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THE INFLUENCE OF SURFACE ON THE
PROPERTIES OF MATERIALS

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PROPERTIES OF MATERIALS

While the contributions of solid state science to the under-
standing of the behavior of materials are many and varied there are some
problems which are not susceptible to solution from solid state princi-
ples; these are regions which are specifically excluded from their
analyses, the surfaces. These surfaces can be of two types; interior,
the grain boundaries, or exterior, the free surfaces. These surface
atoms are in an unbalanced force state relative to the atoms in the
solid and their coordination is on the average much less. As a result
these surfaces have a marked affinity for environmental atoms or for
one another giving rise to what is normally termed surface tension, sur-
face activity, surface energy, etc. These surfaces can and will influ-
ence all the properties of the materials we use as engineers. In many
cases the influence will be slight while in others it may be very great.

To illustrate the importance of internal surfaces we might
look at the determination of the mechanical properties of a brass. A
standard test specimen is made up and this fixes the amount of external
surface. We are aware that grain size is a variable and this is con-
trolled to a given range to fix this variable and the mechanical proper-
ties are determined. We may change the grain size and determine the
resulting change in properties and we do to this extent recognize the
influence of internal surfaces although it is intuitively believed that
what we are measuring are bulk properties and the surfaces play a sub-
ordinate role. If now we repeat the tests but this time merely change

the environment and in place of air substitute a mercurous chloride solu-
tion we obtain quite markedly different results. The yield and tensile
strengths are markedly lowered as well as the ductility as measured by
percent elongation and reduction in area. In this environment the bulk
properties play a subordinate role and the grain boundary surfaces and
free surfaces are much more important. Figure 1 is an illustration of
how different identical brass test specimens appear after testing in
air and in a mercurous nitrate environment. Admittedly this is a severe
change in environment and as a matter of fact is a standard ASTM test
to determine the presence of residual stresses in copper and copper-base
alloys, but it does illustrate very graphically the importance of in-
ternal surfaces.

An example of where free surfaces and their adsorbed films
produce a desired property is to be found in graphite. Most of us are
aware of the lubricating properties of this material and attempts are
sometimes made to relate this property to the layer-lattice structure
and the disparity in strength between layers and across layers. The
work of Savage is quite definitive in proving that this is not the case.[1]
He has shown that it is the presence of adsorbed films of water vapor or
oxygen that produces the low coefficients of friction as shown in Figure
2.

Granted then that surfaces play an important part in deter-
mining the properties of materials, what is the status of research in
this field? To be perfectly candid one must admit that the entire pic-
ture of research on surface is quite confusing. Mathematicians, Physi-
cists, Chemists, Ceramists and Engineers, to mention just a few, are
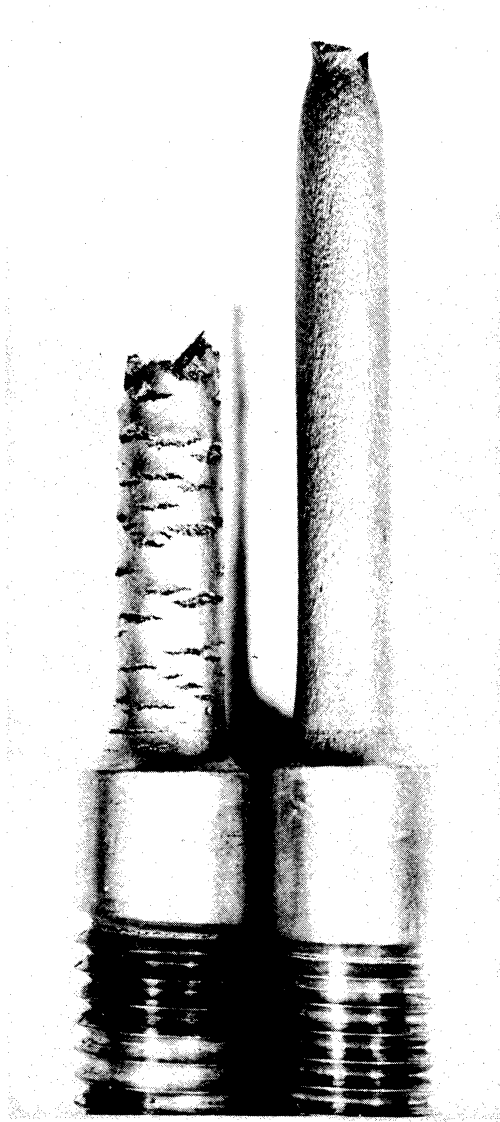
Figure 1. Influence of Surfaces on Properties of Materials.
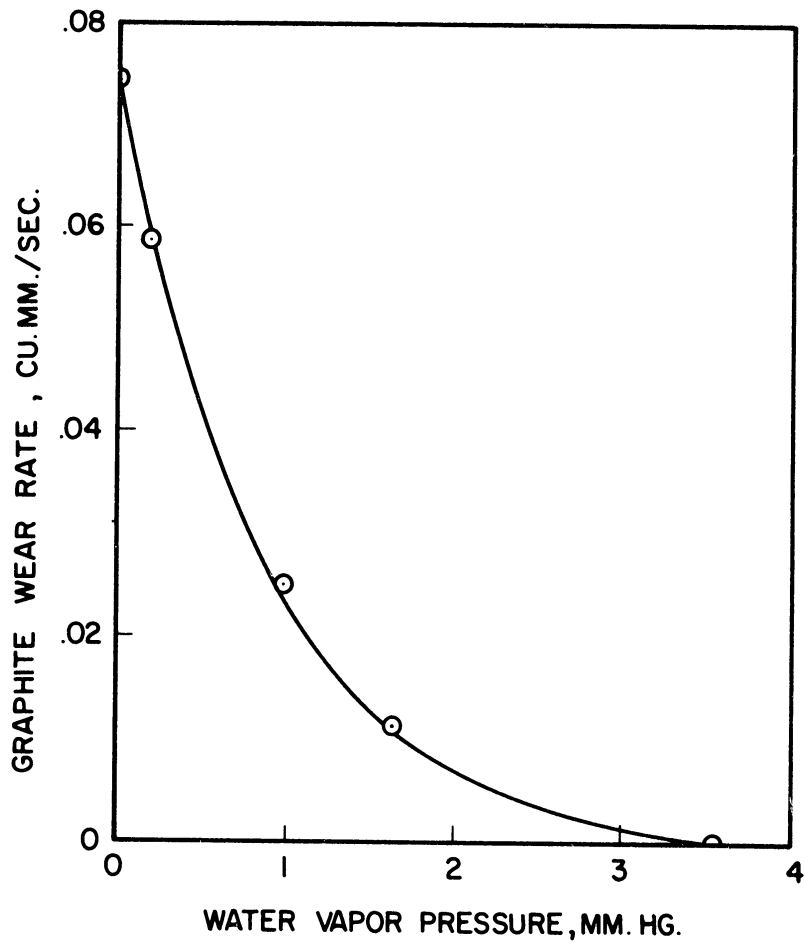
Figure 2.   The Wear Rate of Graphite as a Function of the Water
            Vapor Content of the Test Environment.   (After Savage)

