DEC 29 1945

CLASSIFICATION CANCELLED

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

No. 982

THE CHEMICAL ACTION OF OILS ON SINGLE CRYSTALS OF METALS

By A. T. Gwathmey, H. Leidheiser, and G. P. Smith
University of Virginia

FOR REFERENCE

NOT TO BE TAKEN FROM THIS ROOM

Washington
November 1945

NACA LIBRARY
LANGLEY MEMORIAL AERONAUTICAL
LABORATORY
Langley Field, Va.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE NO. 982

THE CHEMICAL ACTION OF OILS ON SINGLE CRYSTALS OF METALS

By A. T. Gwathmey, H. Leidheiser, and G. P. Smith

I. SUMMARY

The chemical action of oils on large single crystals of metals in the presence of various gases has been studied, with special emphasis placed on the influence of crystal plane. The studies primarily have been concerned with four metals: silver, copper, lead, and iron; and four types of oil: pure hydrocarbons with mineral oil as representative, oiliness agents with stearic acid as representative, chemical polishing agents with tricresyl phosphate as representative, and commercial oils with new and used aviation oils as representatives.

It was found that the rates of all surface reactions, which have been tested, vary with crystal plane, although this variation may be obscured at high rates by the influence of other factors such as diffusion. The reactions tested include oxidation, etching and consequent roughening, carbon formation, rearrangements due to gaseous catalysis, crystal growth, electrolytic reactions such as electrodeposition and galvanic action. Wetting in a few cases varies with plane.

The methods used in preparing large single crystals of various metals are briefly discussed.

II. INTRODUCTION

The beneficial effect of some oils is due to their ability under certain conditions to attack metals in varying degrees, while under other conditions chemical attack, if carried to extremes, can lead to corrosion, roughening of the surface, and ultimately to increased friction and wear. The oil also may be unnecessarily decomposed. The chemical

action between metal and oil, therefore, is one of the crucially important factors in the subject of lubrication. It may mean success or failure to lubrication and the machinery which it serves.

An ordinary metal surface consists of many different types of structure, such as crystal faces, edges, corners, and boundaries, and amorphous layers. The properties of a surface are a composite of the properties of these individual parts, and, in order to understand the behavior of a surface, the properties of these parts must be determined.

Since the number of atoms per unit area in a crystal varies with face, many of the surface properties of a metal would be expected to vary with face. In experiments carried out preliminary to this investigation, it was found that oils in the presence of air etched a single crystal of copper preferentially with crystal plane. Both the rate of etching and the degree of roughening varied with plane. It was significant that chemical attack by the same reagent could render one face smooth and another rough. The striking appearance of these etch patterns, due to the directional reactivity of the crystal, seemed to offer a sensitive and relatively simple method of following the course of a reaction between a liquid and a metal.

Therefore the chemical attack of oil on a metal surface has been studied with the aid of large single crystals, special emphasis being placed on the influence of the crystal plane. A single crystal represents the unit of which all metals are composed and serves as an excellent meeting ground for the correlation of the many apparently unrelated but important processes taking place on the surface of a metal. It is believed that many of the processes which are commonly attributed to mechanical or physical causes have their origin in chemical attack.

This investigation, conducted at the School of Chemistry, University of Virginia, was sponsored by and conducted with the financial assistance of the National Advisory Committee for Aeronautics.

III. DESCRIPTION OF APPARATUS AND METHOD OF EXPERIMENT

The method, in general, consists of studying the reaction between oil and large single crystals of metals in the

form of spheres and polyhedra, the surfaces of which are prepared parallel to known crystal planes. The use of spheres has the advantage in the case of face-centered cubic metals of having every possible crystal plane appear parallel to the surface in at least six points on the sphere, the (100) faces appearing at six different points.

Since the single-crystal method of studying surface reactions is a rather new one, some aspects of which have been developed in this investigation, the possible uses of this method should be briefly described. Processes which may be studied by this method are of importance directly or indirectly to friction and wear.

1. One of the very great difficulties in studying surfaces is the inability to obtain surfaces of known configurations. An electrolytically polished surface along a known crystal plane is one of the nearest approaches to a known surface. Of course, no surface is completely smooth, and impurities can never be completely removed; but it is an approach to a surface of known configuration.

2. The formation of faint etch patterns, which may be easily seen, offers a surprisingly sensitive method of visually detecting very slight reactions. For example, by using a highly polished crystal sphere, reactions may easily be detected when the weight loss is considerably less than 1 milligram. In making rapid exploratory tests, especially with oils, to determine whether reaction takes place, time and effort may be saved.

3. Since most all surface reactions have been found to take place with rates which vary with the crystal plane, probably the chief use of this method is the study of reactions on different crystal planes. It is most impressive to examine a copper sphere which has been given a particular treatment and to find one face unaffected and another greatly acted upon just as if the two faces belong to different metals.

In experiments involving etching, growth as in electrodeposition, and rearrangements at high temperatures, the nature and degree of the reaction can be obtained by microscopic examination. Also, in many cases where definite facets are formed, specular reflections may be obtained and identified by a beam of light directed on the sphere. Owing to the symmetry of the crystals the patterns repeat themselves a number of times on the surface of the sphere. For example,

there are eight octants in a sphere, and eight similar patterns are obtained. These patterns not only serve to identify the particular crystal faces but also serve as a check, one against the other.

4. Since interference colors are obtained from thin films of the order of 400 to 1300 angstrom units, these colors may be used to study the variation in rate of formation and the nature of films, especially oxide, formed on different crystal faces. The thickness of these films also may be checked by measurement of the quantity of electricity required for the reduction of the oxide, using small drops of electrolyte on a particular crystal face.

5. Amorphous layers may be identified by the failure of preferential reactions to take place, and the thickness of the layer may be determined by the quantity of electricity required in electrolytic etching to remove this layer. The point at which the layer is removed may be determined by the appearance of preferential patterns.

6. Slip lines, the nature and direction of which vary with crystal face, may be used not only to identify crystal direction but to determine roughly the amount of strain to which a small section of metal is subjected in rubbing.

7. The formation and growth of crystal grains may be studied by following the behavior of one or more crystals formed on a large single crystal which serves as a reference background. In electrodeposition the growth of nuclei vary with plane. The wear on metal surfaces likewise may be studied by examining the scratch formed by rubbing one metal against a single crystal of another.

Finally, various combinations of the foregoing methods may be adopted for the study of most surface phenomena, physical and chemical. A complete reference map may be marked on the spherical surface for the identity of any region.

Growth of Crystals and Preparation of the Surface

Large single crystals of silver and copper, 5/8 inch in diameter and 6 inches long, were grown by lowering slowly a melt of metal from an electrically heated molybdenum-wound vacuum furnace. (See reference 1, pp. 35-42.) A copper crystal, 1½ inches in diameter, also was

grown. Silver and copper were held in graphite crucibles pointed at the lower end. Nickel crystals were similarly grown in the form of a rod, about 5/8 inch in diameter and 4 inches long, and were held in a graphite crucible lined with magnesia cement to prevent the solution of carbon in the metal. Several large crystals were obtained in this rod. Lead and zinc crystals were grown by lowering from a chromel resistance furnace a melt sealed under a vacuum in a pyrex glass tube. Since lead could not be machined without recrystallization into a polycrystalline mass, it was necessary to grow the lead crystal in a small glass bulb with a small tube attached to furnish a handle for the crystal. In order to prevent lead from sticking to the glass vessel, it was necessary to coat the glass with a thin film of carbon by flushing with mineral oil and heating until the oil decomposed. Iron crystals cannot be grown by the usual method of cooling slowly from the melt since it undergoes a phase change in the neighborhood of 900° C. Irregular-shaped crystals, 1/4 by 1/2 by 1 inch, were grown in rods of cold-rolled steel by decarburizing with hydrogen and then stretching and annealing at about 880° C. Growth of iron crystals will be described in Results, since a special study was required which has not yet been completed.

Spheres, 5/8 inch in diameter with a shaft 3/16 inch in diameter by 1/2 inch long, were machined from the rods of silver, copper, nickel, and zinc. Great care was required in machining zinc in order to prevent shearing along the slip planes which are especially pronounced in this metal. Spheres, about 5/16 inch in diameter, were machined from the iron rods. Spheres of the metals, except lead and zinc, were then mechanically polished by pressing emery papers, Nos. 1 through 0000, against opposite sides of the rapidly revolving sphere, the shaft of which was held in a drill chuck attached to an electric motor. The spheres were electrolytically polished in various solutions described in Results. They were rinsed in running water and dried with clean tissue paper. Electrolytic polishing has the advantage of removing the strained layers of metal at the same time that it polishes, leaving the true structure of the metal exposed at the surface. Attempts to remove impurities on the surface are discussed later.

Method of Heating Crystals in Oil

The spheres with shafts downward were alternately exposed to oil and air by raising and lowering about an inch

above and below the level of the liquid at the rate of 15 times a minute. A wire attached to the shaft of the sphere extended to a revolving mechanism above, which raised and lowered the sphere. The oil was placed in an Erlenmeyer flask, usually 125 cubic centimeters capacity, with a neck 6 inches long, which served as an air condenser. For experiments conducted in an atmosphere of hydrogen or nitrogen, the inlet gas tube passed through a rubber stopper at the top of the flask down into the liquid. The gas passed out through a capillary tube in the rubber stopper. The wire attached to the crystal moved up and down through this capillary. The flasks were heated by hot plates, the temperature being controlled in most experiments to ± 5 percent by placing a variable number of thin asbestos pads under the flask. Experiments were conducted at 100°, 200°, and 300° C. The crystals were removed from the flasks at definite periods of time and examined by several different methods.

When a crystal oxidizes, a very striking color pattern is produced, due to the interference colors from the oxide films of various thickness on the different crystal faces. These patterns may be seen best when a tube of white paper is placed over the crystal in order to cut out reflections from the various objects in the room. When the crystal is reacting in the Erlenmeyer flask, these colors may be seen fairly well by placing a piece of white tissue paper around the flask. A second type of pattern is formed when the reacting liquid etches the different faces of a copper crystal at different rates. Some faces will remain smooth and others will become rough at various depths of etching. These etch patterns are examined by two methods. When a beam of light is directed on the crystal in a dark room, not only may alternate smooth and rough regions be seen, but often striking light reflections will flash into view from small facets developed parallel to special crystal planes. From the directions of these specular reflections and from the orientation of the crystal as shown by the symmetry of the etch patterns, the crystal plane along which these facets have formed can be determined. Finally, the various areas are examined under a microscope. In some experiments the crystals were weighed before and after etching in order to obtain an approximate measure of the rate of etching, but such measurements are limited in meaning due to the fact that all crystal planes are exposed and the rate of etching along these planes varies greatly. Even in the case of polyhedra prepared parallel to special crystal planes, these weight measurements have only a very limited meaning, as will be described in Discussion.

From these types of measurements a picture of the manner in which the reaction takes place may be obtained. For example, the formation of the oxide pattern gives a picture of the reaction between metal and oxygen. The removal of this oxide pattern shows the manner in which the acid constituents of the oil attack the oxide. The etch pattern and the specular reflections indicate the manner in which the three materials, metal, oxygen, and oil, react simultaneously.

The crystals were generally heated in oils in both concentrated form and 5 percent in mineral oil. The experiments with the concentrated reagents were carried out in order to determine the effect of one reagent at a time and the differences in behavior between the various types. The experiments with 5-percent reagent in mineral oil were carried out to determine the effect of these materials when used in small amounts as addition agents. A few experiments were conducted with 1-percent addition agent in mineral oil. A few also were carried out with several types added together in mineral oil.

The mineral oil was obtained from L. Sonneborn Sons, New York City. The stearic acid was obtained from Armour and Company. The tricresyl phosphate was technical grade obtained from Eastman & Co. A few experiments were conducted with the pure grade phosphate but this was not used generally due to prohibitive cost. Tristearin, triphenyl arsine, triphenyl stibine, triphenyl phosphine were pure grades. Methyl stearate was technical grade. The used and unused aviation oils were supplied by the NACA Aircraft Engine Research Laboratory. The silver, 99.9 percent fine, was obtained from Handy and Harmon. The copper was electrolytic metal, 99.9 percent pure, obtained from the American Brass Co. Lead was obtained from The National Lead Co. and was described as having a very small percentage of impurities, probably not more than 0.06 percent copper. Iron was prepared by decarburizing with hydrogen cold-rolled steel having a composition of 0.08 to 0.16 percent C, 0.60 to 0.90 percent Mn, 0.09 to 0.13 percent P, and 0.10 to 0.20 percent S. The zinc was reagent metal obtained from Merck & Co., 99.9 percent pure. The nickel, 99.4 percent pure, was obtained from Whitehead Metal Products Co.

