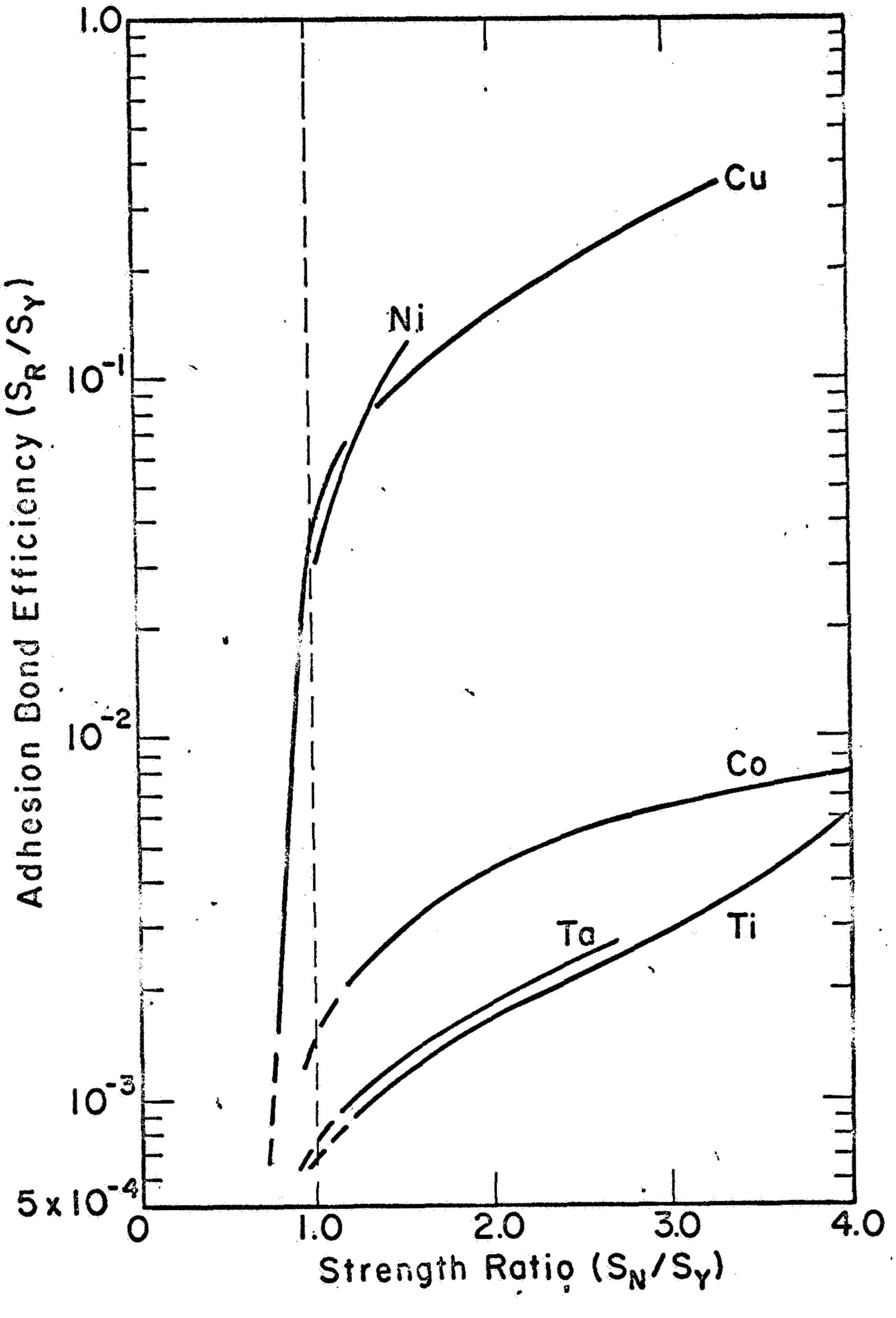
where σ_i is the effective stress developed on the i th asperity junction with a real area A_{ij} and the total force represents the effects of n junctions. The fracture of the i th junction will occur when some critical stress (σ^c) is exceeded in that micro-volume of the junction which will permit a crack to move thus releasing the accumulated applied (σ^a) and the residual stresses (σ^r) as indicated in Equation (4). The necessity for studying the fracture process on a single asperity basis becomes evident, if one considers that the real area of contact is made up of contact points in varying degrees of deformation and further that the contaminant dispersal effect resulting in a metallic adhesion bond strength between these two points can be presented as a function of the contaminant as well as the percent deformation to which the metallic system has been subjected. Since there is no direct evidence on precisely how an asperity undergoes gross deformation in a surface system while subjected to compressive loading and it is through just such a process the contaminant barriers to adhesion are removed, the examination of bulk dispersal mechanisms ought to provide some insight. The roll-bonding studies by Milner et al. (3) serve as a simple example. Such adhesion studies are significant only if we presume that similar processes could be operative at the scale of asperities. The Milner experiments involved the rolling of two slabs of metal in air to some degree of bulk deformation and then testing the interface bond in shear. In this case our assumptions are probably more nearly correct since for the most part the real area of contact is expanded under conditions of constant availability of contaminants and chemical reaction rates tending to disperse the oxide contaminant layer. A portion of the voluminous data developed by Milner from roll-bonding studies of various metal couples is presented in Figure 1. The numerous data points delineating these curves in the original data were left out here for convenience. The curves illustrate several significant points regarding one possible mechanism for the dispersion of oxide films between the two metal surfaces. Firstly, let us consider the case of aluminum in which the variables of temperature, rolling speed and surface structure are held constant. The curve indicates that a threshold of about 40% bulk deformation is required before any bond strength is observed. Between 40-45% deformation, the dispersion rate of the oxide, as well as that of the adsorbed gas