all active investigating various facets of surface phenomena. With so many and such varied interests investigating surfaces it is natural to expect that the picture would be confusing particularly when one recognizes that there is no standard way of describing or characterizing a surface that is acceptable to all groups. If we cannot agree on what are examining or investigating it is quite obvious that the results are apt to be confusing. The Mathematicians, Thermodynamicists and Theoretical Physicists are of course unhampered by these difficulties since one can always postulate a clean surface of known area and proceed from this point. Work of this type is quite important since it is of considerable aid to the experimentalist in attempting to correlate or interpret his results. To date however the correspondence between the experimental and theoretical approaches is rather poor and at best is only qualitative in nature. I do not intend in this paper to go into a review of the theoretical studies since there are several excellent reviews and texts that summarize these contributions. [2,3,4,5,6,7]

Let us look at the properties of materials from an engineering standpoint. In general we are interested in mechanical, electrical and chemical properties. Phenomena such as elasticity, strength, plasticity, conduction or semi-conduction, oxidation and corrosion resistance, catalytic effects, adsorption, lubrication, wetting, etc. occur in everyday engineering practice and are supposed to be under the control of the engineer. Are surfaces involved in these operations? The answer is yes in all cases but they are not necessarily the controlling factor in many applications.

One would not normally anticipate that the elastic properties of a solid would be a function of the internal or external surfaces yet there are many references in the literature which show that this is indeed the case. Table I is a listing of a few of these data. These are very large changes in moduli but this is to be expected when very small diameter specimens are used since it is only in these specimens that the surface atoms become an appreciable proportion of the total volume or cross-section of the sample. These data would indicate that E, the

TABLE I

ELASTIC MODULI IN VARIOUS MEDIA

Material	Environment	E,Dynes/CM^2
Glass	Air	5.22×10^{11}
	Menthanol	4.56×10^{11}
	Water	3.46×10^{11}
Platinum	Air	8.35×10^{10}
	Water	3.59×10^{10}
Steel	Air	23.9×10^{11}
	Water	19.1×10^{11}
Quartz (100μ)	Air	4.9×10^{11}
(1μ)	Air	13.7×10^{11}

elastic modulus should be a function of the surface to volume ratio as the specimen size changes and the internal surface to volume change as the grain size changes. Floreen and Hucke[8] have shown that there are changes in the elastic modulus when the external surface to volume ratio and the internal surface to volume ratio for a given material is varied using sheet specimens of various sizes machined from the same stock or

heat treated to produce various grain sizes. They also showed that vary-
ing the environment in which the specimens were tested produced changes
in the elastic modulus for a given internal or external surface to volume
ratio. A summary of these results is given in Figures 3, 4, and 5. It
is true that in these larger specimens, where the surface to volume ratios
are less than in wire or film specimens, the changes in the elastic moduli
are not as great since the surface makes up a smaller proportion of the
total volume, nevertheless the influences are there and are significant.
Conceivably other testing media may produce even more significant changes
in the surface energy and still more strongly affect the elastic behavior
than the data shown. Another piece of confirmatory information along
this same line are the data of Clauss[9] who showed that a change in the
torsional modulus of wires was a direct function of the degree of gas
adsorption when helium, argon or carbon dioxide is adsorbed on silver
wires.

When one studies the influence of surfaces on the plastic prop-
erties of solids and such phenomena as fracture, yield strength, fatigue
strength and creep strength one encounters an enormous volume of pub-
lished work. It is a well established fact that there is a specimen size
effect in dealing with these properties and many recognize that there are
environmental effects which in some cases are equally as important as
size and bulk properties.