Since the oxidation patterns obtained with copper are important in controlling surface reactions, various treatments were given the metal surface in order to remove possible contaminations obtained from electrolytic polishing and other causes. After electrolytic polishing, crystals were

given various treatments such as boiling in distilled isopropyl alcohol, heating in hydrogen at about 900° C, washing with ether, and cleaning with electrolytic hydrogen by operating as a cathode in caustic solution. In general, the same type of oxidation pattern was obtained after each treatment. Even grease from the fingers by deliberate handling did not influence the etch pattern obtained with stearic acid.

For comparative purposes the photographs of the single crystals given on figures 1 to 8 are oriented in the same direction. Views are normal to surface at (100) pole.

IV. RESULTS

SILVER

Electrolytic Polishing of Silver

Mechanically polished single crystal spheres served as anode in an electrolytic cell consisting of a 400-milliliter beaker and a cylindrical copper cathode. The sphere was supported with shaft downward by means of No. 18 Brown and Sharpe gage silver wire. The polishing medium was a 5-percent-KCN solution to which was added just prior to use 2 milliliters of a 10-percent-NaCl solution per 200 milliliters of the cyanide solution. Polishing conditions were 7 amperes per square centimeter at a potential of 2.0 to 2.5 volts. At slightly higher current densities silver oxide formed on the surface, at increased current densities oxygen evolution with subsequent roughening occurred, while at low current densities an electrolytic etch pattern appeared.

The smoothest surface was always obtained in freshly prepared polishing solutions, the efficiency of the solution decreasing with usage. After admission to the electrolytic cell the current density was increased gradually until the first voltage and current fluctuations were noted. The current density was maintained at this point until a fair polish was obtained. It was gradually decreased until the voltage fluctuations achieved a maximum frequency and a minimum amplitude and maintained at this point until the desired degree of polish was obtained. At the polishing point an orange-yellow film alternately flashed on and off the anode surface in step with the voltage fluctuations. Proof of the single-

crystal character of the surface was obtained by lowering the current density to the point where the electrolytic etch pattern appeared.

Oxidation

No interference color films were obtained on silver crystals heated in dry air, moist air, dry oxygen, or moist oxygen at 100° to 550° C for periods of time ranging up to 48 hours. At 500° C in 18 to 48 hours excellent specular reflections were obtained from the (111) regions and weaker reflections from the (100) in atmospheres of oxygen, air, hydrogen, and in vacuum. Preferential evaporation of silver appeared to be the predominating cause. The fact that the patterns were more intense in air and oxygen suggests that the presence of silver oxide enhanced the preferential evaporation.

Mineral Oil

In an atmosphere of hydrogen.- When a silver crystal was alternately immersed in oil at 200° C and exposed to hydrogen at the rate of 15 times a minute, the crystal was not attacked and the oil remained undecomposed over a period of 24 hours. No sign of a silver film was visible on the flask.

In an atmosphere of air.- Experiments were conducted at 100°, 200°, and 300° C with the crystal alternately immersed in the liquid and exposed to the air at the rate of 15 times a minute. At 100° C a color pattern formed in 5 hours, the (100) regions appearing to be the most active. After 10 hours the color pattern disappeared and a faint roughness pattern took its place. After 10 hours a translucent gelatin-like material appeared on the crystal and on the sides of the flask. This material was slightly soluble in alcohol and very soluble in ether. It was not noted in experiments conducted at 200° and 300° C. The weight loss in 24 hours at 100° C was 0.0021 g. The weight loss was readily verified by noting that a thin film of silver had formed on the base and sides of the flask. At 200° C a bright color pattern formed in 3 hours, the color being very readily removed by rubbing with tissue. Preferential roughening started to occur in 6 hours but this again was followed by a preferential color film pattern. The final pattern after 30 hours consisted of: a brilliant purple square at the (100) regions

surrounded by square silver bands, of small faint red (110) regions, and large circular dark red-brown (111) areas. As in the case of 100° C a large film of silver became visible on the surface of the flask several hours after the experiment was initiated. The weight loss in 24 hours was 0.0014 g. At 300° C a color film formed in 5 minutes but immediately gave way to a preferential roughness pattern. The roughness pattern disappeared after 2 hours and the entire crystal took on a foggy appearance. The weight loss in 24 hours at 300° C was 0.0009 g.

Experiments were conducted at 200° and 300° C with the silver crystal rapidly rotating below the level of the mineral oil. In both cases no signs of color or roughening were apparent; however, at the end of 24 hours a very thin film of silver was noticeable on the base of the flask.

Oiliness Agents

All experiments were conducted by alternately immersing the sphere in the liquid and the atmosphere above the liquid at the rate of 15 times a minute.

Stearic acid in an atmosphere of air.- A very faint superficial etch pattern formed on the surface within 12 hours at 100° C. The pattern after 24 hours consisted of very smooth (111) and small (311) areas, the remainder of the surface appearing slightly misty when viewed with a flashlight in a darkened room. The liquid was only slightly discolored and the weight losses were negligible after 24 hours. At 200° C a very faint etch pattern started to form in 70 minutes. The final etch pattern was similar to that described at 100° C and slightly deeper. Very, very faint specular reflections from the (111) regions were noted normal to (111). The weight loss in 24 hours was negligible. At 300° C an etch pattern consisting of specular reflection from the (111) formed in several minutes. Within 1 hour the pattern became indistinct and the entire surface became roughened. After 3 hours a yellow-tan film formed on the sphere and the acid started to deposit decomposition products. No weight measurements could be obtained due to the irremovable film on the surface. That etching did occur is proved by the immediate formation of an etch pattern and also by the fact that a film of silver was visible on the base of the flask when the liquid was removed.

Stearic acid in an atmosphere of oxygen.- The etch pattern which formed in oxygen at 100° C was about equal in intensity to that noted previously in the presence of air at 200° C. No variation in the weight losses or intensity of the pattern was noted in the comparison of the action of air and oxygen at 200° C.

Five percent stearic acid in mineral oil in an atmosphere of air.- Not the slightest signs of color films or etching were visible after 24 hours exposure to the action of 5 percent stearic acid in mineral oil at 200° C.

Oleic acid in an atmosphere of air.- The surface of the sphere remained perfectly polished during 24 hours exposure to the action of oleic acid at 100° C. A well-developed pattern appeared after several hours exposure at 200° C. The final etch pattern consisted of a strong specular reflection from the (111) regions, a cross at the (100)'s terminating in a small diamond at the (210)'s. The (110) regions remained very smooth and appeared so under a magnification of 600X, while the (100) and (111)'s appeared comparatively rough. Electrolytic etching in the silver polishing solution caused a tan translucent skin to peel off the sphere. This fact perhaps indicates the reason for only superficial development of the etch pattern.

Methyl stearate in an atmosphere of air.- At 100° C the silver sphere had a very faint pink-green color. When viewed in a cone of paper, a very faint color pattern similar to that noted in the case of mineral oil was observed. At 200° C very superficial etching took place in the course of 24 hours. When the crystal was viewed with the aid of a flashlight in a darkened room, four blue dots at the (210) poles were visible when viewed normal to (100) planes, and three green dots at the (311) poles were visible when viewed normal to (111) planes. Although these colored dots were extremely striking in the beam of the flashlight, no preferential surface structure was visible under the microscope to account for this phenomenon.

Chemical Polishing Agents

Tricresyl phosphate in an atmosphere of air.- No etch pattern or color films were visible at 100°, 200°, or 300° C. The weight changes in 24 hours were negligible in all cases.

A protective film was formed on the surface in all cases as indicated by surface film scaling when electrolytically etched in the silver polishing solution.

Commercial Oils

Aviation lubricating oil in an atmosphere of air.- Perfect color patterns presumably due to sulfur in the oil formed in 30 to 60 minutes at 100° and 200° C. The colors went through the series, rose, copper, brown, purple-black, and dark black. The (311) regions appeared to be by far the most active. An atmosphere of hydrogen did not prevent the pattern formation or appreciably reduce the rate. The colors rapidly disappeared when the sphere was dipped in KCN solution, or placed in iodine vapor.

Used aviation lubricating oil in an atmosphere of air. At 100° C a very faint dull gray color pattern similar to that in new aviation oil became apparent in 24 hours. The weight loss was nil. At 200° C a faint color pattern appeared rapidly and a lustrous lacquer formed on the surface in 48 hours. The weight loss was nil. At 300° C a faint etch pattern formed in 2 hours and a black tarlike deposit formed in 5 hours. When the tar was removed by rubbing, a faint color pattern was apparent.

Amines

In an atmosphere of air, etch patterns were formed on single crystals of silver at 200° C by dodecylamine, tetradecylamine, and octadecylamine. In all cases (111) planes were greatly developed, and (100) planes were developed to a lesser extent. The weight losses in 24 hours for a 15-gram sphere of approximately 7 square centimeters were 0.009 g in dodecylamine, 0.007 g in tetradecylamine, and 0.002 g in octadecylamine. No apparent reaction as judged by weight change and surface appearance occurred in dodecylamine and air at 100° C.

Other Evidence of Preferential Etching

Preferential etching of silver-crystal spheres was obtained in the following reagents: 1. Electrolytic etching at low current densities in KCN-NaCl solution; 2. KCN-$(NH_4)_2S_2O_8$; 3. Nitric acid; 4. KCN-air; 5. KI-I_2.

Iodination

A very beautiful and perfect pattern of colors was obtained when an annealed polished crystal sphere was placed in iodine vapor or in a solution of iodine in a solvent such as hexane, ether, chloroform, carbon tetrachloride, or benzene. The variations in rate increased as the color film increased in thickness. The (100) and (311) regions had a high rate of reaction, while the (210) and (111) were regions of low rate.

Rearrangement Due to the Action of Hot Gases

Faint patterns of specular reflection from the (111) regions were visible when 5:1 mixtures of hydrogen and oxygen at a total pressure of 1 atmosphere were passed over a polished crystal at 440° C. The results were attributed to preferential evaporation as noted under Oxidation.

A rearrangement pattern which roughened the (111) region to the greatest extent formed when a 4:3 mixture of oxygen and hydrogen sulfide at a total pressure of 1 atmosphere was passed over the crystal sphere at 200° C.

A mixture of 20 volumes of hydrogen to 1 of chlorine preferentially roughened the (100) regions of a crystal sphere when the gases were passed over the sphere at 250° C and a total pressure of 1 atmosphere.

Although the important result about silver for this investigation is that it is largely unreactive, the films and faint etch patterns formed have been described in some detail in case further studies should be made on silver surfaces.

COPPER

Electrolytic Polishing

Copper single-crystal spheres were electrolytically polished in 42.5-percent-phosphoric acid solution at a current density of 12 amperes/sq dcm and a voltage of 5 volts. The polishing cell consisted of a large vertical glass cylinder to which were attached 2 vertical cylindrical sidearms containing copper rod cathodes. A discussion of the preparation of the surface of copper crystals has been given in reference 1, page 35.

Oxidation

When a polished crystal sphere was heated in air at temperatures above 100° C, brilliant color films formed indicating that the rates of oxidation varied with plane. The relative rates of oxidation in air at 200° C and atmospheric pressure were, in the order of decreasing rates: (100) and (210) regions; boundary lines between two (311) regions; boundary lines between (311) and (110) regions; (111) regions; (110) regions; and (311) regions. (See fig. 1.) In the neighborhood of 500° C there was some change in the order of relative rates but, judging from the color and relative roughness of the oxide film, the (100) and (210) regions continued to be the most reactive. Judged by the continued smoothness of the surface and by the development of definite crystal facets, the (311) regions remained the least reactive. Oxidation of single crystals of copper has been considered previously. (See reference 2.) Further verification was obtained of the fact that the (100) regions were the most active toward oxidation at temperatures of 200° to 300° C. A polished sphere was oxidized in air at 300° C for 3 hours. At the end of this interval the sphere had an adherent black coating over the entire surface. After slowly cooling to room temperature, the sphere was rubbed with tissue. Preferential scaling from a small circular region around the (100) regions occurred, indicating that the deposit was thickest in this region of the surface. Individual grains of a polycrystalline aggregate showed varying rates of oxidation in air at 200° C.

Mineral Oil

In an atmosphere of hydrogen.- When a copper crystal was alternately immersed in oil at 300° C and exposed to hydrogen at the rate of about 75 times a minute, the crystal was not attacked and the oil remained clear and undecomposed over a period of 48 hours. No reaction took place at 100° or 200° C over a period of 23 hours. A small trace of oxygen in the hydrogen (less than 1 percent) will produce an oxide pattern on the crystal as described in the following.

In an atmosphere of nitrogen.- At 300° C over a period of 48 hours, the oil showed no discoloration and the crystal showed a slight oxidation pattern, which was attributed to the diffusion of a small amount of air through the exit tube as judged by a similar experience with hydrogen.