Strength of Roll Bonded Material as a Function of Percent Deformation



is quite rapid as is indicated by the increase in the shear strength of the system, i.e. a sizeable fraction of the real strength of aluminum. At deformations greater than 45%, the oxide dispersal process seems to follow a limiting curve which is representative for the other metals shown. The interfacial strength compares favorably with the bulk metal strength above 80% deformation. It is interesting to compare the aluminum curve with that of lead since the deformation threshold for lead is only 8% deformation yet lead encounters the same limiting curve [cf. Figure 1 - 0,0-A] as that experienced by Sn, Al and Cu. What is suggested by this set of curves is that after the brittle oxide layer is fractured (31), i.e. deformation threshold, which is dependent on the substrate material-oxide characteristics, a limiting rate process of contaminant dispersal is attained which is dependent on the degree and type of deformation and independent of the material which is involved. Since these systems were prepared in a similar manner (wire brushing and severe rolling), one might suspect that the limiting oxide dispersal is a function of asperity interaction (light loads; < 20% deformation) and metal flow patterns along the interface under the severe rolling conditions. In comparing these data with the normal loading interface contact model under discussion, it is unrealistic to carry this analogy too far since in a simple contact process extrusion type flow, i.e. parallel to interface, would not be expected to such a severe extent. Furthermore, during roll-bonding the interfacial area is grossly expanded whereas in normal adhesion relative motion in the interface is quite small. Milner et al. have clearly examined other models of energy input, e.g., the deformation threshold decreases with increasing temperature and extension of the duration of exposure to roll pressure. They have also examined the effects of limiting contaminants, e.g., the deformation threshold of aluminum was reduced to about 2% by brushing in medium range vacuum. The softer metals indicated a lower deformation threshold except for magnesium which did not respond to the simple analysis as presented for Figure 1 since the limiting curve was very low.

Although roll-bonding studies do not simply represent the state of affairs in a normal contact problem, they do clearly demonstrate the contaminant dispersal effect that has been interjected into the contact fracture argument. Vacuum adhesion studies presented by Hordon (32) in Figure 2 were obtained by wire brushing two small flat plates of the respective metals in very high vacuum (1 nTorr), subjecting the plates to near normal loading and then testing the welded system in tension. The data are shown as the relative strength of the interface bond (S_R) to the yield strength of the material (S_Y) based on the nominal area of contact which is compared to the normal loading force (S_N) ratio with S_Y. The general character of the curves is precisely what would be predicted. For example, the natural surface roughness of the samples insures asperity interaction which will provide an exceedingly small real area of contact until at least a few percent plastic deformation is attained, i.e. a nominal load in excess of the yield point; 1.0 on the abscissa of Figure 2. It is evident that normal loading does not provide the rapid oxide dispersal which accompanied roll-bonding experiments as indicated by the lack of a simple symmetrical limiting curve. More severe interfacial dispersing is, however, observed in the softer metals Ni and Cu when compared to the harder metals Co, Ta, and Ti. Hordon also observed that by increasing the ambient temperature the bond strength at a fixed load was also increased. The amount of contamination present on the


Adhesion Bond Efficiency (S_R/S_Y)
Strength Ratio (S_N/S_Y)
1.0
10^{-1}
10^{-2}
10^{-3}
5×10^{-4}
0
1.0
2.0
3.0
4.0
Cu
Ni
Co
Ta
Ti

wire brushed metal surfaces in ultra high vacuum (Hordon) was impossible to ascertain; however, the degree was certainly considerably less than that present in the roll-bonding experiments. Another important unknown in the analysis of the adhesion system is emphasized since no technique has been successfully applied to ascertain the exact amount, or character, of the contaminant phase available for the interruption of adhesion during the study of interface bond strength relative to fraction of deformation.