In preparing this survey I had intended to avoid involvement
in mechanisms; not that they are unimportant but in surface research
there are as many mechanisms as there are investigators and one can loose

Figure 3. The Variation in Elastic Modulus of Copper as a Function
of the Grain-Boundary to Volume Ratio for Three Sizes
of Test Specimens. (Floreen and Hucke)

Figure 4. The Variation in Elastic Modulus of Copper as a Function of the Surface Area to Volume Ratio for Specimens of Three Different Grain Sizes. (Floreen and Hucke)
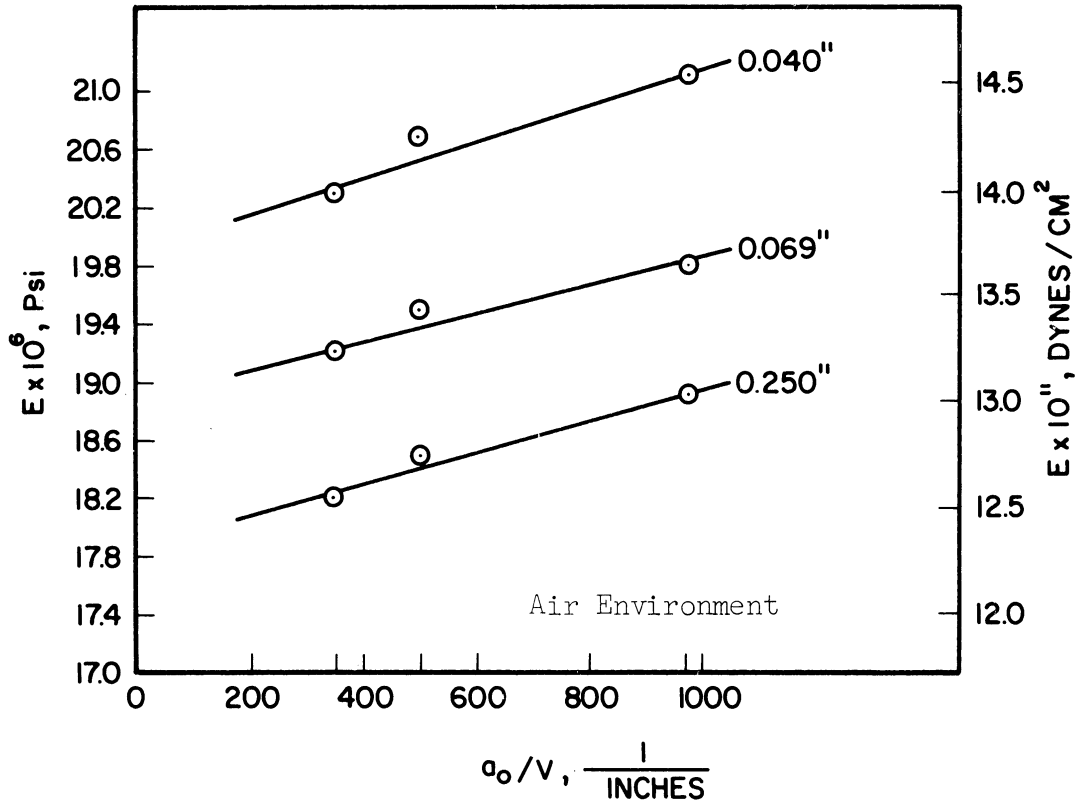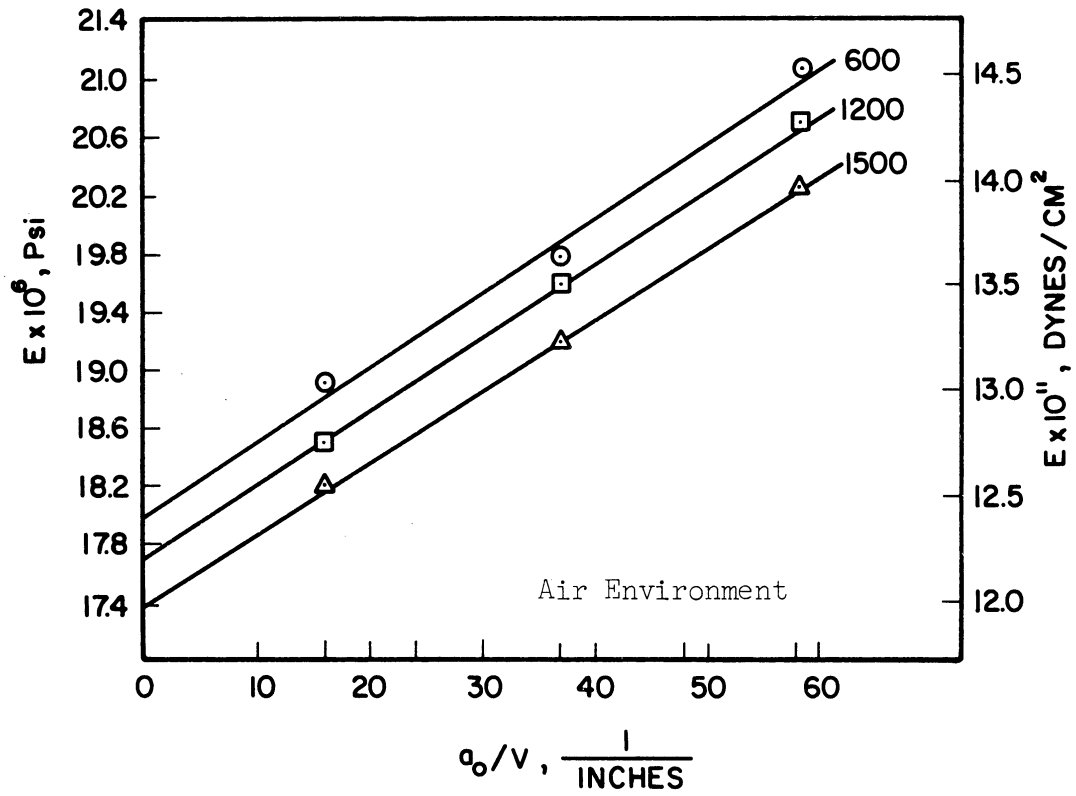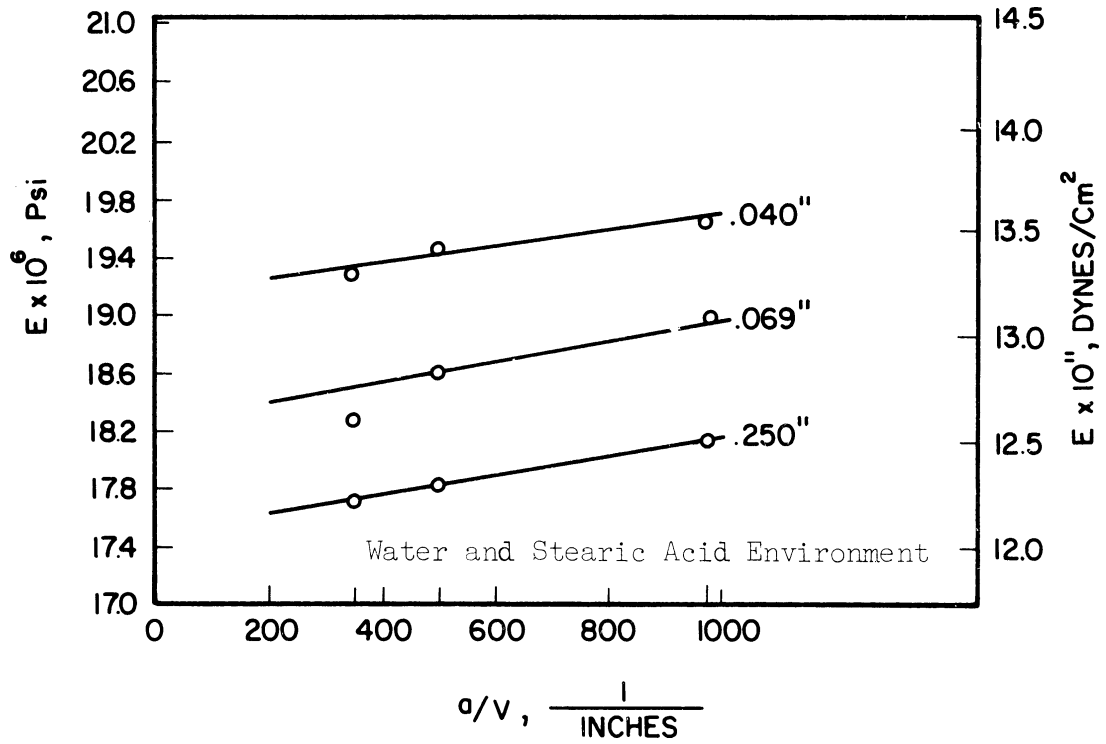
Figure 5. The Variation in Elastic Modulus of Copper as a Function of the Grain-Boundary to Volume Ratio for Three Sizes of Test Specimens. (Floreen and Hucke)

