Meetings

Surface Phenomena

Characteristics of solid surfaces and general problems related to surface phenomena were the subjects of the second annual symposium on fundamental phenomena in the material sciences, held in Boston, Massachusetts.

This year's symposium covered many aspects of surface phenomena and dealt with all solid material types, regardless of whether they are metallic or nonmetallic. Surface phenomena were treated in a broad sense, with emphasis on the surface characterization and properties, rather than on the generic basis, of specific material types. The choice of subject matter was, of course, somewhat arbitrary. Consequently, important branches of the subject have been omitted and hopefully will be covered in the third annual symposium to be held 25–26 January 1965 in Boston.

The symposium dealt with solid surfaces in which the surface of the solid as distinct from the solid as a whole, plays a particularly significant part. For example, in a classic experiment, when a sheet of glass is carefully cleaned with soap and water, the water completely covers and wets the glass. If the glass is dried with a towel and again immersed in water, the water will run off and leave dry patches behind. The glass looks greasy; tiny traces of grease have been transferred to it from the towel and have markedly altered its wettability. This effect is clearly confined to the surface, because grease cannot penetrate into the interior of the glass.

Sometimes, however, the important role played by the surface may not be as obvious. The strength of a brittle solid (for example, glass), and to a certain extent that of a metal, is profoundly affected by the state of its surface. The presence in the surface of minute cracks too small to be seen by the naked eye will greatly reduce the strength. In rock salt, for example, the measured tensile strength is many hundreds of times lower than that to be expected from the known structure of the substance because of surface imperfections of this kind. The adhesion of one solid body to another, which makes possible the welding of hot metals and the sintering of powders, should also be mentioned.

Many of the participants broached the question of a satisfactory definition of the term "surface" or "interface" (which may be a better word than "surface" because—unless the solid is suspended in a vacuum—it is in contact with a gas, a liquid, or another solid, and it is the interface between the solid and the other body which is the focus of interest in surface phenomena). The literature does not contain any useful definition of this term. The term "surface" or "interface" can be defined only if one considers the characteristics of the bulk material, the condition of the surface under discussion, the environment, and its reaction with the surface. The emphasis, however, should be given to the problem under which the surface is discussed. In this way the basic question can be answered as to whether a surface is two-dimensional or whether it has depth and is, therefore, three-dimensional.

H. C. Gatos (Massachusetts Institute of Technology) discussed the structure and electronic configuration of crystalline surfaces. He covered three different aspects of surfaces—their chemical behavior, their structural properties, and their electronic properties. With respect to chemical behavior, the interrelationship between unsaturated bonds and lattice configuration is of prime importance. In a diamond cubic configuration, as was shown in a model, the degree of unsaturation or, in other words, the density of free bonds, varies with the respective crystalline surface. In the *(111)* surface of Fig. 1, only one unsaturated bond goes upwards, whereas three bonds go into the bulk or downwards. In the case of the *(100)* surface, two unsaturated bonds go upwards, and two go into the main bulk. In the *(110)* surface, the very top atoms have two bonds with two other surface atoms, one with the bond up and one dangling bond. With respect to the chemical characteristics, the more dangling bonds present on the surface the more reactive the surface should be. This variation of the unsaturated bonds with the various surfaces permits drawing conclusions with respect to the chemical behavior of respective surfaces. The theoretical configuration has been verified experimentally. It was pointed out by Gatos that, for experiments with meaningful results, specimens have to be prepared and kept in a vacuum of 1×10^{-10} torr or better. He also pointed out that the difficulties in coping with aspects of surfaces in a quantitative way are virtually insurmountable. However, approximations and working models can be successful and can serve to explain some of the facts and as a guide to further experimentation.

A new concept—a tool with which one can investigate the nature of crystal surfaces—was described by L. H. Germer (Cornell University). He talked about the present and proposed uses of low energy electron diffraction in studying crystal surfaces. Germer believes that this method will be the most important technique for the investigation of crystalline surfaces. Most of the present commercial electron diffraction equipment for the investigation of thin films and surface layers uses fast electrons which penetrate the material

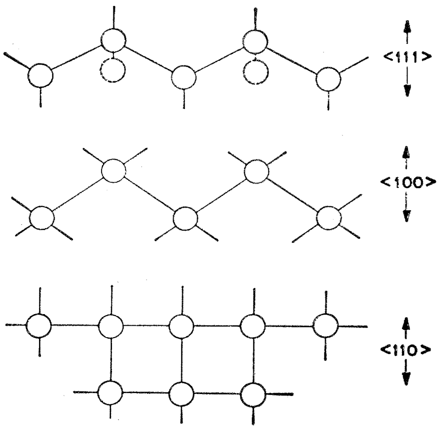


Fig. 1. Saturated and unsaturated bonds in the surface of diamond cubic lattice configuration.