In an atmosphere of air.- When a copper crystal was alternately immersed in oil at 300° C, and exposed to air 75 times per minute, a regular oxide pattern of interference colors appeared in 30 minutes and increased in intensity for 8 hours. This oxide pattern is similar to that obtained in pure air with no oil present. (See fig. 1.) At the end of 20 hours the crystal was completely covered with a black tarry material. At 200° C an oxidation pattern appeared in about 2 hours and continued for about 19 hours at which time the pattern of interference colors gave way to one of dark red and black deposits. When this crystal was heated in hydrogen at 450° C, black deposits remained in certain regions, indicating that the formation of carbonaceous materials varied with crystal plane. When air was bubbled through mineral oil at 200° C, in order to accelerate the oxidation of the oil, an oxidation pattern first formed on the crystal but this soon gave way to a striking etch pattern within 24 hours, indicating that the etching varied with crystal plane.

Oiliness Agents

Stearic acid in an atmosphere of hydrogen or nitrogen. When a very rapid stream of hydrogen or nitrogen was passed through the liquid in order to prevent diffusion of even a small amount of air through the exit tube, the crystal remained unattacked, and the oil, clear after heating at 300° C for 48 hours. A crystal also was unattacked at 200° C.

Stearic acid in an atmosphere of air.- Photographs were taken and losses in weight were determined at 3, 24, and 48 hours. When a crystal was heated in stearic acid at 100° C, the surface showed a very slight etching in 1 hour and a definite pattern in about 6 hours. At 200° C a definite etch pattern began to form in about 1/2 hour, and at the end of 10 hours a pattern typical of stearic acid was obtained. A photograph of such a pattern is shown in figure 2. The (110) regions were very rough and the rest of the surface was relatively smooth. Photomicrographs of (110) and (111) regions are shown in figure 3. At the end of 48 hours the loss in weight of a crystal of about 15 g was 490 mg. At 300° C the typical etch pattern was fully developed within 2 hours, when a black deposit soon began to form on the crystal. This greatly reduced the rate of etching and within 24 hours the crystal was covered with a thick, tarry deposit which could be easily wiped off. When a crystal was heated at 200° and 300° C in a 5-percent solution of stearic acid in mineral

oil, the results obtained were similar to those with pure stearic acid. The rate of pattern formation was slower and the loss in weight less, but the differences were not so great as would be expected.

In all etching experiments with stearic acid it was found that the pattern changed with time until a constant type, having a rough striated surface at the (110) regions and smooth surfaces at the (100) and (111) regions, finally was obtained. In order to determine whether this change in etching with time was a result of the changing composition of the liquid as oxidation proceeded, the acid was renewed every 3 hours using the same crystal continuously for 12 hours. It was found that the typical pattern was obtained in about 6 hours and continued until the end of the experiment in 12 hours, indicating that the change which took place in the composition of the liquid over a period of 3 hours did not change appreciably the etching characteristics of the acid.

In order to investigate the method of attack of stearic acid on films of copper oxide, a crystal with three flat surfaces, about 3/16 inch in diameter, parallel to the (100), (111), and (110) planes was oxidized in air at 200° C and then heated at 200° C in 5 percent stearic acid in mineral oil in an atmosphere of nitrogen. At the beginning, each surface exhibited the color of the oxide film characteristic of that crystal plane, the (100) having the thickest film. As the reaction proceeded, the change in colors on the various faces could be observed, the rate of change being a measure of the rate of etching of the oxide. Finally, all colors disappeared, and the varying degrees of roughness produced by the etching of films of different thickness could be observed. The nitrogen was then replaced by air, and other crystal planes became roughened, the etch pattern shifting over to that of a different type. This suggests that the positions of greatest oxidation in air alone are not the positions of the greatest rate of etching by stearic acid. This experiment is primarily described in order to indicate how the single crystal method of study can be used to study intermediate reactions with special emphasis on the directional properties of crystals. It has been impossible in these studies to take full advantage of such possibilities.

Three polyhedra, a cube with faces parallel to the (100) planes, an octahedron with faces parallel to the (111) planes, and a dodecahedron with faces parallel to the (110) planes were alternately immersed in stearic acid at 200° C and

exposed to air at the rate of 15 times per minute. The polyhedra were removed and weighed at the end of 1/2, 3½, 6½, and 24 hours. Four similar experiments were carried out with these polyhedra, but the results were not consistent. Possible reasons will be discussed later.

As has been stated, no etching occurs in atmospheres of pure hydrogen or nitrogen. If the hydrogen contains a small amount of oxygen (less than 1 percent), however, the etch pattern obtained is quite different from that obtained in air when the experiments are run for periods of time giving approximately equal weight losses. The weight loss in an atmosphere of air after 1½ hours was equal to the loss obtained in hydrogen containing a small amount of oxygen after 24 hours. The etched crystal, with an atmosphere of air above the stearic acid showed rough (100), striated (110), and smooth (111) regions. With a small amount of air in hydrogen, smooth (100) regions, extremely smooth and bright (110) regions, and slightly rough (111) regions were obtained.

Very, very faint specular reflections were apparent when a copper single-crystal reacted with stearic acid in an atmosphere of unpurified tank carbon dioxide. The weight loss in 24 hours was negligible.

Slight but detectable currents were found with pure stearic acid when a potential was applied between a copper single-crystal anode and a cylindrical copper or lead cathode. The magnitude of the currents was as follows: At 300° C and an anode-cathode distance of 1 centimeter, the currents were 30 microamperes at 115 volts and 1 microampere at 4 volts. The current increased to 2.2 microamperes at a potential of 4 volts when the anode-cathode distance was reduced to 2 to 3 millimeters. At 200° C the magnitude of the current varied between 18 to 20 microamperes at a potential of 115 volts and an anode-cathode distance of 1 centimeter. The amount of current doubled in value as the anode-cathode distance was decreased to 2 millimeters. No noticeable difference was apparent in the etch pattern or in the wetting characteristics developed by the stearic acid at 200° C when a current of 18 microamperes at a potential of 115 volts was allowed to flow to a copper sheet cathode for 6 hours as the copper single-crystal sphere was alternately immersed and raised in the air above the liquid.

Rubbing an electrolytically polished copper single crystal, prior to etching, with metal foils such as aluminum, tin, copper, nickel, or lead did not alter the final etch

pattern developed in 24 hours. The customary pattern developed very rapidly when the surface was rubbed with tin or lead foil, in 4½ to 5 hours when rubbed with copper foil, and 10 to 15 hours when rubbed with nickel or aluminum foils.

The size and degree of roughness of the (100), (110), and (111) areas, obtained by etching with stearic acid at 300° C, differed from the customary pattern if the surface of the copper crystal was coated with a film of silver by rapidly dipping the crystal in a 0.01 N solution of silver nitrate. Observation indicated that the major reason for the difference in pattern was due to the preferential ability of the silver to adhere to the copper surface in the presence of the acid.

A very well developed hydrogen-oxygen catalytic pattern was obtained on a copper crystal by exposing it to a 5:1 mixture of hydrogen and oxygen at 400° C for 16 hours. The sphere was then alternately immersed in stearic acid at 300° C and exposed to the air above the liquid. The catalytic pattern entirely disappeared in 1 hour and the well-defined stearic acid pattern first appeared in 4 hours. The pattern resulting in 24 hours was identical with the customary stearic acid pattern.

Oleic acid in an atmosphere of air.- When a copper crystal was heated at 100° C, a faint pattern appeared within 2½ hours and continued for 24 hours. At 200° C strong specular reflections were obtained from the (110) regions and the (311) regions, indicating that crystal facets parallel to these planes had been developed. The crystal remained entirely wetted.

Methyl stearate in an atmosphere of hydrogen.- No appreciable reaction took place over a period of 12 hours.

Methyl stearate in an atmosphere of air.- A very definite etch pattern appeared in about 1 hour and continued until the end of the experiment in 12 hours. The weight loss over 12 hours was 34 milligrams. A 5-percent solution of methyl stearate in stearic acid produced a faint etch pattern in 12 hours.

Tristearin in an atmosphere of air.- With a 5-percent solution in mineral oil at 200° C a definite oxidation pattern formed in about 15 minutes and continued for 48 hours. No etch pattern formed, and the loss in weight was negligible

over a period of 75 hours. When a polished crystal was heated in this used liquid for 17 hours, it was completely covered with a tar which, when wiped off, revealed a definite pattern of carbon formation at the (110) regions.

Chemical Polishing Agents

Tricresyl phosphate in an atmosphere of hydrogen or nitrogen.- When a rapid stream of hydrogen was passed through the liquid at 300° C, no appreciable reaction took place within 24 hours. The liquid decomposed slightly as indicated by a change in color to a light orange and by the formation of a few large black flakes on the bottom of the flask. The crystal remained smooth and shiny.

Tricresyl phosphate in an atmosphere of air.- Experiments were conducted at 100°, 200°, and 300° C, with the crystal alternately immersed in liquid and exposed to air at a rate of 15 times per minute. In general, an oxidation pattern first formed, followed by very faint etching, and a brown insoluble film which is not preferential with crystal plane as far as could be judged. Finally, at 200° and 300° C the crystal was completely covered with a heavy black deposit at the end of 24 hours. At 200° C the dull brown film began to form in about 5 hours and continued to the end of 24 hours when the heavy black deposit formed appreciably. When this deposit was removed by rubbing with tissue paper, the used tricresyl phosphate etched the crystal preferentially and deeply, the thin, brown, protective film failing to form. When a new crystal was heated in tricresyl phosphate which had been heated previously with copper in contact with air, no film was formed, but a very striking etch pattern formed in about 10 minutes. At the end of 15 hours the pattern was very distinct, the (110) regions being smooth and shiny as shown in figure 8. Small shiny spots were located at the (100) and the (111) poles, and the rest of the surface appeared frosted. Five percent tricresyl phosphate in mineral oil at 200° and 300° C formed films similar to those obtained with the concentrated material. The rates were slower. At 200° C the oxidation pattern formed in 20 minutes and the brown film in about 5 hours. At 300° C the oxidation pattern formed almost immediately and the brown film in about 20 minutes. Five crystals, heated successively at 200° C in the used 5-percent phosphate which had been heated at 200° C, formed protective films. A sixth was etched slightly.

Triphenyl phosphine, triphenyl stibine, and triphenyl arsine in mineral oil behaved similarly to tricresyl phosphate. An oxidation pattern first formed and this was followed by the formation of a brown protective film. No appreciable etching took place. With 5 percent triphenyl arsine in mineral oil an oxidation pattern formed, but no appreciable film formed in 42 hours.

Commercial Oils

When a crystal was heated in unused aviation oil at 200° C, an oxidation pattern formed but no appreciable etching or carbon deposition took place within 48 hours. If air was blown through unused oil, a faint etch pattern formed within 48 hours. This should be compared with a definite etch pattern formed with mineral oil heated under similar conditions for 24 hours. Used aviation oil in air preferentially etches a copper crystal with the development of (111) planes at 100°, 200°, and 300° C, and forms preferential carbon deposits as described in the paragraph on carbonization.

Amines in an Atmosphere of Air

Concentrated ethanolamine at 100° C produced an etch pattern almost immediately. Concentrated cyclohexylamine at 100° C produced a faint etch pattern. Concentrated diphenylamine at 200° C did not etch the crystal appreciably over a period of 24 hours, but an oxidation pattern formed. Concentrated hexadecylamine at 200° C produced a definite etch pattern. When a beam of light was normal to the surface at the (110) pole, definite specular reflections were obtained over an entire hemisphere, indicating that facets parallel to the (110) planes were developed. Faint reflections were obtained when a light beam was normal at the (111) pole. Total loss in weight over a period of 24 hours was 16 milligrams. With concentrated octadecylamine at 200° C definite specular reflections were obtained over a hemisphere when the light beam was normal at a (100) pole. Total loss in weight over a period of 24 hours was 10 milligrams. In 5 percent hexadecylamine in mineral oil at 200° C, a definite oxidation pattern appeared, which continued until the end of the experiment in 40 hours. No appreciable etching took place, and the crystal became completely covered with a black deposit.

Ability to Wet

A copper crystal was immersed in stearic acid and exposed to air at a rate of 15 times a minute at 200° C. The customary etch pattern soon formed and, after the etching had taken place for periods of time ranging from 3 to 6 hours, the liquid rearranged itself into definite drops on the (110) poles when the crystal was raised above the liquid. If hydrogen replaced the air, the liquid wet the entire surface of the crystal. If air replaced the hydrogen, the drops again formed at the (110) regions. Only a small amount of air in the hydrogen was sufficient to produce this formation of drops. This formation of definite drops was obtained above 160° C and up to at least 270° C where the film immediately broke into small drops. If the preferred wetting had occurred, additions of mineral oil up to 50 percent did not affect the results. If a freshly polished crystal was immersed in old stearic acid which had been heated previously, as described, the drops immediately formed on the highly polished crystal at the (111) regions. After the etching had proceeded for periods from 3 to 6 hours and the regular stearic acid pattern had been developed, the drops collected at the (110) regions. If a freshly polished crystal was immersed in new stearic acid and exposed to pure oxygen at a rate of 15 times a minute, the drops formed in a short time (several minutes to an hour) at the (111) regions. Palmitic and myristic acids under the first conditions described previously showed a similar preferential collection of drops at the (110) regions. The unsaturated acid, oleic acid, did not show the formation of drops under the same conditions. Five-percent solutions of calcium stearate, aluminum stearate, and zinc stearate in stearic acid exhibited preferential wetting of the (110) regions in 8 to 10 hours.

