NACA TN No. 1460

13 JUL 1949

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

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By Allan T. Gwathmey, Henry Leidheiser, Jr.,
and G. Pedro Smith

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June 1948

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INFLUENCE OF CRYSTAL PLANE AND SURROUNDING ATMOSPHERE ON CHEMICAL ACTIVITIES OF SINGLE CRYSTALS OF METALS

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SUMMARY

A general survey has been made of the influence of crystal plane on the chemistry of the oil-metal interface. Single crystals of 13 metals have been grown, converted into spheres, and their surfaces specially prepared. Five chemical processes important to the operation or manufacture of lubricated surfaces have been studied. It may be concluded in general that the rates of these five processes with 13 metals vary with plane in different degrees. In some cases there is more difference between the chemical behavior of two different faces on the same metal than between the behavior of polycrystalline surfaces on two different metals. The significance of this variation with plane is great both in regard to an understanding of the mechanism of surface processes and in regard to the practical use of metals.

The complete list of the 13 metals studied is given according to crystal structure as follows: (1) face-centered cubic structure - aluminum, copper, gold, lead, nickel, and silver; (2) body-centered cubic structure - chromium and iron; (3) hexagonal close-packed structure - cadmium and zinc; (4) rhombohedral structure - bismuth; (5) body-centered tetragonal structure - tin; (6) face-centered tetragonal structure - indium.

The processes which have been studied, and the rates of which in general vary with plane are:

1. Oxidation in air.

2. Corrosion by oils. This produces two distinct effects: one, the amount of metal removed varies with plane; and two, some regions are roughened and others remain smooth. Increased roughness may produce other effects such as mechanical wear.

3. Wetting of the surface by stearic acid with copper, nickel, and iron.

4. Rearrangement and roughening of the surface due to the action of hot gases in many cases.

5. Electrochemical processes, including deposition, etching, replacement, and in a few cases, galvanic action.

The nature of the surrounding atmosphere was found, as in the case of copper, to have a far greater influence in controlling chemical action at the oil-metal interface, especially in the case of etching and wetting, than the literature on this subject indicates.

Although the preparation of the crystals was undertaken as a means to an end, the information and experience obtained with crystal growth, recrystallization under mechanical strain, the process of shear, and formation of slip lines are an important addition to the chemical information obtained in the studies of processes 1 to 5. Physical as well as chemical processes are influenced by crystal plane, and a comprehensive knowledge of both must be brought to bear on the over-all process of friction and wear.

All crystals, except those of iron and chromium, were grown by slowly lowering the melt in a vacuum furnace. Iron was grown by the strain-anneal method, and chromium was ground from large crystal lumps. Lead, zinc, tin, and indium could not be machined without recrystallization and were generally grown in spherical form. The mechanically strained and roughened layers were removed by electrolytic polishing, it being necessary in some cases to develop special solutions.

An attempt has been made to find some basis for correlation of results. Although each reaction pattern is characteristic of the particular reaction, there are certain similarities in the patterns for metals of any one crystal system. For example, the regions of high and low rates of oxidation with those face-centered cubic metals, the oxides of which can be readily reduced, are in general the same. Likewise, the regions of high and low rates of oxidation for the hexagonal close-packed metals are similar. The etching and wetting characteristics of the various metals have been summarized, and the variations in the rates of the several processes are given. The results of these studies with a number of processes on a number of metals of greatly different properties suggest the universal dependence of surface processes on crystal plane. Also it is believed that many of the difficulties of lubrication commonly attributed to mechanical causes may have their origin, at least, in chemical processes.