sight of the data in attempting to interpret it. I had envisioned this paper as one that would present the fact that there are important surface phenomena but would leave their interpretation to others. I might say in passing that in surface phenomena we do not have the equivalent of that universal cause of all solid state behavior, the dislocation. In order to bring some coherency to the large volume of data on the plastic behavior of solids as influenced by their surface it will be convenient to go into mechanisms and to subdivide solids into classes of glasses, ceramics and metals.

To explain the mechanical behavior of glasses one is usually forced to a Girffith crack mechanism which essentially postulates the existence of microcracks or imperfections in the surface of the glass. This then relates the strength to the size in that with decreasing sizes there is a lowered probability of finding a crack which would produce failure to give the relationship observed experimentally that the strength is inversely related to the size. The influence of environment on the strength is usually explained by either of two alternate mechanisms. Stress corrosion at the root of the surface cracks, or a change in surface energy due to the adsorption of the environment onto these surfaces. Note that both of these mechanisms involve surface phenomena rather than any intrinsic property of the glass as a solid although the bulk properties can be modified to produce property changes.

In the case of ceramics, Al_2O_3, MgO and ionics such as NaCl the same type of size effect as noted in glasses is observed, i.e., the tensile strength is inversely proportional to size. Environmental factors are probably more significant in affecting the plasticity and

strength of these materials. The work of Joffe[10] on testing of NaCl in water and obtaining greatly increased strength and the work of Polanyi and Ewald[11,12] showing increased plasticity when surfaces are wet, are well known. Other media also have quite as marked effects; Parker and others[13,14] work on gas adsorption for example shows the same phenomena. There are three mechanisms proposed for the behavior of these materials. The healing or dissolution of microcracks by wetting of the surfaces, the penetration or wetting of the internal boundaries by the environment, or the barrier quality that the surface offers to dislocation flow or generation.

Turning to metals these same size and environmental effects that have been noted in glasses and ceramics have been detected. The size effect is more generally believed to be due to surface restrictions to the emergence of dislocations while the environmental effects can either be explained by dislocation theory which postulates the blockage of their flow by surface films of oxides, hydroxides, sulfides or even synthetic plastics,[15,16] or by a Russian concept known as the Rebinder Effect. This latter theory, based on the studies of Rebinder and his associates,[17,18,19] showed that when materials are immersed in surface active environments the environment adsorbs onto the surfaces to lower the surface energy which in turn produces a marked decrease in the extent of plastic flow and lowers the fracture stress. Both of these mechanisms involve surface films but there are data which show environmental effects even in the absence of a film. The testing in acid, for example, of bismuth and germanium produces marked increases in strength.[20,21]

In some respects the less ductile metals or metalloids are more sensitive to surface conditions than the ductile metals.

Turning now to electrical properties once again one can show that in many applications the influence of surfaces, either internal or external is quite significant. The earlier work of Langmuir and Volmer on the study of surface diffusion showed that the work function was definitely related to the surface concentration of impurity atoms. The development of the field emission microscope has enabled significant advances to be made in studies of surface diffusion in the last few years.[22,23] It should be marked in passing however that most of the surface diffusion data is concerned with metallic surfaces; the phenomenon has been noted on glasses, plastics, polymers and other types of surfaces, but quantitative data are absent.