A copper single crystal containing a perfect stearic acid etch pattern which had developed in 12 hours at 200° C was transferred to fresh stearic acid. The crystal showed preferential wettability of the (110) regions after 6 hours, a time interval comparable to that necessary to develop preferential wetting on a freshly polished crystal.

A polycrystalline sphere of copper exhibited wetting results similar to the single crystal sphere at 200° C. In fresh acid the liquid first began to exhibit nonwetting of the surface in 5 to 6 hours. Stearic acid previously heated in contact with copper for 12 hours showed no signs of wetting the copper surface for the total running time of 3 hours. An etched surface reacted in the same manner as an unetched

surface, the stearic acid wetting the sphere for 5 to 6 hours, then no longer wetting it. The surface remained completely wet in atmospheres of hydrogen and nitrogen after 24 hours when the experiment was concluded.

An attempt was made to correlate the wetting of a copper single crystal by stearic acid with the wetting of a platinum spade dipper at 200° C. The platinum dipper was cleaned by heating to redness in a Bunsen flame, it was cooled in air and dipped in the stearic acid. The first signs of preferential ability to wet with copper were noted after 5½ hours of heating and continued for 11 hours. The first signs of a finite contact angle of stearic acid on platinum were noted in 7 hours, the magnitude of the angle increasing with time until a total of 11 hours. With a sample of stearic acid heated out of contact with copper, the first signs of a finite contact angle of the stearic acid on the platinum dipper were noted in 22 hours. These results appear to indicate that an oxidation product of stearic acid is responsible for the preferential wetting of the copper surface.

Monomolecular layers of oleic acid were put on freshly polished slices of a (100) plane and polycrystalline copper and the contact angle of water measured by the method of Langmuir. (See reference 3.) Consistent results were obtained with the (100) slice, the contact angle of the water drop varying from 81° to 84°. The results with the polycrystalline slice were not so consistent, the magnitude of the contact angle varying from 48° to 71°, apparently with the degree of polish. The possible significance of these results will be considered under Discussion.

Carbonization

When a single crystal of copper was alternately immersed in used aviation oil at 200° C and exposed to air at the rate of 15 times per minute, carbonaceous residues of varying kinds deposited on the crystal. The nature of the deposits varied with the atmosphere above the liquid, and with the time and temperature of heating. In atmospheres of hydrogen and nitrogen, neither carbon formation nor etching occurred. In atmospheres of oxygen or circulating air, colored lacquers rapidly formed preferentially with plane and remained for periods of time up to 20 hours before preferential etching started. In atmospheres of still air the results varied with time as described in the following paragraphs.

There seems to be four distinct possibilities:

1. Formation of a colored lacquer which is completely irremovable

2. Formation of a heavy dark brown lacquer which can be removed preferentially with plane

3. Formation of a heavy black deposit which can be preferentially removed

4. Strong preferential etching without strong adherence of the carbon deposits to the metal

Colored lacquer.- This formation occurs in short intervals of time, generally in 3 to 8 hours. The crystal appeared very bright and lustrous and exhibited a rather ill-defined interference color pattern. In moving air and moving oxygen, lacquer formation predominates for long intervals of time, occasionally to 20 hours. In the latter case severe rubbing with tissue will induce a pattern, due to the preferential scaling off of the deposit in certain areas. The fact that the areas which scale off in the (100), (210), (123), and (110) regions are small suggests that the lacquer is predominantly oxide, since these areas are the most active toward oxidation at 200° C. Oxygen and moving air may prolong the life of the colored lacquer, since oil is a dilute solution of acid and the excess oxygen may inhibit the loosening action of the acid. The initial rapid rate in oxygen may form a more compact oxide surface which resists the attack of reactive acid molecules.

Heavy brown lacquer.- This formation occurs in 5 to 7 hours, and the deposit is very definitely preferential in its ability to be removed by rubbing. Prior to rubbing, the surface has a dark brown, slightly lustrous appearance. It does not resemble any color or texture of oxidation in air previously encountered. The preferential removability of this lacquer has been encountered in all stages of development. The various patterns developed with increasing time are:

1. A thin ring around all (111) poles, passing through the six (123) poles, is first removed. The removed ring widens in time, occasionally most rapidly toward (111), or most rapidly toward (100) and (110) poles.

2. The ring has widened to such an extent that all the deposit is removed except a large square at (100) and a small circle at (111) poles.

3. The only deposit removed is a wide circular area surrounding and including the (111) region.

4. All the deposit is removed except a small triangular area at the (111) pole. The patterns described in (2), (3), and (4) apparently occur depending on the rate of the ring widening described in (1).

In all cases of heavy brown lacquer formation the traces of the used aviation lubricating oil etch pattern were becoming apparent. This fact indicates that the method of deposit loosening is a direct attack upon the copper-deposit interface. It appears that diffusion through the deposit and attack at the interface always occurs most rapidly at the (123) pole positions.

The phenomenon of heavy brown lacquer deposition definitely is not due to expansion-contraction effects. Similar results were obtained if the crystal were wiped while hot, agitated in a sand-oil mixture below the level of the oil, wiped after cooling in air, wiped after cooling below the level of the oil, rapidly cooled in tap water before wiping, and rapidly cooled in aviation oil at room temperature before wiping.

Heavy black deposit.- This type of deposit only occurred if etching had not occurred to an appreciable extent. It is noted in time intervals of the order of 12 to 24 hours. The ease of removal, in order of decreasing ease, is (110), (100), and (111). Generally, only a large area surrounding the (111) pole retains its deposit after vigorous rubbing with tissue. (See fig. 6.) It appears that this effect is largely an expansion-contraction effect since the heavy deposit is only encountered after rapid cooling, the deposit appearing like a frozen mass. If the crystal is wiped while hot, the deposit, which would have been rigid if rapidly cooled, has the texture and appearance of thick grease. Beneath this readily removed grease layer the crystal has a dull gray lacquerlike appearance, the lacquer being much darker at the (111) areas.

Etching.- When strong etching occurs no lacquer or heavy black deposit is encountered. Etching will always occur in time intervals greater than 24 hours, but will quite

often occur in shorter intervals of time. The (111) planes are developed. Apparently the occurrence of the preceding four phenomena is dependent upon the correct acid-oxygen ratio, the time inconsistencies being explained on this basis.

Wear Experiments

A polished copper single-crystal sphere was clamped in a chuck attached to a motor, rotated at 1725 rpm, and rubbed with a strip of lead foil. A pattern of triangular dark gray areas in the (111) regions resulted. This was attributed to lead which had scaled off the foil and preferentially adhered to the (111) areas due to the predominance of slip lines in these areas. Slip lines were readily visible under a magnification of 135X, and in the majority of instances lead could be seen to have piled up like snowdrifts along these lines. Similar preferential adherence to the (111) areas was noted in the presence of used aviation lubricating oil as indicated below: A polished copper single-crystal sphere was attached to a rotating mechanism and pressed against a lead sheet immersed in used aviation lubricating oil heated to 200° C. The contact pressure was regulated by means of a guide wire which ran over a pulley to a balance pan on which weights were placed. The sphere served as anode and the lead sheet as cathode, and a current was passed through the circuit. When a load of 200 grams was applied and current of 2.25 amperes at an applied potential of 50 volts, the potential drop across the lead-copper contact was 0.3 to 0.4 volt. A negligible amount of scratching and no lead adherence occurred. However, when the load was reduced to 50 grams, sparking occurred which apparently melted the lead and caused it to adhere preferentially to the (111) regions along the band of rubbing. A preponderance of slip lines was visible in the (111) regions.

Several interesting facts were noted when the apparatus described was used in the presence of stearic acid at 200° to 300° C. The results may be briefly summarized:

1. The sphere became badly scored and scratched in time due to the deposition of copper on the lead, the latter scratching then being due to the rubbing of copper on copper.

2. Sparking readily caused the lead to melt and to adhere here to the copper sphere.

3. When a copper cathode was used and sparking conditions chosen, the stearic acid decomposed and formed a very thick adherent layer of carbonaceous material.

4. Under nonsparking conditions the lead rubbed off and adhered preferentially to the roughest areas of the rubbing surface.

Mixtures of an Oiliness Agent and a Chemical Polishing Agent

Three experiments were carried out at 200° C with a mixture of 10 percent stearic acid and 90 percent tricresyl phosphate, and three, with 90 percent stearic acid and 10 percent tricresyl phosphate. With the 10 percent stearic acid, an etch pattern characteristic of the acid formed in about 20 minutes, and an insoluble film formed in about 1½ hours. Weight measurements indicated that appreciable etching took place until the film began to form, but that etching was appreciably reduced by this film. The 10 percent phosphate mixture showed a greater film-forming tendency than the 90 percent. In general, tricresyl phosphate appeared to reduce the preferential etching by the acid and produce a smoother surface.

With 5 percent stearic acid and 5 percent tricresyl phosphate in mineral oil at 200° C, the customary stearic acid pattern appeared in 1 hour and the customary phosphate film in about 22 hours. In 24 hours no appreciable preferential etching was noticeable.

5 Percent Salicylic Acid in Tricresyl Phosphate, 5 Percent Phosphoric Acid in Tricresyl Phosphate, and 5 Percent Benzoic Acid in Tricresyl Phosphate

An attempt was made to identify the etching compound present in used tricresyl phosphate by comparing the pattern obtained from used phosphate with the pattern produced by a known compound. Salicylic acid solution reacted like undiluted tricresyl phosphate. The phosphoric acid solution pitted the crystal but gave no definite pattern. The solution of benzoic acid produced a very definite pattern within

2 minutes which was similar to that obtained with used tricresyl phosphate. This latter experiment suggests, but does not prove, that one of the oxidation products of tricresyl phosphate is benzoic acid.

A Copper Crystal Plus 5 Percent Calcium Stearate and 5 Percent Tricresyl Phosphate in Mineral Oil at 200° C

Two experiments were conducted using the alternate-immersion-and-exposure-to-air method, and one, allowing the crystal to remain in the liquid which was stirred vigorously and through which air was bubbled. Blanks of 5 percent tricresyl phosphate in mineral oil were run at the same time for comparative purposes. In the two alternate immersion experiments the crystal first became oxidized and then etched preferentially. No trace of any film was found on the crystal, the calcium stearate appearing to function as a detergent. At least, it prevented the formation of the usual film. In the experiment in which the crystal was continually immersed in the liquid, at the end of 24 hours it was covered with a very heavy tar which was easily removed by rubbing. When the tar was removed, a definite etch pattern was seen and no film underneath was noticeable as was the case when calcium stearate was absent.

Etching by a Series of Paraffin Acids

In order to determine the effect of increasing complexity of molecule on etching characteristics, the first experiments carried out in this project were those on the etching of copper by a series of paraffin acids. Acetic, propionic, n-butyric, n-valeric, and myristic acids were studied. The crystals were alternately immersed in acid and exposed to air at the rate of 75 times per minute. Since the lower members of the series boil at temperatures slightly above 100° C, all experiments were conducted at 100° C. Micrographs of the major planes of the first four acids were taken at the end of 3, 24, and 48 hours, micrographs of planes of the last two, 24, 28, and 72 hours. Each acid gave a distinct pattern, but there appeared to be no systematic change in the pattern in passing from one acid to the next higher member in the series.

Rearrangement Due to Action of Hot Gases

Very striking surface rearrangements were obtained on a highly polished copper crystal due to the catalytic reaction of gases at temperatures considerably below the melting point of the metal. The reactions were highly specific with the gas. In some regions very striking facets were developed, in others, irregular roughness was obtained, while other regions seemed to be completely unaffected. Such rearrangements may be of considerable importance to those parts of an engine which are subjected to the action of hot gases. Not only is the surface roughened in some regions, which would increase wear, but a considerable amount of metal is evaporated during these reactions. Very striking rearrangements were produced on copper by the reaction between hydrogen and oxygen at a gas temperature of 400° C, by ammonia and oxygen at 500° C, and by the action of ammonia alone at 500° C. The single-crystal method of study is especially suited for detecting and following the course of such reactions. Photographs of a copper surface, on which the hydrogen-oxygen reaction has taken place, are shown on figures 9 to 16.