INTRODUCTION

The processes which take place in lubricated machinery may be divided, for convenience in study, into chemical processes and mechanical processes. In these studies chemical processes are considered to include all ordinary chemical changes, such as oxidation and corrosion of the metal surface, plus the processes of adsorption, orientation of oil molecules, and electrodeposition. Mechanical processes, which involve the action of forces on metals, are considered to include such processes as friction, wear, and shear. It should be emphasized that this classification is simply for convenience in isolating and studying one variable at a time. A comprehensive

understanding of over-all lubrication would be greatly aided by a knowledge of these individual processes. The present investigation includes all chemical processes taking place at the surface of large individual crystals of metals unaccompanied by mechanical friction and wear. In order to relate the consecutive parts of this study, a brief review of the project as a whole will be given.

An ordinary metal surface consists of crystal faces, edges, corners, boundaries, and disturbed layers. Each type of surface has its characteristic arrangement of atoms which influences its reactivity. The properties of a surface are a composite of the properties of these individual parts, and measurements made on ordinary polycrystalline surfaces have a limited meaning, especially for purposes of understanding the mechanism of surface processes. Therefore, in order to understand the behavior of a metal surface, the properties of the different types of structure must be understood.

From preliminary measurements made in this laboratory with lubricating oils, it was suggested that corrosion of metal surfaces and other processes important to lubrication might vary with crystal plane. Proposals were made that the processes of lubrication, friction, and wear be investigated by a study of large single crystals in the form of spheres on which different faces of known structure could be identified. This method also has the advantage of being concerned with the unit crystal of which all metals are composed and therefore offers special opportunities for the correlation of many apparently unrelated processes. The importance of the preparation of the surface cannot be overemphasized. Many careful surface measurements are of little value because they have been made on surfaces of unknown structure. In the method used in the present study all strained layers are removed by electrolytic polishing, which leaves the known structure of the base metal exposed to the action of the reacting oils and gases. It is possible to follow slight changes in the surface by the appearance of symmetrical patterns against a highly polished background. Through the use of crystals in the form of spheres, it is possible, in effect, to study chemical changes on a surface having a complete set of spherical coordinates inscribed on it for identification of structure and for following the course of the reaction. It was appreciated at the outset that, in the study of lubrication by this method, the over-all conditions in an actual engine were not reproduced, but it was thought that the underlying principles which control the behavior of metals in an engine could be effectively studied and that much valuable information on mechanism of surface processes could be obtained. At the same time the desirability of using oriented crystal surfaces could be investigated, with due consideration of the possibility that this study might even show that an oriented surface is just what is not desired.

A project for one year, beginning Oct. 1, 1943, was approved, the purpose of which was to obtain fundamental knowledge on the chemistry of the oil-metal interface of lubricated systems and its dependence on crystal plane. The oils to be studied were: pure hydrocarbons, oiliness addition agents, chemical polishing agents, and commercial oils. The metals were to be copper, silver, and iron if possible. The temperature range was room to 300° C. Emphasis was to be placed on dependence on crystal plane.

The first year was devoted largely to a study of copper and the development of the method. Results were also obtained with silver and lead and a few results with iron, nickel, and zinc. In the case of copper it was shown that the rates of reaction varied with plane for the five chemical processes listed in the SUMMARY plus the catalytic decomposition of oils. Each of these processes is important to the operation of aircraft engines, and hence their variation with plane is important. For example, both friction and wear vary with the thickness of the oxide film up to a certain point, and corrosion by oils depends greatly on the oxidation characteristics of the metal. The rate of oxidation of one face of a copper crystal is at least five times that of another. The nature of the surrounding atmosphere was found to play a controlling part in chemical action at the oil-metal interface.

A few additional effects were studied, which were thought to be important to lubrication and which readily lent themselves to this method of study. They were: formation of slip lines and their effect on corrosion by oils, rubbing of one metal against another whereby the softer metal adhered preferentially to the harder one, the effect on etching of rubbing two metals together, and the electrochemical displacement of one metal by another in oils and aqueous solutions. The etching of copper by three lower members of the paraffin series of acids, acetic, propionic, and butyric, was studied to determine any similarities between the etching characteristics of a series of acids, but no striking similarities were found. Each acid produced its characteristic pattern.