Electronic conduction in metals is largely a volume controlled process but the interfering effects of grain boundaries are well known. If however the dimensions of the conductor are reduced to where the size is of the order of the mean free path of the conduction electrons, the external surface once again plays an increasingly more important role. This effect is apt to become quite significant from an engineering standpoint as we drive further towards miniaturization of our electronic gear. The theory of what should happen when conduction occurs in thin films has been quite thoroughly presented; effects on thermal conductivity, thermoelectric power, influence of magnetic fields, Hall effects, optical property changes, etc. On the other hand the experimental verification of any of these studies is quite scarce. What data are available

seem to indicate that if extreme care is taken to prepare films of high
purity with smooth and parallel faces, one can then show that these
have the same properties as the bulk metal. Unfortunately, however,
the introduction of impurity atoms, adsorption effects, non-coherency
of the films, etc., all produce what are termed "anomalous behavior",
i.e., the data don't agree with the known behavior of the massive metal.
As Dr. Mayer has stated "Among 5000 papers dealing with thin film since
the beginning of their study, a great number tell of the great pains the
authors took and still take, not beforehand, but afterwards, to trace
out extraneous physical factors and to relate them to certain observed
properties."[24]

In the field of semiconductors the presence of interfaces is
even more important than in conductors. It was the study of surface
state theory in semiconductors which led to the invention of the tran-
sistor. Surface states on germanium were suggested by Bardeen to account
for the observed facts that the contact potential, the work function and
the rectification characteristics appeared to be independent of the metal
that was used for the reference or contact. The exact character of the
surface state of the semiconductor is not usually specified; they may be
merely work-function differences between metal and semiconductor, chemi-
cal barrier layers, surface contamination due to adsorption, or combina-
tions of these factors, etc. As in the case in so many phenomena in-
volving surfaces, ways have been devised to analytically handle the
description of their behavior without actually determining basic mecha-
nisms. One cannot tolerate internal surfaces in semiconductors since

they also produce anomalous effects; they may form a highly conductive region if the bulk is highly insulating, or it may act as a high resistance layer in a conducting bulk phase. In addition they also act as regions of high recombination. Since they are a disordered region they also act as scattering centers and lower the electron and hole mobilities. It is for these reasons that semiconductor devices are almost invariably single crystals. These same effects can of course be generated at external surfaces but since these cannot be eliminated their presence has to be tolerated but they can also introduce some extraneous effects of their own, so much so that environmental conditions such as humidity, cleanliness etc., must be controlled in order to produce commensurable components.

Materials which are dielectrics or insulators are also subject to surface property changes. Many of the engineering failures of insulators are not due to intrinsic breakdown of the dielectric but are primarily caused by structural discontinuities which produce internal surfaces, subsequent internal heating chemical deterioration and eventual loss in insulating properties. The external surface is particularly susceptible to chemical change by way of adsorption, aging effects and eventual chemical decomposition which results in tracking failures, crazing, and finally failure. Many of the effects which are noted in the electrical, magnetic and optical properties of materials are really traceable to the changed chemical properties of internal and external surfaces. By their very nature these surfaces are bound to produce anomalous effects. Since they consist of poorly coordinated bonds

which are satisfied either by physical or chemical adsorption of environ-
mental atoms, are points of high stress, are preferential loci of im-
purity atoms, their resulting influence on the properties of materials
should not be surprising. The fact that we cannot accept in an im-
perfect manner characterize these regions is no reason for ignoring them.

External surfaces more strongly affect the chemical behavior
of materials than any other property. This is to be expected since the
surface a solid presents to a liquid, gas or to another solid actually
consists of a barrier or series of barriers which must be penetrated
before chemical reactions can occur. Most of us are aware of this from
the extensive studies that have been made and continue to be made on
the oxidation and corrosion of metals. Corrosion is generally thought
of an occurring by one of three basic mechanisms: direct chemical attack,
galvanic attack; or oxygen depolarization. In direct chemical attack
the metal reacts with the medium and supposedly goes directly into solu-
tion. While some systems are this simple many of them are not. The
solution of copper, for example, in acid ferric chloride is the basis of
the treatment of plates for the photoengraving industry and in preparing
printed circuitry in the electronic industry. A person simply immerses
copper in the acid solution and the copper is dissolved. Because the
etching obtained commercially was not of sufficiently high quality an
investigation was made of the actual mechanism with a view to improving
it. This study showed that the dissolution of copper is not a simple
reaction but consists of two separate and distinct steps. First a mono-
film of Cu_2Cl_2 forms on the surface of the copper and is insoluble in

the depleted acid film near the copper. As the solution is replenished via diffusion from the bulk of the liquid the Cu_2Cl_2 dissolves and forms $CuCl_2$ which is soluble and the process proceeds. A study of the metallic variables such as purity, orientation, grain size, cold work, etc., showed that none of these variables had any effect on the dissolution rate. The controlling factor is the kinetics of the formation and dissolution of the surface films, not the properties of the underlying metal.

In corrosion by galvanic attack most people are aware that a change in environment or merely the concentration of the environment will change the positions of the elements relative to one another in the electromotive series. Here again this is obviously a surface phenomenon since nothing has been done to the metal, only the environment, yet the stability of the metal has been changed. The very mechanism of corrosion by oxygen depolarization, the removal of oxygen from solution to react with the hydrogen released at the anode, is intimately tied to the surface.