Electrochemical Reactions

The electrodeposition of copper on a single crystal of copper has been found to vary greatly with crystal plane. With an electrolyte containing copper sulfate and sulfuric acid at a low current density of 2 milliamperes per square centimeter for 450 hours, a single crystal in the form of a sphere was converted into a polyhedron, exposing largely the (111) planes. At a current density of about 20 ma/cm^2 the deposit followed the orientation of the underlying crystal in some regions, but in others, new randomly oriented nuclei were formed. Thus, after about 5 hours of deposition, part of the sphere was covered with a single-crystal deposit and part of it was a polycrystalline deposit. If the current density was increased to about 80 ma/cm^2, the entire surface became covered with a polycrystalline deposit in a short while.

Galvanic action between two metals in aqueous solutions varied with plane. When a single-crystal sphere of copper in a solution of copper sulfate was connected electrically to a crystal of zinc in zinc sulfate and the two solutions connected by a bridge of potassium sulfate, copper was deposited preferentially with plane on the copper crystal and zinc was etched preferentially from the zinc crystal. This effect has not yet been tested in oils.

LEAD

Electrolytic Polishing of Lead

Lead spheres were electrolytically polished as anodes in a cell consisting of a cylindrical lead cathode in a 150-milliliter beaker. The solution was stirred vigorously, and the current density was 20 to 25 amperes/sq dcm at a potential of 5 to 8 volts. Fluctuations of the voltage occurred at the polishing point. This treatment gave a fine finish if the initial surface had been made smooth by mechanical polishing, but it was impossible to rub lead with emery papers due to recrystallization. Small indentations that formed in the surface during growth due to air bubbles were, therefore, preserved during electrolytic polishing.

The polishing liquid had to be renewed frequently to prevent the formation of lead dioxide on the anode. Tarnishing of the surface was reduced by removing the sphere from the liquid before cutting off the current, and the sphere was immediately placed in distilled water, washed with alcohol, and dried in a current of warm air. A clean, bright surface was maintained for several hours.

Oxidation

Faint oxidation color patterns as shown on figure 21 were formed in several minutes by heating lead crystals in air and oxygen at 150° to 250° C. The patterns did not consist of well-defined bright colors like those obtained with copper, but in general, lead was oxidized only slightly preferentially with plane. This may be due to the tarnish layer which forms so readily on the surface prior to heating in air.

Mineral Oil

Mineral oil in an atmosphere of air.- A color pattern consisting of circular (100) areas started to form at 100° C in 2 hours and was very striking at the end of 5 hours. After 14 hours yellow-orange flakes began to scale preferentially from the (100) regions and in time the entire surface of the sphere showed this scaling phenomenon. The weight loss in 5 hours was 0.004 g and in 24 hours, 0.024 g. Results at 200° C were similar to those obtained at 100° C. A

color pattern of active (100) areas formed within a few minutes, and preferential scaling in these areas occurred in 90 minutes. In 3 hours the entire sphere exhibited this scaling property. Electrolytic etching in the lead-polishing liquid after 5 hours heating in mineral oil at 200° C developed a yellow circular area around the (100) region. The facts that scaling started preferentially at the (100) and etching developed the (100) regions indicated that the oxide, or the mineral oil-oxide complex, was thickest at these regions. The loss in weight in 24 hours was 0.028 g.

Oiliness Agents

Stearic acid in an atmosphere of hydrogen.- At 200° C in unpurified tank hydrogen a crystal sphere lost 0.015 g in 5 hours. In a comparable length of time in hydrogen purified by passing over heated copper wire, the lead crystal lost 0.003 g. These values should be compared with 1.047 g lost in 5 hours in an atmosphere of air. In spite of the small weight loss in hydrogen, an etch pattern consisting of strong specular reflection from a large area surrounding the (111) regions was noted. Since this pattern was similar to that obtained in pure air, it suggests that the small weight losses in hydrogen were due to traces of oxygen.

Stearic acid in an atmosphere of air.- Lead was greatly attacked by stearic acid, but the reaction was only slightly preferential with plane. Crystals reacted very similarly at 100° and 200° C. The weight loss in 5 hours at 100° C was 0.3467 g and at 200° C, 1.047 g. In both instances weak specular reflections from the (111) areas became apparent soon after the experiment was initiated. Six narrow bands radiating from the (111) pole had the power of diffracting a beam into colors depending upon the angle at which the surface was viewed. The entire surface of the sphere appeared very smooth and only under inspection at the highest magnifications could minute facets parallel to the (111) plane be noted. When the crystal was raised above the level of the liquid, the film of liquid broke rapidly and formed into drops which rolled off the crystal.

Five percent stearic acid in mineral oil in an atmosphere of air.- The weight loss in 5 hours at 200° C was 0.405 g, and a pattern of specular reflections from the (111) regions developed in 5 minutes, remaining until the end of the experiment. Drop formation occurred when the lead sphere

was suspended above the level of the liquid, the drops appearing to be preferentially wetting the (111) regions. This result was uncertain since all drops rolled rapidly from the sphere.

Oleic acid in an atmosphere of air.- Similar results were obtained at 100° and 200° C. During the entire experiment the lead crystals remained wet when suspended above the level of the liquid and the surface appeared very bright and smooth. When viewed with a flashlight in a darkened room, very weak reflections from isolated minute spots appeared normal to the (111) poles, and diffraction patterns of six bands radiating from the (111) poles, as described in the case of stearic acid, appeared. The weight loss in 5 hours at 200° C was 1.8953 g.

Methyl stearate in an atmosphere of air.- The weight loss in 5 hours at 200° C was 0.852 g. A pattern of specular reflections from an entire hemisphere normal to the (111) planes developed in several minutes and continued until the end of the experiment. In one case when a copper supporting wire was used, a thin film of copper deposited on the lead sphere.

Polishing Agents

Tricresyl phosphate in an atmosphere of air.- Tricresyl phosphate preferentially etched a lead single-crystal sphere at 100° and 200° C. No heavy lacquer or surface film could be detected with the eye. The weight loss at 100° C was 0.0067 g in 5 hours and 0.024 g in 24 hours. At 200° C the weight loss was 0.0032 g in 5 hours and 0.0035 g in 24 hours.

Commercial Oils

New aviation lubricating oil in an atmosphere of air. Negligible weight losses were detectable at 100° and 200° C. The surface rapidly became dark and remained so until the end of the 24-hour period.

Used aviation lubricating oil in an atmosphere of air. Used aviation lubricating oil very slightly attacked a lead single-crystal sphere at 100° C, the weight loss being 0.0008 g in 24 hours. No signs of etching or carbon deposition were apparent. The weight loss in 24 hours at 200° C

was 0.044 g. No carbon deposition was visible, but strong preferential etching occurred with the development of (111) planes.

Amines

Dodecylamine in an atmosphere of air.- No signs of preferential etching appeared when a lead single-crystal sphere was subjected to the action of dodecylamine for 5 hours at 200° C. The weight loss in this interval was 0.008 g.

Other Evidence of Preferential Etching

Striking preferential etching occurred in the following reagents.- (1) Electrolytic etching at low current densities in the lead-polishing solution. (2) Acetic acid-hydrogen peroxide mixture. (3) Acetic acid-nitric acid-water mixture.

IRON

Growth of Single Crystals

Owing to the inability to grow large crystals of iron by the conventional method of slowly cooling, it has been necessary in this study to make a special investigation on the preparation of iron. At the present time, irregular-shaped crystals about 1/4 by 1/2 by 1 inch have been obtained. Since larger crystals have not yet been grown elsewhere as far as can be determined and since the subject is of interest to the science of metals, a brief review of the present state of this subject is included along with this description of results.

It was originally thought that large single crystals of iron could not be grown by slowly cooling the melt due to the fact that iron changes its crystalline structure at about 900° C, thereby converting any large crystals of one kind which might have existed above this temperature into small crystals of another kind. It has been shown that such a change does take place when the metal is cooled without special treatment. Furthermore, single crystals of 3-percent silicon-iron alloy, which does not undergo a phase change, have been grown by slowly cooling a melt.

Prior to 1924 it had been found that if carbon was removed from iron or steel and the metal deformed in some manner, such as by stretching or rolling or even stamping, and then heated for at least several hours at a temperature close to but below 900° C, abnormally large grains grew in the deformed region. In the middle twenties, Edwards and Pfeil (reference 4) and Gries and Esser (reference 5) made extensive studies of the formation of these large grains. They attempted to remove the carbon from the iron by heating for long periods in hydrogen at temperatures from 950° to 1050° C and found it very difficult to remove the carbon from the interior of thick pieces of the metal. Thin strips, about 1/8 inch thick, finally were adopted. After removing the carbon the bars were deformed by pulling or rolling and finally annealed in hydrogen at temperatures a little below 880° C. Both groups were able to produce fairly large grains some of which extended several inches along 1/8- by 1/2-inch bars and occupied the entire cross section. There were always a few tiny crystal grains imbedded in the large ones. The two groups were not in complete accord as to the details of procedure, especially the exact amount of deformation. Gensamer has recently attempted to repeat the work of Edwards and Pfeil and found that, "The preparation of large crystals of iron by this method is much more difficult than it appears to be" (reference 6). He was unsuccessful in applying this method to the purest available iron and found it necessary to decarburize mild steel in hydrogen for over 2 weeks. The production of the crystals was found to be somewhat sensitive to the manner in which the metal was cooled. The best crystals were only 3/4 inch long and not quite 1/2 inch in diameter. In accord with the other experiments it was impossible to avoid a number of minute crystallites in the large crystals.

In 1934, Tangerding (reference 7) showed that, if one is working with sufficiently pure iron, the strain in the distorted crystal lattice at the grain boundaries may be sufficient to promote grain growth to a marked degree. The results also indicated that impurities other than carbon may have a marked influence upon single-crystal formation. Moreover, Cioffi of the Bell Telephone Laboratories in a private communication describes experiments which show that by employing the proper method and the proper kind of iron the strain produced in going from the gamma to the alpha phase is sufficient to produce enhanced grain growth.

In all the foregoing studies the purpose has been either to find what measures might be taken to prevent grain growth or to produce grains satisfactory for studying the magnetic

properties of single iron crystals. In no cases have crystals been produced which would be satisfactory for machining into spheres for chemical study, and all crystals produced have contained imperfections in the form of tiny crystallites. The conditions under which any particular piece of iron will yield large crystals have not been established nor is there any satisfactory explanation for the observed grain growth.

In most of the experiments conducted in this laboratory, the method of Edwards and Pfeil has been used. The metal employed was a cold-rolled steel, containing 0.08 to 0.16 percent carbon. It was decarburized in moist hydrogen for periods varying from 18 to 72 hours at temperatures varying from 950° to 1050° C, elongated from 1 to 4 percent by increments of 0.5 percent and annealed in moist hydrogen for periods varying from 18 to 48 hours. All combinations of the preceding factors have by no means been tried. The greatest trouble has been encountered in removing the carbon from the thick (1/2- to 3/4-in.) rods. If the steel had not been decarburized long enough, the carbon on the interior prohibited grain growth, thereby producing a rind of very large grains about a core of minute ones. Grain growth starts at the surface of the bar, and the grains proceed to grow radially toward the center. The trace of carbon and other impurities in the grain boundaries is apparently pushed ahead of the growing grain and is concentrated in the decreasing boundaries until sufficiently concentrated to stop grain growth. Further heating has been found to have no effect on grain growth. This method, which at present has produced grains 1½ inches long and extending to the center of a 5/8-inch rod, should be studied further to determine more exactly the optimum strain in rods which have been drastically decarburized. A few experiments have been conducted with Armco iron using this same method without success. This possibly may be attributed to a poor initial grain size. Other experimenters have found that good results can be obtained only with an initial grain size of 120 to 140 grains per square millimeter, and the Armco specimens studied had an initial grain size of about 90 grains per square millimeter. It may be possible to produce smaller grains by suitable deformation and heat treatment. Preliminary tests have been made on Cioffi's "gamma-alpha strain" method, and a decided grain growth had been obtained in large bars of Armco iron without any mechanical strain. The grains produced were not, however, larger than 1 square millimeter. To determine whether or not this result could be attributed to unremoved carbon, 1/8-inch slices of 3/4-inch Armco rod were heated for several days in moist hydrogen at 1000° C and after

annealing at 880° C for about a day yielded grains which had grown through the slice and occupied as much as one-fourth its area. Cioffi found it necessary to heat the bars to 1480° C in order to remove satisfactorily the carbon from thicker specimens. A molybdenum-wound furnace is now under construction in order to use this method.

Carbonyl and electrolytic iron have been obtained in order to study further the gamma-alpha strain method and also Tangerling's method of employing the strain normally found at a grain boundary.