Before this information on the chemistry of the oil-metal interface could be profitably applied to the problem of friction and wear or before a detailed quantitative study of any one of these processes was justified, it seemed advisable to determine first whether this variation in rate with plane was a universal property of surface reactions. If this variation in rate with plane were a universal property of metal surfaces, this fact would have great significance. If it were simply a property of one or two metals, it would be of interest but would have limited significance. Accordingly, proposals were approved for a continuation of these studies for 1 year. The first 6 months were to be devoted to preparing and studying, by the same methods developed for copper, six additional metals. Actually 10 additional metals have been studied. This part of the study, including a discussion of all chemical studies carried out, is described in the present report. The second 6 months of this second year were to be devoted to studying the effect of crystal plane and atmosphere on friction and wear and to applying the chemical information previously obtained to this problem. This part of the study is given in reference 1.

The consecutive parts of the entire study, including references 1 and 2, are summarized as follows:

1. During the first year the method of study was developed, and the influence of crystal plane was studied with a number of processes important to the oil-metal interface. The rates of oxidation, corrosion, wetting, rearrangement due to the action of hot gases, electrochemical reactions,

and formation of carbonaceous deposits were shown to vary in different degrees with crystal plane for copper and lead. Silver was largely unreactive.

2. During the first half of the second year, five of these processes were studied with single crystals of 10 additional metals of greatly different properties in order to determine whether variation in rate of reaction with plane was a common property of surface reactions. This part has been completed and is described in the present report.

3. During the second half of the second year, the influence of crystal plane and atmosphere on friction and wear between metal parts was studied. The chemical information obtained in steps 1 and 2 of the entire study was used in selecting the most suitable conditions for these experiments and in interpreting the results. This part is covered in reference 1.

4. Since the general importance of crystal plane and atmosphere has been determined for a number of processes involved in the operation or manufacture of lubricated parts, it is now desirable to study on a quantitative basis the more important of these processes. Since oxidation is a controlling factor in many of these processes, it is specifically recommended that a quantitative study be made of the oxidation process for two or three metals by using color films, electrolytic reduction of the oxide, and electron diffraction as means of study. It is also recommended that the present studies on the influence of crystal plane and atmosphere on friction and wear be continued.

This work was conducted at the School of Chemistry, University of Virginia, under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

METHOD OF EXPERIMENT

The method of experiment is the same as that described in reference 2. It consists essentially in preparing single crystals of metals in the form of spheres and studying their reactivities with hot gases and oils. The advantages of this method of experiment and the types of information which may be obtained have been discussed in detail in the aforementioned report.

With the exception of iron, all single crystals were grown by slowly lowering a melt of metal from an electrically heated furnace. Iron crystals were grown by the strain-anneal method. Spheres, approximately 5/8 inch in diameter, with shafts 3/16 inch in diameter by 1/2 inch in length extending from one side, were machined from the single crystal rods. This was done with the aid of a special ball-turning apparatus which moved the tool on the arc of a circle as the single crystal rod was turned in the lathe. In a few cases in which machining produced recrystallization, it was necessary to grow the crystals from the melt in the shape of a sphere. The spheres were mechanically polished, whenever possible without

recrystallization, with emery papers numbers 1 to 0000 and then electrolytically polished in order to remove the strained layers at the surface. Since the growth, machining, and polishing of the various crystals varied in details, the significant features for each metal are described under RESULTS.