The voluminous and seeming never-ending flow of papers, symposia, research proposals and programs dealing with corrosion is due principally to the fact that the problem is inherently one that is surface controlled and simply cannot be handled by considering only the bulk metal as the system; the bulk composition is only one variable and generally not the most important one. It is somewhat naive to believe that the chemical analysis or the physical structure of a solid alone determines its subsequent behavior in various media. The strong feelings that engineers have relative to the merits of one type of stainless steel over another; 316 vs. 347, 304 vs. straight chromium steels, etc., are based on the

behavior of these materials in various corrosive media. While all engineers will admit that the passivation, (doing something to the surface), is the principal reason for the corrosion resistance, they seem to associate this passivity with the base analysis of the metal. The fine work of Rhodin[25] in analyzing the surface of stainless steels, as shown in Figures 6 and 7, clearly indicates that while there are changes in the major constituents of Fe, Cr, and Ni, the minor constitutents show an even greater change and in this fashion as he states "a minor constituent can become a major constituent of the surface." Undoubtedly the composition of the bulk phase determines the composition of the surface films but the straight bulk analysis is not the only criterion since the treatments used to produce different types of surface films are equally as important.

In the fields of adsorption and absorption on surface there has been and there continues to be a great deal of activity. The major portion of work in this field is of the variety where the solid surfaces are cleaned, then subsequently exposed to a given media, usually a gas, and the process of adsorption followed through pressure changes. This is of course the basis of the famous BET technique for the measurement of surface area. While studies of this type are informative and important they unfortunately do not shed too much light on the behavior of real materials. As engineers we are forced to work with surfaces before they are cleaned and in this respect we are more interested in what comes off the surfaces than what is readsorbed. An example of this is the material graphite which is finding considerable use in the nuclear fields as well as in extreme temperature applications. The
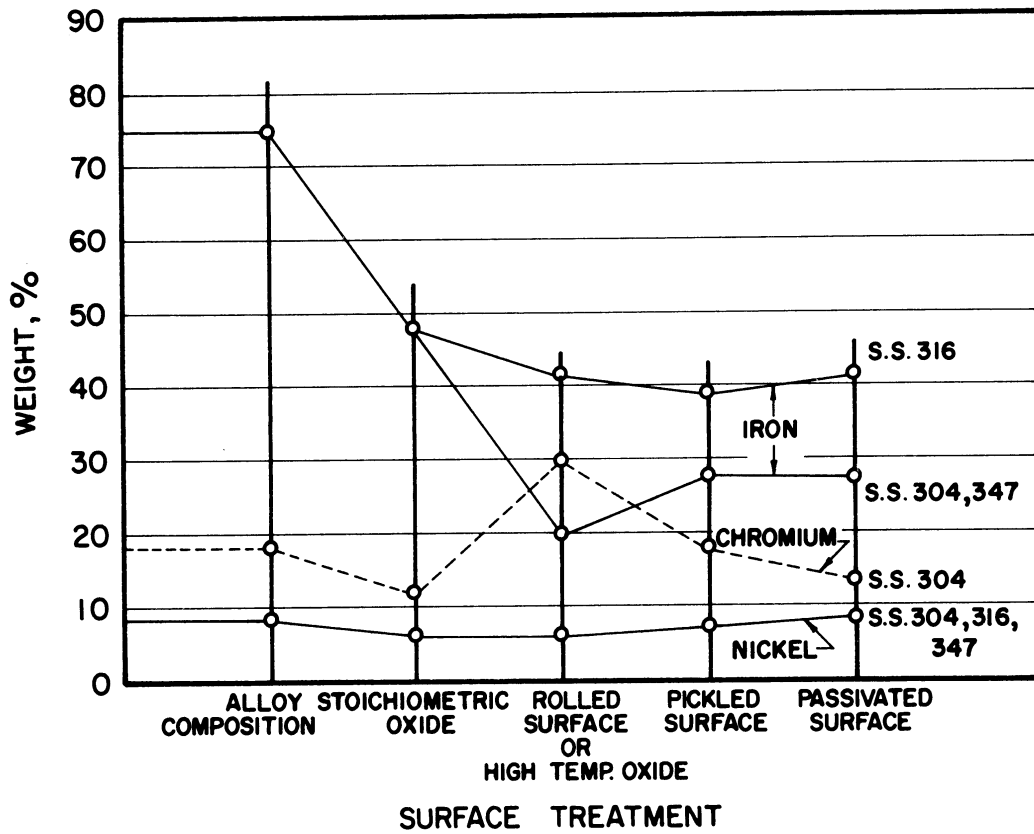
Figure 6. Changes in the Surface Concentration of the Elements in Stainless Steels as a Function of Their Prior Treatment. (After Rhodin)
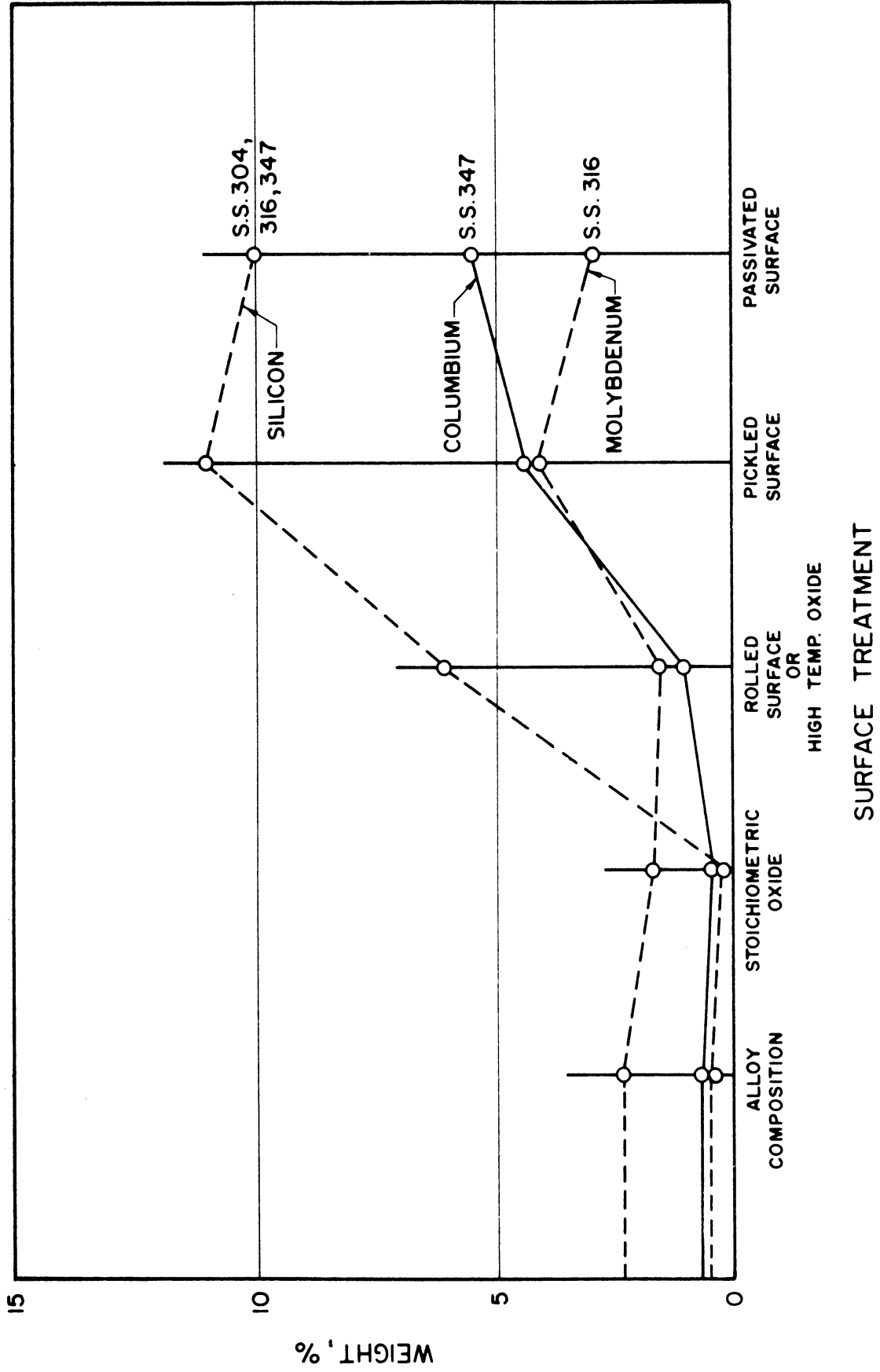
Figure 7. Changes in the Surface Concentration of the Elements in Stainless Steels as a Function of Their Prior Treatment. (After Rhodin)