and therefore give very little information on the true nature of the surface. The low energy electron diffraction method has been developed during the last 4 years and commercial equipment will be available within the next few months. Germer considers that the most significant result of the new test methods is the conclusion or proof that when foreign atoms are adsorbed into a clean metallic surface a complete rearrangement of the surface metal atoms occurs, even if the adsorption concerns only a fraction of the monolayer.

In a discussion of the effect of oxides and hydrocarbons on sliding friction, P. M. Ku (Southwest Research Institute) emphasized low temperature effect. He pointed out that measured friction of like-pair pure metals, such as copper on copper or aluminum on aluminum, can be accurately measured and changes very little in the temperature range from room temperature to −250°C. The measured friction between the oxidized metals, however, scatters widely; the scattering increases with the thickness of the oxide film up to a film thickness of 2000 Å. Organic films between copper surfaces in pure helium atmosphere lower the friction with increasing temperature during the experimental procedure. Friction is at a minimum just below the melting point of the organic film. Above the melting point, sliding changes to stick and slip, metal damage increases sharply, and friction rises abruptly.

F. F. Ling (Rensselaer Polytechnic Institute) presented new ideas on the deformational and geometrical aspects of surfaces in sliding contact. Based on rather simple experimental work on the friction between two cones of similar or dissimilar materials (Fig. 2), of which one cone is rotating and the second one is stationary, Ling developed a calculation of the friction characteristics in the absence of adhesion. He showed the effects of the cone angles on the friction characteristics between a variety of materials. Ling has developed a modified equation which can be useful in selecting materials for a variety of friction conditions. Ling's finding permits calculation of the heat flux generated in the moving, as well as in the stationary, body and is based on the dissipation capacities of these bodies.

In discussing the influence of surface energy on sliding contact, E. Rabinowicz (Massachusetts Institute of Technology) emphasized that the real lubrication problem in any sliding contact is the wear of the sliding parts and the effect of the lubricant on this wear. Wear can best be expressed in terms of the size and the amount of particles that are taken off during the sliding action. He also found that ball milling of solid materials with the lubricant added resulted in the formation of fine particles. The size of the particles is practically identical with the particles produced by the sliding action. In both cases, the addition of the lubricant reduces the surface energy of the solid and the lowered surface energy reduces the size of the wear particles. There is a close correlation between the roughness of the surface due to friction and the size of the wear particles. Materials which produce low surface energy in the solid are those which give low friction coefficients.

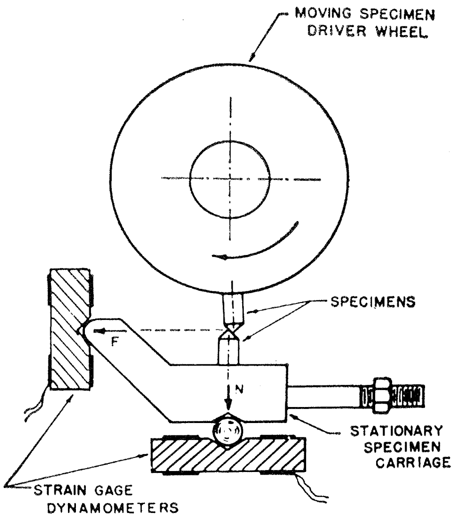


Fig. 2. Experimental set-up for friction between two cones of similar or dissimilar materials.

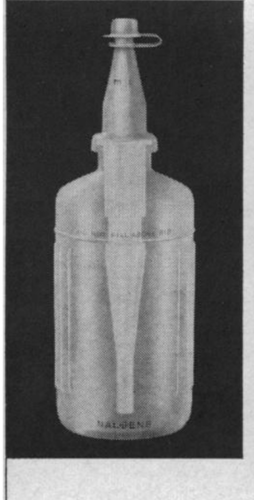
Imre Farkass, (Ilikon Corporation, Natick, Massachusetts) reiterated the statement by Gatos that in order to do meaningful experiments relating to surface phenomena one has to perform these experiments in extremely good vacuums of 10^{-10} torr pressure or better. Farkass discussed the problems of producing a clean surface by degassing in ultrahigh vacuum and again emphasized the necessity of perfect vacuum chambers for any experiments on a truly clean surface. He gave a considerable amount of data on surface outgassing in a vacuum of about 10^{-11} torr, and he also discussed in great detail the design and construction details of commercially available vacuum chambers which are able to produce pressures of about 10^{-11} torr.