The spheres with shafts pointing downward were alternately exposed to mineral oil and air by raising and lowering the spheres about an inch above and below the level of the liquid at the rate of about 15 times a minute. Some experiments were conducted in an atmosphere of hydrogen or nitrogen. The conditions of experiment and the methods of examining the crystals have been previously described in reference 2. In brief, the crystals are examined by three methods. Oxidation patterns were studied by examining the interference colors which appeared when the crystal was examined within a tube of white paper. Etch patterns were examined by means of the specular reflections obtained when a beam of light was directed at the crystal in a darkened room. Light reflections flashed into view from small facets developed parallel to certain crystal planes. From the directions of these reflections and from the orientation of the crystal as shown by the symmetry of the etch patterns, the crystal plane along which these facets formed was determined. The details of the etching in any one area were examined with a microscope. The direction, depth, and cross-sectional dimensions of the etch structure could be measured. In most etching experiments the crystals were weighed before and after etching in order to obtain a rough measure of the degree of etching, but such measurements are limited in meaning because of the fact that all crystal planes were exposed and the rate of etching along these planes varied greatly. However, these weight measurements are of value when combined with information on the etch patterns.

It should be emphasized that, although care was taken in the preparation of the surfaces used in these studies, there is still a great need for a special study to be made on the preparation of metal surfaces mechanically smooth and chemically clean. In reference 2 various treatments for cleaning the surface of copper were described. It is believed that the surfaces used in this present study are satisfactory for the tests made, but the point should be made that the advancement of our knowledge of surface chemistry, and especially the correlation between theory and experiment, is dependent on the preparation of a surface of known structure which is more nearly mechanically plane and chemically clean. This is not an easy task.

Stearic acid was one of the oiliness agents used and tricresyl phosphate was one of the polishing agents used. A few experiments were conducted with pure-grade phosphate but this was not generally used because of excessive cost. The used and unused aviation oils were supplied by the NACA Flight Propulsion Research Laboratory in Cleveland. The purity of the metals used is described in RESULTS.

RESULTS

The pertinent facts about the growth, machining, polishing, and chemical reactions are given for each metal. In describing the chemical reactions, it is necessary to describe in some detail the various patterns obtained. Although this makes difficult reading because of both the inherent complications of the patterns and the large number of reactions studied, this method of description is necessary in first recording the chemical properties of the individual crystals. It is from this type of information that the conditions for subsequent detailed studies must be selected. The number of tests made and the information obtained vary somewhat with the metal, the number of tests made depending on the importance of the metal and the difficulties encountered. The metals are grouped according to the lattice spacing in which they crystallize. They will be considered in alphabetical order within any one lattice spacing. Temperatures are expressed in degrees centigrade.

The photographs given in the present report (figs. 1 to 21) are oriented in the same directions for crystals of any one structure in order that the patterns may be compared. The views of crystals of the face-centered and body-centered cubic structure are looking normal to the surface at the (100) pole. Tables I to III give results of oxidation, etching, and wetting.

FACE-CENTERED CUBIC STRUCTURE

Aluminum

The aluminum used had a listed purity of 99.4 percent aluminum. The melting point of the pure metal is 660°.

Growth.- Crystals in the form of rods, 5/8 inch in diameter by 6 inches in length, were grown by lowering a melt at the rate of 1/2 inch per hour in an electrically heated molybdenum-wound vacuum furnace. The crucible consisted of a graphite rod into which was drilled a hole with a tapered point at the lower end for the formation of a single nucleus.

Machining.- Spheres, 5/8 inch in diameter, with a small shaft 3/16 inch in diameter by 1/2 inch in length extending from one side, were machined from the rod. Single crystals are much softer than the polycrystalline material and great care is usually required in machining. In the case of aluminum, chips of the metal adhere readily to the work so that a bad surface finish results. This can be prevented by machining slowly and using carbon tetrachloride as a cutting oil. The tool should have a large positive rake of 40° to 60° and a side rake of 60°. The clearance should be 8° to 10°. If this angle is too small, the side of the tool will rub against the work and generate heat and distortion in the underlying metal; if too large, it will tend to cause digging. The

nose radius should be small since only light cuts can be made. In all cases it is essential to have keen cutting edges and highly polished faces which are free from burrs. The tools should be finished on a fine wheel followed by a very fine oil stone. Since aluminum expands greatly when heated, drilling should be done very carefully to prevent gripping of the drill. A good lubricant of one part lard oil to one part kerosene should be used and the drill should be withdrawn frequently to dispose of chips.