properties of this material are quite well known but it is not generally

recognized that this material has a very extensive surface. It's

theoretical density is 2.25 g/cc but this is never obtained; most

graphites are of a density of 1.85 g/cc. Some of this defect in density

is due no doubt to point and planar defects but the great bulk is in-

ternal porosity. While the quantity of gas adsorbed per square centi-

meter on these internal surfaces may be small the total square centi-

meters of internal surface is enormous. This means that considerable

quantities of gases can and are adsorbed in graphite and can and will

change the properties of the graphite particularly where graphite is

being used for its chemical stability. These are not lightly held gases

since desorption is still occurring at temperatures as high as 2200°C

and furthermore the desorption is not irreversible since on re-exposure

to the atmosphere the graphite readily readsorbs approximately 50% of

the gas desorbed. The principal gas desorbed in this material is water

vapor. This adsorption is not something which is restricted to a defect

material such as graphite. Powdered metals and ceramic materials parti-

cularly when in a size range where there is a very large extended sur-

face, readily adsorb or absorb gases on their active surfaces. In some

cases the bonding is rather weak and this is known as physical adsorp-

tion while in other cases strong bonding occurs and this is termed chemi-

sorption. Subsequent release of these adsorbed atoms during such opera-

tions as sintering causes problems in dimensional stability, density and

the various physical properties. Here again the properties of the bulk

material do not determine what composition the surface adsorption will

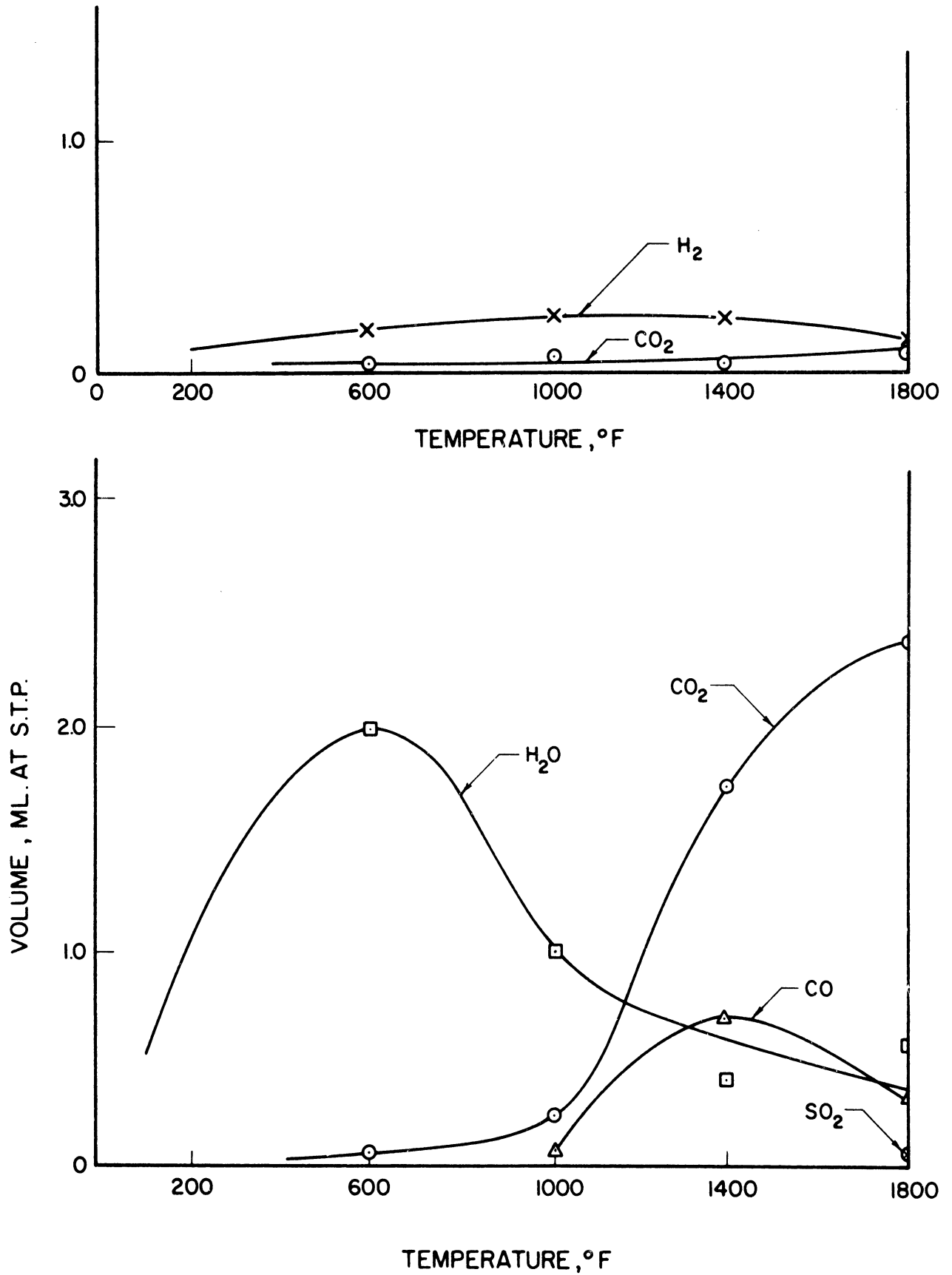take. Figure 8 shows the desorption analysis obtained on nickel powders

Figure 8. The Composition of the Gases Desorbed from Nickel
Powders as a Function of the Temperature of De-
sorption. The upper curves are for steam scattered
nickel into a nitrogen atmosphere; the lower curves
are for steam scattered nickel into an air atmos-
phere.

that had been manufactured by the same technique but in different
atmospheres. To still further complicate the picture if these same
powdered metals are given different surface treatments, either chemi-
cally or mechanically, their subsequent readsorption characteristics
are modified. Copper powders for example when cleaned in ammoniacal
solutions, rinsed and dried are stable in air for weeks while the
same powder cleaned in nitric acid, rinsed and dried, will interact
almost immediately with the atmosphere to produce a surface stain.
Vacuum cathodic etching of uranium also produces this stabilization
of the surface to atmospheric corrosion while untreated uranium will
tarnish almost immediately on exposure to the atmosphere.

One of the most important and at the same time most compli-
cated of all phenomena associated with surfaces is that of heterogeneous
catalysis. These are chemical reactions which are carried out in the
liquid or gaseous state by contacting a solid catalyst. Catalysts are
usually defined as promoters of a chemical reaction which do not appear
in either the feed or product streams. They don't contribute energy to
the system, they do not change the equilibrium of the system, they are
capable of regeneration, and their essential characteristic is that
they change the kinetics of a reaction. While catalysts have been rec-
ognized and used for well over a hundred years and the last ten years
have seen an enormous amount of effort put into research to understand
the phenomenon, it is still safe to say that other than recognizing
that it is a surface phenomenon, the basic mechanisms are unknown.
There are many reasons that can be given for this lack of understanding;

the phenomenon is entirely surface controlled, not all the catalyst surface is active, addition agents called promoters and poisons can markedly change the characteristics, temperatures, pressures, compositions, dispersions, prior treatments, types of carriers, modes of regeneration are but a few of the many variables which are known to affect the catalytic behavior. Many concepts have been investigated in order to gain some insight into the mechanisms involved. Relationships between contact potentials, work functions, electronic configurations, paramagnetic properties, atomic sizes, lattice imperfections, influence of impurity atoms, conducting or semi-conducting properties, particle sizes and distributions, orientations or crystal faces, presence of adsorbed films, etc. have all been investigated. Weak interrelationships can sometimes be found but for the most part the problem is still unsolved from a mechanism standpoint.

I have mentioned three or four fields in which the presence of surface is of considerable significance but this by no means is a complete listing nor even the most important but they are fields in which active research is being carried forward at an accelerated rate. Other fields which are concerned with surfaces are those dealing with fibres and films, polymers and plastics, coatings, paints, emulsions, adhesives, lubricants and cements. All solids, liquids and gases that we handle as engineers are contained within some confined volume and produce interfaces where surface phenomena can occur.

In symposia such as the present one there is a tendency to put our best foot forward and show how we are making real progress.

You will note that in my discussion I have been taking what might be termed a negative attitude. There are advantages in seeing where you have been but I feel that it is more important to look forward to see where we should be going. While there is no doubt that progress has been made and will continue to be made along the line of current research programs I have the strong feeling that more time, effort and funds should be devoted to basic studies on surface phenomena if we ever expect to obtain a real understanding of the behavior of real materials in engineering practice.

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