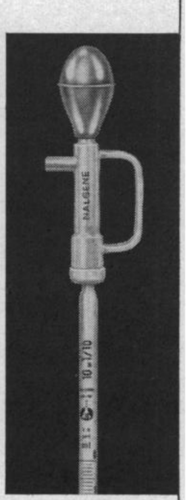
In a paper on adsorption on heterogeneous and homogeneous solid surfaces, S. Ross (Rensselaer Polytechnic Institute) differentiated between localized and mobile adsorbed films and referred to De Boer's book, *The Dynamical Nature of Adsorption*, published in 1963. Special emphasis was given to the phenomena one should expect with Van der Waals type of two-dimensional gas at a phase change of the absorptive layer as the temperature decreases.

Ross disclosed that, in an alkali halide with ethane adsorbed at 90°K, he actually had observed the phenomena theoretically foreseen by De Boer. A discontinuity of the adsorbed film was observed with krypton and alkali halide when the amount of adsorbent corresponded to the close-packed monolayer. If the coverage was more than 60 percent, the first monolayer began to develop into a multilayer and the experimental data hardly permitted any theoretical analysis.

Frederick M. Fowkes (Sprague Electric Company) discussed the determination of intermolecular forces between adjacent materials by surface chemical techniques. A reference was made to Hildebrand's work, in which he predicted molecular interactions from the solubility of one material into the other. The intermolecular forces between adjacent surfaces include the ever-present dispersion forces, dipole and ionic interactions of various kinds, hydrogen bonding, and metallic bonding. Surface tension can also be used as a measure of intermolecular forces, he reported. Means were offered to evaluate the magnitude of interacting forces in the measurement of contact angle, interfacial tension, or free energy of immersion or adsorption.

In an analysis of solid-to-solid adhesion, J. J. Bikerman (Massachusetts Institute of Technology) noted that if two solids are pressed together for a short time and then separated, the force needed for separation usually is due to one or a combination of three effects—Stefan's apparent adhesion, capillary attraction, or electrostatic attraction. If the pressing occurs in air at atmospheric pressure, the two metal surfaces would be covered by adsorbed air and moisture. No solid-to-solid contact exists, but there is contact between the adsorbed layers of contamination on the structures. If, however, pressing occurs in vacuum of 10^{-11} torr or better, it would take a very long time until a solid surface is contaminated and the forces for bonding would





be considerably smaller. Adhesion between solids actually depends on the viscosity of the medium between them or the transfer of charge between the solid surfaces or both. Long-time pressing will result in mutual diffusion, sintering, or recrystallization; separation cannot be achieved without cohesional break of one of the solids.

C. M. Adams, Jr. (Massachusetts Institute of Technology) offered a new concept for spreading of a liquid metal on a solid surface and developed equations which strongly indicated the similarity in the thermodynamics of wetting and penetration. In partial wetting, there will be no spreading. If the interfacial energy is low enough for spreading, it certainly will be low enough for penetration. Observed velocities of a pure copper liquid spreading on a solid copper surface are in the range of several hundred centimeters per second. Low velocities of spreading were observed in the system liquid tin on solid copper. This system is controlled by "surface" diffusion. For example, an alpha solid solution of tin and copper has to be formed before reasonable spreading can be observed. In addition, Adams reported, it was found that the process depends on the presence of a very small concentration of oxygen, which seems to be vital for this type of wetting. A complete absence of oxygen inhibits wetting. This was somewhat contrary to our customary belief that oxygen is detrimental to some processes, such as brazing.

After the formal presentation of the papers, a discussion developed about the value of a meeting of this type and how much stimulation the theoretical papers gave to speakers who discussed more practical aspects of surface phenomena. The majority of the audience and the authors stated the definite need for this type of meeting. Several hours' discussion among the speakers and between the speakers and the audience indicated that a symposium of this kind cannot only be informative but also extremely useful, as it tends to formulate definitions and clarify theoretical aspects of this field.

A symposium volume is being prepared. Requests for this volume should be addressed to Ilikon Corporation, Natick, Massachusetts.

L. J. BONIS

Ilikon Corporation
Natick, Massachusetts

H. H. HAUSNER

Brooklyn Polytechnic Institute,
Brooklyn, New York