Polishing.– The spheres were mechanically polished with emery papers numbers 1 to 0000 and paraffin in kerosene was used as a lubricant. Electrolytic polishing was carried out by the method of Jacquet (reference 3), the electrolyte being a mixture of 7 volumes of acetic anhydride and 2 volumes of 70-percent perchloric acid. The cell consisted of a 250-milliliter beaker containing a cylindrical aluminum cathode and a glass stirrer. The current density was 3 to 4 amperes per square decimeter at a potential of 40 to 60 volts. The solution was stirred during the removal of the strained layer produced by mechanical polishing but was not stirred toward the end of the process. A bright surface was obtained in several minutes. The single crystal nature of the sphere was determined by noting the sharpness of the pattern obtained when etched in 10-percent sodium hydroxide.

Oxidation.– No visible change was produced when a crystal was heated in air at 500° for 15 hours. When it was heated in oxygen at 550° for 2 days and then examined under a beam of light, a faint but definite pattern of foggy and bright regions could be seen. Under the microscope the foggy regions appeared slightly rough and disrupted, and the bright ones appeared relatively smooth. Apparently the roughened regions were produced by penetration and reaction of the oxygen below the surface.

The roughest regions consisted of circular bands around the (100) poles and small connecting bands joining the (100) poles and passing through the (110) poles. Within the circular band at the (100) pole was a smooth region and at the center of this was a small rough spot. Large areas around the (111) poles remained bright and smooth. Thus, from the roughness of the surface, it appears that the regions around the (100) and (110) poles had the greatest rates of oxidation and those around the (111) poles, the lowest.

Mineral oil.– No visible change or weight loss was obtained after alternate immersion in mineral oil for 24 hours at 200° in an atmosphere of air, and the surface remained completely wet by the liquid.

Oiliness agents.– No visible change or weight loss was obtained after heating by alternate immersion in stearic acid for 24 hours at 200°, and the crystal remained completely wet. At 300° in an atmosphere of air a slight tarnishing occurred in 3 hours, but no weight loss occurred. In order to determine whether the inactivity of aluminum was due to an anodic film formed during the electropolishing, a crystal was etched for 7 minutes in 10-percent sodium hydroxide solution. An excellent etch pattern developed. After heating by alternate immersion in stearic acid for 24 hours at 200°, no visible change or weight loss was found.

No visible change or weight loss was found after heating by alternate immersion in oleic acid for 24 hours at 200° in an atmosphere of air. An attempt was made to determine the effect on etching of continually removing the protective oxide film by mechanical means. A crystal was revolved at a rate of 100 rpm in a flask containing oleic acid at 200° and about 1 inch of sea sand on the bottom. Within 3 hours small particles of aluminum appeared at the surface of the liquid and small scratches could be seen on the crystal. After 22 hours the crystal lost 0.0142 gram (0.14 g/sq dm), but from the appearance of the surface it seemed probable that there was no loss due to corrosion.

Chemical polishing agents.– After heating by alternate immersion in tricresyl phosphate at 200° for 20 hours in an atmosphere of air, a crystal became covered with a black, tar-like material which was readily removed by rubbing. After a total of 24 hours no weight loss was found, and the surface was unchanged.

Commercial oils.– After heating by alternate immersion in new aviation oil at 200° for 24 hours in an atmosphere of air, no visible change or weight loss was found.

A very slight weight loss and nonpreferential tarnishing were detected after heating by alternate immersion in used aviation oil at 200° for 24 hours in an atmosphere of air. The crystal remained completely wet.

Amines.– No weight loss or visible change in the surface was apparent after heating by alternate immersion in dodecylamine at 200° for 24 hours in an atmosphere of air.

Copper

The copper used had a listed purity of 99.90 percent copper plus silver. The melting point of the pure metal is 1083°. (See reference 2.)