To determine further what recent work has been done in this country on the growth of iron crystals, correspondence has been carried on with the research laboratories of United States Steel and Westinghouse Electric & Manufacturing Company, neither of which has done much work in this field; also with the laboratories of the Bell Telephone Co. and the Carnegie Institute of Technology, whose work was described in this discussion.

Electrolytic Polishing

Very bright and smooth surfaces of iron were obtained by the electrolytic polishing method of Jacquet and Rocquet (reference 8). Mechanically polished iron spheres served as anode in a cell consisting of 100 to 125 milliliters of the polishing liquid in a 250-milliliter beaker. The cathode was a cylinder of aluminum sheet fitted inside of the beaker. The cell was immersed in a bath of ice water for maintaining the temperature below 25° C, and the solution was stirred vigorously. The polishing medium consisted of: acetic anhydride - 76.5 percent, 70-percent perchloric acid - 18.5 percent, and distilled water - 5 percent by volume. The current density was 4 to 6 amperes/sq dcm at a potential of 25 to 30 volts.

Oxidation

An electrolytically polished polycrystalline disk of Armco iron was annealed in hydrogen at 550° C and oxidized in air for several minutes at 250° C. Microscopic examination indicated that definite colors were associated with each crystal grain, the color depending upon the orientation of the grain. A sphere consisting of several large single crystals was treated similarly and oxidized for 3 minutes at

300° C. Definite patterns were visible on the three larger grains, but it was impossible to identify the most active regions. It may be concluded, however, that the rate of oxidation of iron is highly preferential with plane.

Mineral Oil

When a sphere containing several large grains was alternately immersed in the liquid at 200° and 300° C and exposed to the air above, color films were obtained similar to those obtained in pure air. No etching occurred within 48 hours.

Oiliness Agents

Stearic acid in an atmosphere of hydrogen.- Preferential etching occurred in 3 hours at 200° C, although it was impossible to identify the planes developed due to the small size of the grains. The sphere remained entirely wet in an atmosphere of hydrogen, and the loss in weight in 24 hours for a 9-gram crystal was 0.019 g. No pitting occurred.

Stearic acid in an atmosphere of air.- At 200° C in 24 hours the weight loss in a 10-gram crystal was 0.266 g. Thus the loss in air was approximately 14 times that in an atmosphere of hydrogen. Etching along certain planes was obtained, but the most striking fact about the experiment was the predominance of a large number of uniformly distributed pits over the entire surface. Etching within the pits was also preferential as shown by parallel ridges visible under the microscope. Color films could be seen in the regions immediately adjacent to the pits indicating the presence of an oxide film. This fact suggests that etching in air depends in part upon electrolytic action between the oxide-covered region acting as cathode and the pit acting as anode. The nature of these pits should be studied further.

Polishing Agents

Tricresyl phosphate.- A preferential oxide color film formed on the surface in several hours at 200° C, and within 20 hours a heavy black sludge formed which was readily removed by agitating below the level of the liquid. A slight gain in weight in 24 hours was noted.

Commercial Oils

Unused aviation oil.- When the sphere was alternately immersed in liquid and exposed to air, a preferential oxide color film formed in several hours at 200° C and remained until the end of the experiment in 24 hours. No etching was visible on the surface, and the weight change was negligible.

Used aviation oil in atmospheres of carbon dioxide and hydrogen.- No etching or color films occurred at 200° C. The sphere remained bright and shiny and the weight loss was negligible.

Used aviation oil in an atmosphere of air.- No sign of etching or carbon deposition was noted after 48 hours at 200° C. A preferential oxide color film formed in several hours and remained to the end of the experiment in 48 hours. At 300° C a preferential color film formed in 5 minutes, and within 2 hours the surface became covered with a heavy, greaselike covering which was readily removable by rubbing with tissue. When this layer was removed, the surface was covered with a black, lacquerlike covering which could not be removed with intense rubbing. The sphere gained 0.001 g in 24 hours.

Displacement of One Metal by Another

A polished iron sphere was placed in a solution of copper stearate in stearic acid at 200° C. Copper deposited on the iron very rapidly but no signs of preferential action were noted.

Rearrangement Due to Hot Gases

A polished iron sphere consisting of several large crystals was heated at 440° C in a stream of a 5:1 mixture of hydrogen and oxygen for 48 hours. Microscopic examination indicated that the surface had recrystallized into a number of small grains of approximately grain size No. 5, A.S.T.M. Specifications. The surface gave the impression that a strained film first had developed on the surface and that later it had uniformly snapped, forming a number of crevices which served as grain boundaries. Etching for 5 minutes in concentrated hydrochloric acid removed these small grains.

Since the size of the iron crystals has not been of sufficient size for the proper identification and study of the crystal regions, these results with iron should be considered as preliminary only.

ZINC

A few preliminary results were obtained.

Machining of Zinc

Due to recrystallization and ease of shearing, great care must be used in machining zinc. A number of single-crystal rods was destroyed. Several spheres were grown in a small spherical glass vessel with a shaft extending from one side, but the best spheres were finally made on the lathe by making very, very fine cuts with the cutting tool.

Electrolytic Polishing

Zinc was electrolytically polished by a modification of the method of Vernon and Stroud. (See reference 9.) The cell consisted of 75 milliliters of a 25-percent solution of potassium hydroxide in a 150-milliliter beaker with a cylindrical zinc cathode. The solution was agitated by passing air through it, and the crystal was supported shaft downward by a zinc wire. The current density was 50 amperes/sq dcm at a potential of 6 volts. At higher current densities the surface became roughened due to adherent gas bubbles, while at lower current densities preferred etching occurred.

Oxidation

Faint preferential color films formed on heating in air at 300° C for 24 hours. A hexagonal region surrounding the (1000) pole appeared to be the most active, and there was no fine structure to the pattern.

Oiliness Agents

After immersing for 1 hour in stearic acid at 200° C, the crystal, weighing 12 g and having a total surface area of 7 square centimeters, lost 0.540 g. Definite preferential etching along the (1000) planes was obtained immediately after the crystal was placed in the liquid, but this became less pronounced with time and the surface became roughened all over. When the sphere was raised out of the liquid, it remained wetted during the course of the experiment.

When a sphere, which showed pronounced slip lines due to machining, was placed in stearic acid at 200° C, increased reaction as shown by excessive evolution of hydrogen could be seen to take place along these lines.

Galvanic Action

Galvanic etching of a zinc crystal has been described previously in the section on Copper.

Formation of Slip Lines

Slip lines parallel to the basal hexagonal planes occurred very readily when zinc crystals were scratched or pricked with a pin. Striking pressure figures, consisting of three main slip lines making angles of 120° C with each other, were obtained when a pin was pressed into the hexagonal plane. Similar lines also could be seen on two sections of the crystal which had sheared apart in machining.

Preferential Recrystallization

When a sphere, which had been machined from a bar, was electrolytically etched in polishing solution, it was noted that preferential recrystallization had occurred. Two bands of small crystals, about 3 millimeters wide and 14 millimeters long, ran parallel to the cleavage planes near the top and bottom of the crystal. Etching for 10 minutes at a current density of 50 amperes/sq dcm removed these small crystals, and the entire surface exhibited a crystalline character.

NICKEL

A few preliminary results were obtained.

Electrolytic Polishing

Bright and smooth surfaces were obtained by electrolytically polishing in a sulfuric acid solution, 75 percent by weight. The cell consisted of a 250-milliliter beaker containing 100 to 125 milliliters of the polishing liquid, a cylindrical aluminum cathode, and a stirring mechanism designed for moderate agitation of the liquid. Agitation was necessary in order to prevent severe pitting due to adherent gas bubbles. The nickel sphere, supported shaft upward by means of a nickel wire, served as anode, and the current density was 20 amperes/sq dcm at a potential of 6 to 8 volts.

Oxidation

A brilliant oxide color pattern, very much like that initially obtained with copper, formed at 450° C in air in 30 minutes and remained for many hours. The oxidation was very preferential with crystal plane. The colors of the various regions after 3 hours oxidation in air at 450° C were as follows: (100) and (210) - purple, (111) - blue, (110) - dark brown, and (311) - straw. This indicates that the oxidation rates at 450° C in order of decreasing rate were: (100) and (210), (111), (110), and (311).

Oiliness Agents

A faint pattern due to preferential etching and roughening appeared on a nickel sphere when it was immersed in stearic acid at 200° C. The (111) regions were the smoothest. The loss in weight in 40 hours at 200° C was 0.015 g. It has not yet been tested for preferential wetting.

Rearrangement Due to Hot Gases

A rearrangement pattern due to catalytic reaction of gases was visible on the surface of a nickel crystal after heating for 3 hours at 420° C in a 5:1 mixture of hydrogen and oxygen. Faint specular reflections were apparent and crystal facets were visible under the microscope at a magnification of 600.

V. DISCUSSION

Before discussing the individual results, a few preliminary remarks should be made about the general nature of the experiments. These experiments necessarily have been of an exploratory or qualitative nature for making a general survey of any factors which might enter into the chemical reaction between oil and metal surface. Special emphasis has been placed on the influence of crystal plane. An attempt also has been made to obtain information of other types which might be related to the subject of friction and wear and which would lend itself to the single-crystal method of study. Until the importance of these factors could be determined and their interrelationships understood in a qualitative way, it seemed undesirable to attempt quantitative studies of any one of these factors. Obviously, the entire

time of a small group during 1 year could be devoted to the careful study of the influence of any one of these factors, such as crystal plane and surrounding gas, on any one of the processes, such as etching, wetting, and roughening, with any one of the six metals. Thus, a large number of varied tests has been made to determine ways in which crystal plane might influence surface reactions.

It is believed that it is fair to say that the over-all purpose of this project, in relationship to the practical problem of reducing friction and wear in aircraft engines, is to determine, as far as possible, the principles controlling the chemistry of the oil-metal interface. This information is required in order to point out those factors which must be taken into consideration in the design of new machinery having decreased friction and wear. It is believed that these studies have indicated the importance of crystal plane and surrounding gas. Although the immediate application of this knowledge was not a definite part of this assignment, yet the question well may be asked at this point, "Could friction and wear in lubricated machinery be reduced by a control of the crystal plane, and if so, is it possible to control the plane?" The answer to the first of these questions is that the plane and surrounding gas have been shown to be important in studies with isolated metals but that only further tests with rubbing parts can determine whether friction and wear would be reduced by a control of plane. The answer to the second question will depend on the particular planes which are desired. Mechanical treatment and addition agents in electroplating can be used to obtain special orientation of surface crystals. (See reference 10.) Furthermore, if an appreciable improvement could be obtained, it is believed, from the experience of growing crystals in these studies, that very large crystals could be grown and any desired face cut.

However, regardless of the practical applications which the control of crystal plane may have, it should not be lost sight of that the chief use of this method is to study the properties of the metals and to obtain information on the mechanism of surface processes, physical and chemical. The results will now be discussed.

Considering the metals in ascending order of their position in electromotive series, a brief comparison of their reactivities at 200° C is as follows:

(a) <u>In an atmosphere of air.</u>- Silver, as would be

expected, was very unreactive and not appreciably etched by any of the four types of oil. It was the only one of the four metals studied which was completely wet on all crystal faces by stearic acid in air.

The reactions of copper were highly preferential with plane. These included oxidation in air and etching by mineral oil, oiliness agents, and commercial oils. Roughness of the surface produced by etching also varied greatly with plane. Chemical polishing agents, when new, formed protective films but, after being heated in air for about 24 hours, etched copper greatly and preferentially. Stearic, myristic, and palmitic acids wet some planes and not others while the unsaturated acid, oleic acid, wet all the planes completely. The formation and removal of carbon deposits in used aviation oil varied with plane.

Lead was by far the most greatly etched of the four metals studied. It was deeply etched by mineral oil, stearic acid, and used aviation oil. The reactions were only slightly preferential with plane except at lower temperatures when slow rates and preferential etching were obtained. Lead was not readily wet on any of the crystal planes by stearic acid, and no appreciable carbon deposits formed in used aviation oil.

Only small crystals of iron, about 1/4 inch in diameter, which are not entirely satisfactory for test purposes, have yet been obtained. Preliminary results indicated that iron, in general, was not greatly reactive, but the weight loss with stearic acid was appreciable and pitting was pronounced. Oxidation in air and etching by stearic acid were preferential with plane. It was not wetted readily by stearic acid when raised above the liquid.

The results of these chemical studies, including weight losses, are summarized in the following tables. The weight losses are useful for comparative purposes only since they represent composite values for the many faces exposed on the surface of a sphere. Results are given for 200° C. Results at 100° and 300° C are, in general, similar, with corresponding differences in rates.

(b) In an atmosphere of hydrogen.- The electronegative metals, silver and copper, were not etched appreciably, and the weight losses of the electropositive metals, lead and iron, were small fractions of the losses obtained in air.