Since the real area of contact formed in the contact zone during the compressive mode (Equation 2) of the adhesion test is identical to that operated upon during the removal of the compressive force (Equation 5) and possibly the same as that during the tensile test of the adhesion junction, the total interfacial force may be written as:

$$F_{(T)} = \sum_{ij}^{n} \sigma_i \; (k_{ij})_x W^{x_{ij}} \tag{6}$$

where k must be evaluated under the conditions of x which is due to the deformation process involved at the i th asperity. For example, if the i th asperity is undergoing simple plastic deformation in compression, we might assume $(k = \frac{1}{3Y})$ and $(x = 1)$; however, if the i th asperity is under tension $x = 0$ and $k = \frac{W_{max}}{3Y}$ might be assumed as a first approximation until the critical stress (σ^c) in the i th asperity is exceeded. Under any circumstances when the compressive load is reduced infinitesimally portions of the system may be exposed to a tensile stress even though the entire system is still considered as being under a compressive load. If the tensile stress experienced by the asperity contact area exceeds the critical fracture stress (σ^c) of the interface, a crack will propagate through that region to relieve the internal stress but will stop when the balance ($\sigma^c = \sigma^a + \sigma^r$) is achieved.

The path of the crack will, of course, follow the path of least resistance which will couple a minimization of molecular bond strengths with a maximization of regional tensile stress. The chemical composition, therefore, of the free surfaces resulting from fracture can not simply represent the pre-contact surfaces since material transfer is expected in all cases. For example, in the case of severely oxidized metal surfaces adhesion should be expected between some of the oxide particles in contact; however, on fracture the path of least tensile force resistance may not include such an adhesion junction. Material transfer would result. A situation quite similar to this state of affairs was clearly described by Bowden and Tabor (1) in their discussion of "released elastic stresses" during normal hardness measurements. Johnson and Keller (9,10) also reported a similar phenomena in adhesion studies between similar and dissimilar couples under contaminated conditions.

If a very weak boundary exists all over the interface, e.g., σ^c is very small, a plot of the variation of contact area with applied load from maximum load to zero load should very nearly superimpose on the loading curve provided no massive plastic flow of either system has been effected. Plastic flow would provide a larger real area of contact on unloading than was available on loading depending on the magnitude of residual elastic stresses in that region.

Next, let us consider the real area of contact developed between two atomically clean surfaces such that each contact point becomes a welded junction; a case which closely resembles a clean grain boundary (14). Since compressive loading prior to a tensile test tends only to slightly distort the tensile stress-strain diagram of the metal under consideration, one would predict (14) that the strength of each asperity adhesion junction would be approximately that of the tensile strength of that metal based on that real area of contact. The relationship of the junction strength to impressed load is only through the asperity deformation necessary to expand the contact area. If, for example, atomically clean and flat surfaces were brought into intimate contact without an impressed load, the junction strength would still be the tensile strength of the metal still based on the real contact area, which in this ideal case would be the nominal area.

Another important aspect for the consideration of Equation 7 lies in the fact that the distribution and the degree of contaminant dispersal is a function of the degree of deformation. As a consequence, the critical fracture stress (σ^c) will vary with the contact point area depending on the amount and type of contaminant present at that point and the degree of dispersal experienced by that point during the compressive mode. Studies directed toward the evaluation of specific contaminants and their ability to interrupt the adhesion process ought therefore to be conducted in a system in which rigorous control is maintained over all secondary impurities, surface roughness, and loading variables such as contact time, temperature, and rate. One suggested configuration (11) was to evaluate Equation 6 under atomically clean conditions at various maximum loads and then compare these values with those observed under one specifically contaminated condition maintaining all of the other variables constant in the test system, e.g.,

$$\eta = \frac{\left[\Sigma\ \sigma_i\ A_{ij}\right]\ \text{contaminated}}{\left[\Sigma\ \sigma_i\ A_{ij}\right]\ \text{atomically clean}} \qquad (7)$$

Such an approach and the assumption that the only change in the system is (σ^c) permits a rather simple analysis. Extensive details of the value of this assumption and a detailed analysis have been presented by Westwood (33).