Gold

The gold used had a listed purity of 99.95 percent gold. The melting point of the pure metal is 1063°.

Growth.– A gold single crystal in the form of a rod, 1/2 inch in diameter by 4 inches in length was grown by lowering the melt in a graphite crucible in a molybdenum-wound vacuum furnace at the rate of about 1/2 inch per hour.

Machining.– Gold must be machined with the greatest care since it is soft and tough and therefore susceptible to digging of the tool and bending of the entire crystal rod. In its general machining properties it is very

much like copper. Also, chips tend to weld to a clean surface, and sulphurized oil is used as a cutting oil. The depth of cut should not exceed 0.005 inch.

Polishing.– The gold single crystal was mechanically polished with numbers 1 to 0000 metallographic emery papers coated with a solution of paraffin in kerosene. The greater portion of the strained layer was removed electrolytically in dilute hydrochloric acid at a low current density, the sharpness of the etch pattern indicating when the greater part of the layer had been removed. The final polish was produced electrolytically by the method of Kushner (reference 4). The electrolyte consisted of a mixture of 67.5 grams of potassium cyanide, 15 grams of Rochelle salt, 15 grams of potassium ferrocyanide, 22.5 grams of phosphoric acid, and 2.5 milliliters of ammonia per liter of solution. The bath was maintained above 60° and the voltage was kept between 9 and 10 volts. The cell consisted of a 250-milliliter beaker with a cylindrical copper cathode. The solution was stirred vigorously. Current densities of about 150 amperes per square decimeter were used, but the rate of gold solution was very slow because of the low current efficiency.

Oxidation.– No change occurred with gold crystals on heating in air at 200° and 550° for 24 hours.

Mineral oil.– A crystal turned a lustrous green-black color within 30 minutes after being alternately exposed to the air and immersed in mineral oil at 200°. No pattern was visible and the weight loss was negligible after 24 hours. Some of the surface coloring could be removed by vigorous rubbing. The tip of the shaft, which always remained below the level of the liquid, was colored only slightly, this fact indicating that exposure to the air promoted the formation of the colored material.

Stearic acid, oleic acid, tricresyl phosphate, new and used aviation oils, and dodecylamine.– There was no change visible and no weight loss measurable after alternate exposure to air and immersion in stearic acid, oleic acid, tricresyl phosphate, new and used aviation oils, and dodecylamine at 200° for 24 hours.

Etching in aqua regia and electrolytic etching in hydrochloric acid or potassium cyanide.– Very striking preferential etching was obtained after etching in aqua regia and electrolytic etching in hydrochloric acid or potassium cyanide.

Rearrangement due to action of hot gases.– The gold crystal was inactive in a 7:1 mixture of hydrogen and oxygen at 440°. No visible change took place on the surface.

Lead

The lead used had a listed purity of 99.94 percent lead. The melting point of the pure metal is 327°. (See reference 2.)

Nickel

The nickel used had a listed purity of 99.4 percent nickel. The melting point of the pure metal is 1455°.

Growth.– A single crystal rod, 1/2 inch in diameter and 4 inches in length, was grown by lowering the melt in a molybdenum-wound vacuum furnace at a rate of about 1/2 inch per hour. Since carbon dissolves in nickel, it was necessary to use magnesium oxide as a refractory. Several different methods of preparing small crucibles were tried, the most successful consisting in lining the inside of a graphite crucible with magnesia cement. This was done by painting successive layers of cement on the inside of the crucible with a small paint brush. The final inside shape with a tapered point was obtained by twisting a mandrel of the desired shape down into the crucible and then applying more cement to the low places. A smooth surface was finally obtained.

Machining.– The machining of nickel is in general similar to that of copper.