For example, the loss with copper in stearic acid in air at 200° C was 5.47 g/sq dcm/day. In an atmosphere of tank hydrogen the loss was 0.0017. The loss with lead in air was 60 while in tank hydrogen it was 0.86 and in hydrogen purified by passing over heated copper it was 0.17. The surface of all four metals was wet by all the liquids, and no carbon residues formed, the liquids appearing to be unchanged at the end of 48 hours.

With the exception of wetting, preferential reactions similar to those obtained with single crystals were identified on the individual crystals of polycrystalline specimens.

Silver was conspicuous by its nonreactivity with oils in the presence of air. Although referred to as a "noble" metal, it should not be concluded that it is unreactive with respect to all compounds, especially gases. Its unreactive quality may be largely attributed to its failure to be attacked appreciably by oxygen, but it is most sensitive in its preferential reactions with iodine vapor or in solution, with chlorine, and with sulfur compounds. The successful use of silver as a bearing is probably largely due to its resistance to oxidation, indicating the importance of the chemical properties of the surrounding gas. If oxygen were not present, the chemical nature of many metals would appear to be quite different. It is interesting that a highly preferential color film was obtained when silver was heated in new aviation oil. This may be due to small traces of sulfur compounds. The results with silver suggest that gold, at least as far as chemical attack is concerned, might be beneficially used in rubbing parts. The complicated nature of surface reactions was shown in experiments with silver by the preferential formation of gelatinous films with mineral oil in an atmosphere of air. No such films were formed in air alone or in mineral oil from which air was excluded. Apparently a complex of silver, oil, and oxygen first formed which scaled off, leaving the surface increasingly rough. The complex then decomposed, giving free silver which deposited on the walls of the flask. All the reactions with silver, which were found to take place, were preferential with plane.

Copper was the most highly preferential in its reactions of the metals studied. Since oxygen was known to accelerate greatly the attack of a copper surface by oil, as a starting point, experiments were conducted on the attack of oils in an atmosphere of hydrogen at 100°, 200°, and 300° C. Neither the basic hydrocarbons nor several types of addition agents,

Metal	Oxidation in air 300° C	Etching at 200 C (Figures give weight losses in g/sq dcm/day)					Carbon residue formation in used aviation oil 200° C	Wetting by stearic acid 200° C	Surface rearrangements due to catalytic reactions with hot gases. Patterns are specific with gas
		Mineral oil	Stearic acid	Tricresyl phosphate	New aviation oil	Used aviation oil			
Silver	No oxidation as shown by no color film. Minute facets parallel to (111) planes form after heating for 20 hours in O_2 at 500° C.	Preferential color film followed by slight preferential etching. 0.02	Very faint etch pattern. 0.001	Slight lacquer formation (not preferential). 0.000	Preferential sulfide color film. 0.000	Slight nonpreferential lacquer formation in 48 hours. Slight etching at 300° C. 0.000 at 200° C	Slight nonpreferential lacquer formation in 48 hours.	In air or hydrogen all faces are wetted.	$H_2S + O_2$ at 200° C $H_2 + Cl_2$ at 250° C
Copper	Oxidation varies greatly with plane, (100) and (210) having the greatest and (311) the lowest rates. Oxide scales off at (100) after heating, 300° C.	Preferential oxidation followed by preferential etching. 0.03	Preferential etching, roughening, and wetting. (111) smooth, (110) rough. 5.47	Protective film forms followed by preferential etching when film removed. 0.07	Preferential oxidation followed by very slight preferential etching. Negligible loss.	Preferential etching. Rate of etching variable due to carbon formation. 0.18 to 0.77	Preferential lacquer formation in about 6 hours followed by heavy tarry deposit and etching. Deposit removed preferentially.	In air the (110) faces only are wetted by stearic, palmitic, and myristic acids. In hydrogen all faces are wetted.	$H_2 + O_2$ at 400° C $NH_3 + O_2$ at 500° C NH_3 decomposition at 500° C
Lead	Oxidation varies slightly with plane. Faint color film forms in few minutes.	Preferential color film. Particles scale off certain regions. 0.29	Etching not preferential at 200° C, but becomes so at lower rates. (111) developed. Extrapolation loss: 60.24	Preferential etching. 0.04	Preferential etching after 3 days. Negligible loss in 1 day.	Etching slightly preferential. 0.53	None	In air no faces are wetted. In hydrogen all faces are wetted.	
Iron	Oxidation varies greatly with plane as shown by color films.	Preferential oxide color film. 0.000	Preferential etching plus deep pits formed over surface. 4.18	Preferential oxide film. gain of 0.005	Preferential oxide film. gain of 0.002	Preferential oxide film. 0.000		Same as lead.	$H_2 + O_2$ reaction at 440° C causes formation of small crystals at surface.

by themselves, attacked the copper surface. When a copper crystal was heated in mineral oil in air, it was surprising to find that the copper crystal oxidized in a manner very similar to that obtained in pure air with no oil present. The rate of oxidation was, of course, considerably slower. Apparently oxygen readily diffused through the oil surrounding the crystal and reacted with the crystal. The acid constituents of the oil reacted with the oxide, producing a faint etch pattern. Blowing air through the oil greatly accelerated this etching because of the more rapid oxidation of the oil. As the oil began to form a tar, the deposition of the tarry material varied with the oxidation pattern.

This variation in oxidation with crystal plane is of the greatest importance in controlling the action of oils on a metal surface. In an aqueous solution the effect of oxygen has been shown previously to be important. (See reference 11.) If copper was immersed in water through which carbon dioxide was bubbled and exposed to air, the crystal was etched preferentially at room temperature. If carbon dioxide and hydrogen were passed through, no etching took place. The etching was attributed to two reactions, the oxidation of the copper and the reaction between copper oxide and carbonic acid; or looked at in another way, the oxygen removed the hydrogen, thereby facilitating the solution of the copper. The same type of reaction has been found to take place with lower members of the fatty acid series, acetic, propionic, and others. Therefore, it would be expected that the oiliness addition agents, stearic and oleic acids, would etch copper preferentially at 100° C or higher in an atmosphere of air. Not only did the rate of etching vary with crystal plane but the roughening of the surface varied greatly with plane. Although the etching action could account for the removal of an appreciable amount of material, the preferential roughening of the surface by this etching might possibly account for even more, due to increased wear between the rough surfaces. Figures 2 and 3 show the preferential roughening of the surface with crystal plane. Figure 4 shows the variation in roughening on the individual grains of a polycrystalline surface. It appears that the orientation of the individual grains can be identified by the appearance of the surface, although X-ray examination is required to confirm this conclusion.

The etch pattern produced by stearic acid changed during a period of 6 hours until a characteristic pattern was obtained. By renewing the acid every 3 hours, it was shown that the change in pattern was not produced by the changing

composition of the acid over a period of 3 hours. There is no ready explanation for this. One possible explanation is that etching is dependent on a certain critical angle between the geometric surface and a particular crystal plane as shown by the fact that sometimes facets parallel to the (111) planes will be developed in the (110) regions and not in the (100) or even the (111) regions. Thus, as the smoothness of the surface is changed due to etching, the etching characteristics may change. Another possible explanation is that some material is slowly absorbed from the decomposing stearic acid, and this may change the etching characteristics up to a certain point. These changing patterns which are sometimes produced by other reagents are often more apparent than real.

The fact that an etch pattern was obtained with stearic acid in the presence of chlorine gas, showed that an electronegative gas will promote the etching of an acid of a metal below hydrogen in the electromotive series.

Less time was spent on experiments with the polyhedra prepared parallel to special planes than was at first planned. As previously pointed out in the proposals for this project, the results with polyhedra can have at their best only limited meaning. The surface which roughens may appear to have the greater rate due to the fact that it exposes a greater surface while actually it may have a lower rate per unit of area exposed. Furthermore, it is impossible to eliminate corners and edges which may have unusually high rates of etching. The reasons for the inconsistency between the two sets of experiments with the polyhedra possibly may be explained as follows. In order to speed up etching and facilitate more accurate weight measurements, the crystals were alternately immersed in liquid and exposed to the atmosphere above. The rate of etching possibly varied with the manner in which the polyhedra entered and passed through the liquid. The rate of flow of liquid past the crystal will depend on whether a corner, edge, or face entered the liquid and on the shape of the polyhedra. Also the rate of etching will depend on the wetting ability of the various faces, and it could be easily seen in these experiments that the adherence of drops to the surface varied with the plane. These experiments should be repeated with the crystal continuously immersed in the liquid in order to prevent any variation in the flow of liquid adjacent to the crystals. The duration of the experiment must be increased in order to obtain sufficient etching for accurate weight measurements.

The ability of a film of liquid to rearrange into

definite drops at particular regions of a crystal has been designated by the term "ability to wet," although it is not certain that this is the proper classification. At least the film which temporarily formed on the surface broke and receded to definite positions symmetrically arranged on the sphere. It is not known to what extent all traces of liquid were removed from the bare regions but they appeared to be completely dry as compared with the large drops formed at particular positions. The photograph in figure 6 in which the drops are shown as four large black spots does not adequately illustrate this striking experiment. This photograph was taken after the crystal had been removed from the flask and cooled, and the drops of stearic acid had solidified. The failure of the drops to form in an atmosphere of hydrogen and their immediate formation in pure oxygen indicates that oxidation plays a controlling part. This is also borne out by the fact that, in order to initiate the formation of the drops, it is sometimes necessary to allow the crystal to stand in air above the liquid for about a minute. The formation of drops in a few minutes in an atmosphere of pure oxygen with new stearic acid indicated that no decomposition product of the acid, at least over a period of about 20 minutes, was responsible for the phenomenon. The inability of the drops to form when the temperature of the liquid was below about 160° C may have been due to the slow rate of oxidation of the surface, or the slow rate of formation of some oxidation complex, below this temperature. The shift in the formation of the drops from the (111) regions to the (110) with time may have been due to the final formation of many facets at the (110) regions which were approximately parallel to the (111) planes. Thus, if the stearic acid molecules were attracted to the (111) planes, they may ultimately have been drawn to the (110) regions where a greater total surface of (111) planes was exposed than at the (111) regions. After the crystal had been etched for at least 3 hours, the (110) regions became rough and the remainder of the surface relatively smooth, but the ultimate formation of the drops at these rough regions was not due to the roughness in itself, for no preferential formation of drops took place in an atmosphere of hydrogen. It seems more reasonable that the preferential formation of these drops was due to some selective fitting of the stearic acid molecules into the copper oxide lattice. Electron diffraction studies of the different crystal faces should give valuable information on this subject. It was noted that stearic, palmitic, and myristic acids exhibited preferred wettability, while the unsaturated oleic acid did not. Also stearic acid solution in mineral oil, up to 50 percent mineral oil, showed preferred wetting.

The formation of an insoluble protective film on the crystal was the most interesting feature of the tricresyl phosphate experiments. The formation of this coating appeared not to be preferential with plane but actually it may be. The coating may first form as a thin film on the more active regions, thereby tending to give the surface equal activity and appearance overall. At low temperatures, below 200° C, where the decomposition of the tricresyl phosphate does not take place appreciably, this film even on rubbing parts might protect the surface from etching by acid constituents. Experiments with mixtures of stearic acid and tricresyl phosphate indicated that the film reduced the etching by the acid and produced a relatively smooth surface. The smoother surface should distribute the load more evenly. At the higher temperatures, on the other hand, where the decomposition of the tricresyl phosphate takes place, it is a striking fact that the etch pattern produced by the tricresyl phosphate is exactly the opposite of the pattern produced by stearic acid. The rough regions on one are the smooth regions on the other as can be seen in figures 2 and 5. It has been shown elsewhere that a combination of tricresyl phosphate and stearic acid in mineral oil is especially effective in reducing wear. It remains undecided whether the effective action of tricresyl phosphate in actual practice is produced by its film-forming action at lower temperatures or by the etching action of high spots by decomposition products at high temperatures. Oxygen is necessary for either effect. Possibly the film may be rubbed off the high spots where high-temperature etching can take place to produce a smoother surface. It does not seem that the theory of phosphorus alloying with high spots on a metal surface to lower its melting point, is required to explain from a chemical point of view the action of tricresyl phosphate in producing a smooth surface and thereby reducing wear. (See reference 12.) Chemical etching by combination of the two materials will give a smooth surface.

The failure to understand completely the carbonization results was attributed to the complexity of the reactions taking place simultaneously and to failure to control accurately the variables involved, especially the pressure of oxygen and the concentration and nature of the acid constituents of the oil. The formation of deposits is dependent on crystal plane, pressure of oxygen, and oil composition. The removal of the deposits is dependent on the nature and thickness of the deposit, the etching ability of acids in the oil, and in advanced stages on the contraction of the deposit on cooling. The etching ability of the oil is dependent in

turn on pressure of oxygen and composition of oil. Thus unintentional variations in the oxygen supply, the oil composition, and temperature could produce a wide variety of results.