The coefficient of adhesion (α) was developed (1) as the ratio of the fracture load of a nominal adhesion junction to that compressive load utilized in the formation of the interface. The implicit assumption is that, on the average, the area supporting the load is identical to that which resists a tensile force to fracture the system; however, according to a more careful examination this is only the case when absolutely no contamination exists between two metal surfaces. The presence of only a fraction of a monolayer of contamination on either surface immediately invokes the necessity to sum the varying degrees of asperity deformation necessary to generate the real area or the application of a compressive force which will generate complete dispersal at all points. In equation form we can use the maximum force in compression

$$F_{max} = \sum_{ij}^{n} \sigma_i \left[(k_{ij})_x W^{x_{ij}} \right]_{max} \tag{8}$$

as the load to form the junction and Equation 6 that to cause fracture. The coefficient of adhesion (α), thus, takes form

$$\alpha = \frac{F_{total}}{F_{max}} = \frac{\sum_{ij}^{n} \sigma_i \quad (k_{ij})_x W^{x_{ij}}}{\sum_{ij}^{n} \sigma_i \left[(\sigma_{ij})_x W^{x_{ij}} \right]_{max}} \tag{9}$$

The coefficient of adhesion (α), therefore, may vary from zero to infinity depending on the conditions of the experiment. For example, if atomically clean, flat surfaces are brought into forceless contact the denominator approaches zero and if any force of attraction exists between the two bodies the numerator has a finite number and α approaches infinity. On the other hand, a perfect lubricant reduces the numerator to zero at any load or (α) approaches zero. Wide variations in α for the same metal system tested by different experimenters under approximately the same conditions are common, e.g. in the case of copper cf. Buckley (34) for large α values and Ham (35) for small α values. The definition of an α for each i th contact or an average $\bar{\alpha}$ also appears to be a fruitless path because of the difficulty in ascertaining either the precise degree of contamination of the i th contact or the total amount of contaminant dispersion energy available to the system necessary for the dissipation of the contaminant layer which is preventing the two asperities from welding together, and establishing the α for that asperity.

In the utilization of various α values as reported in the literature, it would appear that for the purposes of comparing data produced between ultra clean versus specifically contaminated surfaces which are produced by one investigator utilizing the same technique for each experiment such as is done in the experiments by Gilbreath (17), one could assume a degree of qualitative relationship between the different values of α on similar metal couples at corresponding loads without much error. Interrelating data from different physical systems of study as suggested by Rittenhouse (36) or those between dissimilar metal couples as used occasionally by Buckley (34), however, should be considered dangerous since F_{max} and σ^c are strongly dependent on the test temperature relative to the absolute melting temperature, crystal structure, cohesive strength, etc. of the bulk materials as well as the nature of the contaminants and surface roughness in the system. The F_{max} values cannot, therefore, be related since the deformation mechanisms providing the real area of contact are different due to the different modes of deformation and rates of contaminant dispersal.

The conclusions of the previous discussion can be most simply illustrated as a theoretical curve of an adhesion cycle which proceeds from zero load contact to some F_{max} and then unloading the system to junction fracture as shown in Figure 3. The compressive loads

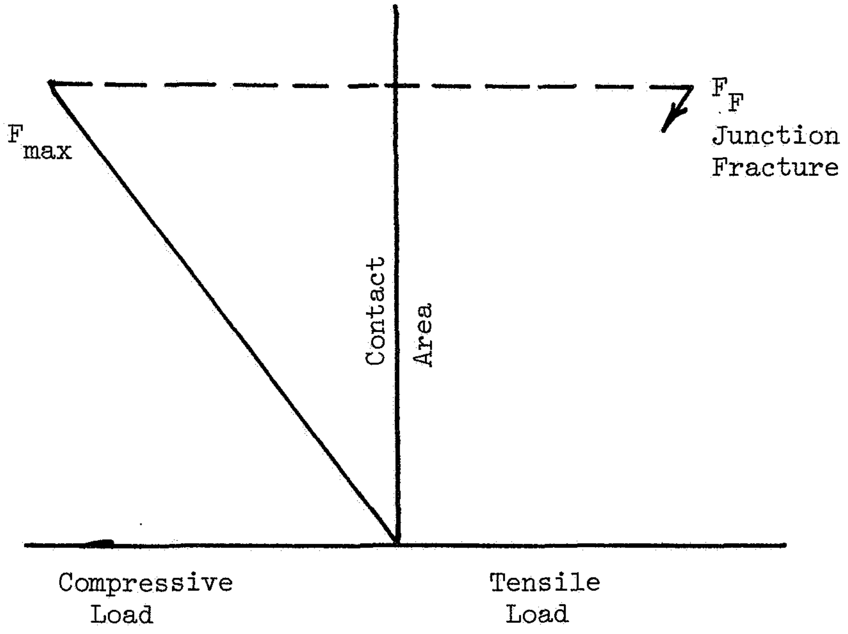


Figure 3 Theoretical loading versus area curve for massive compressive strains below the 0.2% offset point.