Polishing.– The spheres were mechanically polished with emery papers numbers 1 to 0000, thoroughly degreased in alcohol and ether, and electrolytically polished by the method of Hothersall and Hammond (reference 5). The current density was 28 to 100 amperes per square decimeter at 10 to 25 volts, and the cell consisted of a 250-milliliter beaker containing a cylindrical nickel sheet cathode. The electrolyte was 150 milliliters of 70-weight-percent sulphuric acid, and the solution was stirred vigorously. The crystal was supported shaft upward in the electrolyte by means of a number 16 B. & S. gauge nickel wire inserted through a hole in the shaft. Some pitting was obtained, but this was minimized by using a high current density and by rapid stirring, and a bright, smooth surface was obtained. Excellent electrolytic etch patterns could be obtained with this electrolyte at low current densities, but because of deep pitting this solution was not used for determining the complete removal of the strained layer. For this purpose the crystal was etched at low current density in a mixture of dilute nitric and acetic acids.

Oxidation.– Nickel crystals gave excellent interference color patterns when heated in dry air or oxygen at 400° to 500°. Sharp patterns were only obtained when the crystal was preheated at 550° for 24 hours in dry hydrogen prior to admission of the air. At the lower temperature of oxidation, 400°, the first-order straw color appeared only after 24 hours of heating. The relative rates of oxidation of the different regions in order of decreasing rates were: (210) and (110) regions, wide bands connecting the (210) poles and bands connecting the (210) and (110) poles, crosses at the (100) poles, the (111) regions, fine structure bordering the (111) regions, and the (311) regions. A photograph of an oxidation pattern is given as figure 2.

Mineral oil.– At 100° in an atmosphere of air there was no weight loss or visible change after 48 hours when the crystal was either alternately immersed in mineral oil and exposed to the air above or suspended immediately

above the liquid. At 200° on heating by alternate immersion for 24 hours, there was no weight loss or visible change, but on suspending the crystal immediately above the liquid for the same length of time, the crystal lost 0.0002 gram (0.0014 g/sq dm), and the shaft, which for this experiment was pointing downward, showed strong specular reflections, whereas the body of the sphere showed no change. Complete immersion in the oil at 200° for 24 hours resulted in a weight loss of 0.0003 gram (0.005 g/sq dm); apparently all the etching took place on the shaft, for the sphere remained very bright. After heating by complete immersion at 300° for 24 hours, the sphere was covered with a heavy black deposit which was insoluble in ether or carbon disulphide and could not be removed by rubbing. No weight measurements were possible in this case.

Oiliness agents.– At 100° after 24 hours in an atmosphere of air one crystal heated by alternate immersion in stearic acid lost 0.0001 gram (0.002 g/sq dm) and another heated by complete immersion lost 0.0002 gram (0.003 g/sq dm). Both crystals lost their bright finish but showed no signs of preferential etching. At 200° after 24 hours with alternate immersion two crystals lost 0.0087 gram (0.124 g/sq dm) and 0.0086 gram (0.123 g/sq dm). Since the top of the sphere remained very bright and showed no evidence of chemical attack, whereas the bottom of the sphere and the shaft, which pointed downward, showed striking specular reflections, the experiment was repeated with the shaft pointed upward. Preferential etching occurred on the sphere and no visible attack appeared on the shaft. When a crystal was completely immersed below the level of the liquid at 200° for 24 hours, it lost 0.0053 gram (0.076 g/sq dm) and a slight uniform pattern with faint specular reflections from circular (100) regions developed over the entire sphere. Another crystal suspended just above the level of the liquid at 200° for 24 hours lost 0.0017 gram (0.024 g/sq dm) and there was a slight irregular roughening of the surface. At 200° for 24 hours in an atmosphere of hydrogen a crystal lost 0.0029 gram (0.045 g/sq dm). Light reflections were obtained in the (210) regions from facets parallel to (100) planes, from bands connecting two neighboring (210) regions, and from bands connecting neighboring (210) and (110) regions. A photograph of this pattern is shown as figure 9. In an atmosphere of hydrogen purified by passage over hot copper the weight loss was only 0.0002 gram (0.003 g/sq dm) and no sign of etching was visible.