However, several definite conclusions may be drawn:

1. Oxygen is necessary in the formation of a lacquer.

2. A high oxygen concentration increases the rate of lacquer formation and tremendously decreases the attack on the base metal. The decreased rate of attack leads to a firmly adhering lacquer, stable for long periods of time.

3. Chronologically the attack on copper by used aviation oil proceeds as follows: preferential formation of a colored lacquer, thickening of the lacquer, and preferential attack on the base metal.

It is believed that additional information could be obtained on the mechanism of lacquer formation by further study with single crystals.

The electrolytic displacement of one metal by another in oils may be important where the oil circulates in contact with several different metals. A harder metal, like copper, depositing on a soft bearing metal might cause increased wear. Galvanic cells also may be set up between different metals, and although the action would ordinarily be very slight due to the poor conductivity of oils, yet with thin films and high temperatures obtained at elevated spots, the action may be appreciable.

The study of scratches produced by one metal sliding on another may well be studied by this method. The nature of the material within the groove may be studied at various depths below the surface by electrolytic etching and examination with the microscope. An amorphouslike layer may be seen on the surface followed by small grains which have been torn away from the base crystal and rolled along. The depth of the disturbance can be determined by the appearance of the underlying single-crystal structure. This method for studying abrasion has not been fully utilized in these studies.

Lead was conspicuous in being greatly etched by most of the oils studied. Its reactions were preferential with plane only at the lower rates. The oxidation in air was only

slightly preferential as shown on figure 24. This should be compared with the photograph of copper on figures 1 to 8. It is interesting that lead, which is so useful as a bearing material, should recrystalize under the least amount of mechanical strain.

The difficulties of growing iron crystals have been discussed in a special note under Results. The results so far obtained on the chemical properties of iron surfaces should be considered as preliminary. Oxidation in air was highly preferential with plane. The formation of etch pits over the surface appears to be due to galvanic action which is known to be important in the corrosion of iron. Since pure iron is known to form passive films very readily, oxidation and attack by acids should be studied in detail. It should be emphasized that single crystals can be grown by present methods only from relatively pure iron. Care should be exercised in using results with these crystals to interpret the behavior of steel. It is believed that studies with iron, however, will give information of importance. The cracking of the surface film into small grains due to the catalytic reaction of hydrogen and oxygen has been obtained only with iron.

The unique property of zinc crystals was the ease with which shearing was produced by mechanical strain. Slip planes seemed to be centers of increased activity. Zinc was etched appreciably by stearic acid.

It is interesting that the oxidation patterns with nickel were very similar to those obtained with copper, which crystallizes in the same system and has approximately the same atomic spacing.

University of Virginia,
Charlottesville, Va., October 25, 1944.

REFERENCES

1. Gwathmey, Allan T., and Benton, Arthur F.: The Growth, Orientation, and Preparation of the Surface of Single Crystals of Copper. Jour. Phys. Chem., vol. 44, no. 1, Jan. 1940.

2. Gwathmey, Allan T., and Benton, Arthur F.: The Reaction of Gases on the Surface of a Single Crystal of Copper. I. Oxygen. Jour. Phys. Chem., vol. 46, no. 8, Nov. 1942, pp. 969-980.

3. Langmuir, Irving: The Mechanism of the Surface Phenomena of Flotation. Trans. Far. Soc., vol. XV, pt. 3, June 1920, p. 69.

4. Edwards, C. A., and Pfeil, L. B.: The Production of Large Crystals by Annealing Strained Iron, Jour. Iron and Steel Inst., London, vol. CIX, no. 1, 1924, pp. 129-147.

5. Gries, H., and Esser, H.: Über Einkristalle aus Eisen, Archiv für das Eisenhüttenwesen, vol. 2, no, 11, May 1929, pp. 749-761.

6. Gensamer, M., and Mehl, R. F.: Yield Point of Single Crystals of Iron under Static Loads. Tech. Pub. No. 893, Am. Inst. Mining and Metallurgical Engineers, Metals Tech., vol. 5, no. 2, Feb. 1938, pp. 1-6,

7. Tangerding, W.: Kornwachstum in Karbonyleisen und Herstellung von Eiseneinkristallen. Archiv für das Eisenhüttenwesen, vol. 9, no. 2, Aug. 1935, pp. 113-114.

8. Jacquet, Pierre, and Rocquet, Paul: Application du polissage electrolytique a l'examen micrographique du fer et des aciers. Compt. Rend., vol. 208, no. 13, March 27, 1939, pp. 1012-1014.

9. Vernon, W. H. J., and Stroud, E. G.: Electrolytic 'Polishing' of Zinc. Nature, vol. 142, no. 3609, Dec. 31, 1938, p. 1161.

10. Barrett, Charles S.: Structure of Metals, Crystallographic Methods, Principles and Data. McGraw-Hill Book Co., Inc., New York and London, 1st ed., 1943.

11. Gwathmey, A. T., and Benton, A. F.: Some Experiments Showing Directional Reactivities of Single Crystals of Copper. Trans. Electrochem. Soc., vol. 77, 1940, pp. 211-218; discussion, pp. 219-222.

12. Beeck, Otto, Givens, J. W., and Williams, E. C.: On the Mechanism of Boundary Lubrication. II. Wear Prevention by Addition Agents. Proc. Roy. Soc. London, ser. A, vol. 177, no. 968, Dec. 31, 1940, pp. 103-118.

BIBLIOGRAPHY

Chappell, C.: The Recrystallization of Deformed Iron. Jour. Iron and Steel Inst., vol. LXXXIX, no. 1, 1914, pp. 460-[illegible]

Joisten, A.: Einfluss der thermischen Behandlung auf die Korngrösse des Eisen. Metallurgie, vol. 7, no. 14, July 22, 1910, pp. 456-458.

Sauveur, Albert: Note on the Crystalline Growth of Ferrite Below Its Thermal Critical Range. Proc. Int. Assoc. for Testing Materials, vol. 2, no. 11, 1910-12.

Sherry, R. H.: Coarse Crystallization Produced by Annealing Low-Carbon Steel. Metallurgical and Chemical Engineering, vol. X, no. 10, Oct. 1912, pp. 666-667.

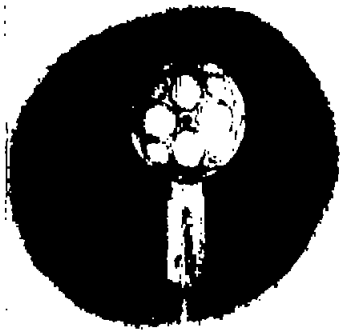


Figure 1.—Oxidation pattern on copper crystal heated in air at 200° for 80 minutes. Normal at (100) pole.

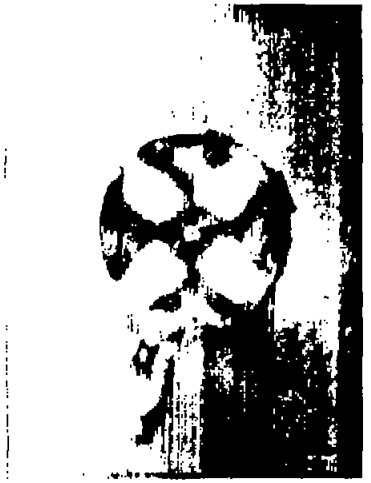
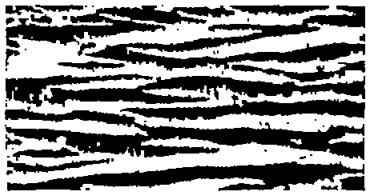


Figure 2.—Etch pattern on copper crystal heated in stearic acid at 200° in air for 24 hours. Normal at (100) pole.

(111) regions



(110) regions

Figure 3.—Photomicrograph of copper crystal etched by stearic acid in air at 200° for 24 hours. Magnification 600.

Figure 4.—Photomicrograph of polycrystalline copper etched by stearic acid in air for 24 hours. Magnification 600.

Figure 5.—Etch pattern on copper crystal heated in used tricresyl phosphate in air at 300° for 15 hours. Normal at (100) pole.

Figure 6.—Preferential formation of drops of stearic acid at the (110) regions on a copper crystal heated in acid at 200° in air for 6 hours. Drops had solidified when photograph was taken.

Figure 7.—Preferential formation of carbon deposits at the (111) regions on a copper crystal heated in used aviation oil at 200° in air for 18 hours.

Figure 8.—Photomicrograph of carbon deposits on surface of polycrystalline copper heated in used aviation oil at 200° in air. Magnification 600.

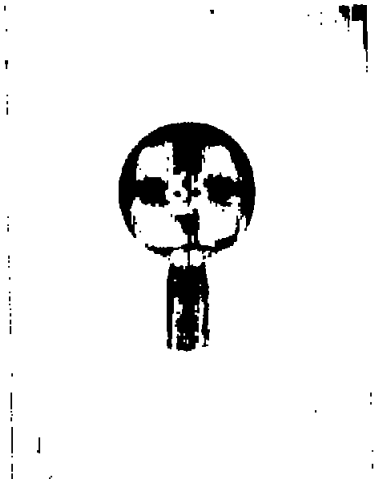


Figure 9.—At (100). Four lights were focused on bright (110)s.

Figure 10.—At (111). Note strong specular reflection from 3-armed area.

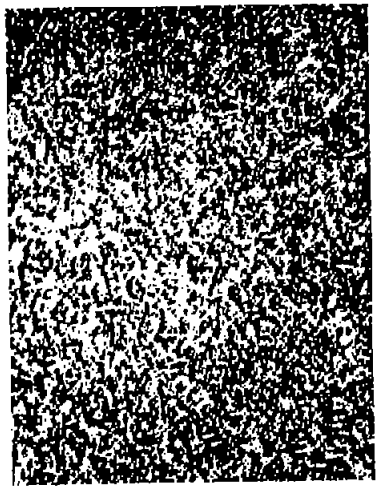


Figure 11.—At (100). Magnification 600.

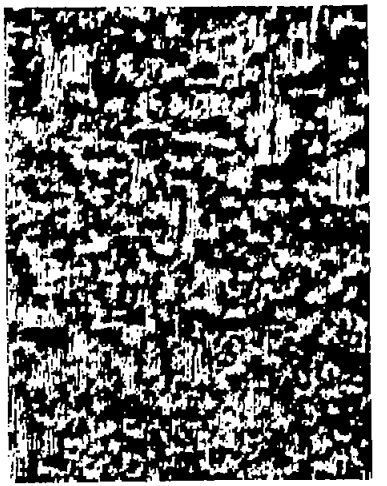


Figure 12.—Near (100). Magnification 600.

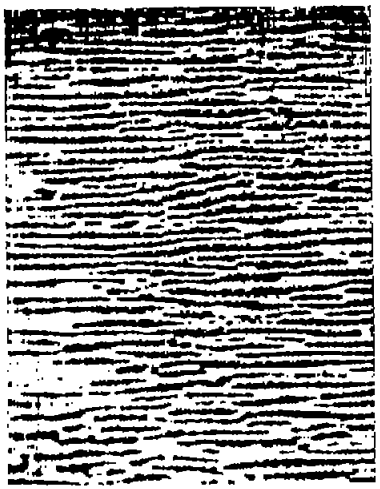


Figure 13.—At (110). Magnification 600. Ridges run perpendicular to line between (100)s.

Figure 14.—At (111). Magnification 600.

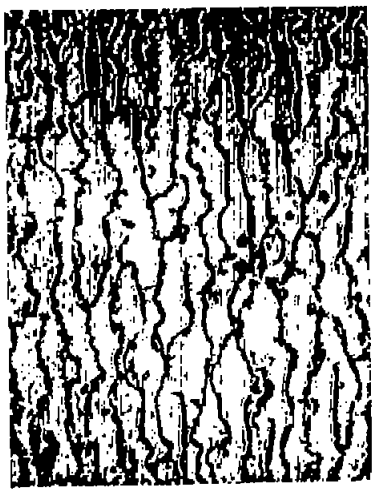


Figure 15.—Near (111). Magnification 600.

Figure 16.—Polycrystalline copper. Magnification 600.

Figures 9 to 16.—Catalytic reaction of hydrogen and oxygen on a single crystal of copper for 16 hours at 400° C.

Figure 17.—Color film formed by mineral oil and air on single crystal of silver. Wide color range. Normal to (100).

FIGURE 18. Action of iodine in hexane on a single crystal of silver. Wide color range. Normal to (111).

Figure 19.—Slip lines formed by pin prick on a (110) plane of silver. Magnification 600.

Figure 20.—Slip lines formed by pin prick on polycrystalline silver. Magnification 600.

Figure 21. Air oxidation of a single crystal of lead at 200° for 10 minutes. Normal to (100).