considered are below the 0.2% offset yield point of the material since massive strains serve only the transport bulk material and institute contaminant dispersal effects. The loading cycle of Figure 3 assumes only plastic motion of the asperities; area is proportional to load in the first approximation. For materials of higher yield point, the case of normal loading could extend into the region of bulk elastic compressive strain which would be represented by a distinct slope change in the $0\text{-}F_{max}$ curve. If in either case, the load at F_{max} was retained for a period of time, creep of the plastically deformed asperities would ensue. Both of these cases are described in the following paper by McNicholas and Keller (12).

The release of the load from point F_{max} will produce an effect which is related directly to the amount and nature of the contaminant along the interface at F_{max}. According to the previous discussion this interfacial contaminant layer at F_{max} is due to the surface state of contamination before physical contact and the degree of its dispersal during the loading process. The limits of fracture are readily fixed: firstly, if at F_{max} the low shear stress contaminant has been undisturbed, the "released elastic stresses" will continuously decrease the required area to support the continuously reducing load, i.e. path $F_{max}\text{-}0$ is followed approximately depending on the magnitude of the interfacial change due to the plastic strain of the asperities. Secondly, in the case where the surfaces are interfaces are automically clean or the contaminants are capable of high shear strength interface formation (solders to rapid set adhesives), the release of the load would not result in a gross area change ($F_{max}\text{-}F_F\text{-}0$) until the tensile fracture stress of the system was realized. In this case one can appreciate that the "elastic stresses" are accumulated along the non-equilibrium interface as stored energy until fracture takes place. Thus, not only is the true fracture strength reduced to some degree; but one can now envision a continuum of possible events between the two limits.

These cases are particularly evident in the McNicholas et al (12) paper which follows while the other cases were described by Johnson et al (9, 10).

Clearly the mechanism of the dispersal rate of the contaminant barrier to metallic adhesion, and its balance with film growth rate, is the key to the overall analytical problem; and until quantitative studies which are initiated with a known degree and type of surface contaminant are undertaken, correlation of data produced by one investigator are not likely to agree in detail with that of another. Under compressive loads below the yield point of the material, several authors (2, 5, 6) have shown that a monolayer of certain contaminants (9, 10) emanating either from the vapor or by diffusion from the bulk (12) can reduce the adhesion strength to zero. The detail with which the original metal surfaces, i.e. prior to specific contamination, must be defined is established through this limitation.

The lack of clear definition of the amount and type of contaminant layer present on a metallic system prior to study has also inhibited our ability to gain any insight into possible cross-correlations between modes of energy inputs for contaminant despersal. For example, the correlation of adhesion data produced by the normal load contact methods (12) cannot be precisely correlated with a normal contact plus some fraction of tangential motion or the comparison of normal contact at some temperature (T) with that at (T + 500°C). If both of these examples could be clearly resolved, a rather significant step toward the understanding of the adhesion theory of friction could be made.

ACKNOWLEDGEMENT

The authors express their gratitude to NASA for the support of the programs which led to the conclusions cited and to J.B.P. Williamson (Director of Research, Burndy, Corp.) for his numerous helpful comments during the preparation of the manuscript.

List of Symbols:

A - real area of contact

A_p - projected area of contact

F - force on asperity

F_T - total force on contact area (A)

k - constant dependent on deformation process

m - materials constant

n - number of asperity contacts

S_N - nominal compressive stress

S_R - nominal fracture stress

S_Y - yield stress

W - impressed normal load

W_{max} - load at maximum compressive stress in adhesion cycle

x - constant dependent on deformation process

Y - yield point

α - adhesion coefficient

σ - total stress

σ^a - applied stress

σ^c - critical fracture stress

σ^r - residual stress

List of Captions:

Figure 1 Roll-bonding studies of various metals in air at room temperature (3). The data are presented as the strength ratio of the interface bond formed by roll-bonding to the solid metal versus percent deformation.

Figure 2 Variation of the relative strength of polycrystalline metals with the degree of compression (32). The ratio of the bond fracture stress (S_R) to the yield stress (S_Y) is plotted versus the reduced compressive stress (S_N/S_Y).

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