At 100° on immersion below oleic acid for 24 hours in an atmosphere of air a crystal lost 0.0004 gram (0.007 g/sq dm) and developed a faint but uniform pattern. When a beam of light was directed normal to the surface at the (111) pole, weak specular reflections were obtained from the (100) areas. The (111) regions showed no sign of attack. At 200° the results were similar to those obtained with stearic acid. On alternate immersion for 24 hours a crystal lost 0.0103 gram (0.172 g/sq dm) and all the etching, as judged by the roughening of the surface, took place on the lower part of the crystal and the shaft. On complete immersion a crystal lost 0.0044 gram (0.076 g/sq dm) and a faint but fairly uniform pattern developed over the entire surface. A crystal suspended immediately above the liquid lost 0.0044 gram (0.076 g/sq dm) and gave a faint pattern. Strong reflections were obtained from a small spot at the very top of the sphere where a drop of

liquid remained during the entire experiment. In an atmosphere of tank hydrogen and at 200° an etch pattern similar to that produced with stearic acid was obtained. The weight loss was 0.0054 gram (0.083 g/sq dm).

Chemical polishing agents.– No visible change in the surface or weight loss was detectable when nickel single crystals were alternately immersed in tricresyl phosphate and air or suspended below the liquid for 24 hours at 200°. A weight loss of 0.0001 gram (0.001 g/sq dm) was noted when the crystal was suspended above the level of the liquid for 24 hours at 200°. The position of the nickel surface nearest the liquid attained a nonpreferential misty appearance.

Commercial oils.– At 100° in an atmosphere of air after 48 hours the weight loss with alternate immersion in new aviation lubricating oil was negligible, with complete immersion was negligible, and with suspension above the liquid was 0.0003 gram (0.005 g/sq dm). Very slight preferential etching was visible with both alternate immersion and suspension above the liquid. At 200° with alternate immersion there was no apparent change or weight loss after 48 hours.

At 100° with both alternate immersion and complete immersion in used aviation oil a slight mistiness was detected after 24 hours. At 200° after 24 hours with alternate immersion a crystal became covered with a uniform dark-brown lacquer. When a crystal was suspended for 24 hours below the liquid, then cooled in air and rubbed with tissue, a definite pattern resulted because of preferential adherence of the carbonaceous deposits to the crystal. The deposit resembled the earlier stages of lacquer formation on copper. The lacquer could be rubbed off wide regions around the (111) poles; the result was a pattern similar to the nickel oxidation pattern. Weight measurements in these experiments were meaningless since both etching and lacquer formation took place simultaneously. In an atmosphere of tank hydrogen at 200° no lacquer formation or change in weight was discernible after 24 hours.

Wetting.– When a crystal was raised above stearic acid in which it had been heated at 200° by alternate immersion for 16 to 20 hours in an atmosphere of air, the film broke in a few seconds and formed definite drops at the (111) regions. The surface of the nickel, unlike that of copper, showed no visible roughening. The regions in which the drops formed were regions of low rate of oxidation in air at elevated temperatures.

Rearrangement due to action of hot gases.– A very striking pattern was obtained because of rearrangements produced by the catalytic reaction of hydrogen and oxygen on a crystal of nickel at 430° for 3 days. The ratio of hydrogen to oxygen was 8:1 and the flow was maintained at approximately 10 cubic centimeters per minute. Square-shaped areas containing a striking fine structure with a cross at the center were developed at the (100) regions, as shown by figure 11. Strong specular reflections were obtained from these areas when a beam of light was directed normal to the surface at the (100) pole, this fact indicating that facets were developed parallel to the (100) planes. Facets parallel to (111) planes were developed in the regions between two neighboring (210) poles. Large areas around the

(111) poles remained smooth and apparently unchanged by the catalytic reaction. The regions which developed facets due to the catalytic reaction were those which had the greatest rates of oxidation at the same temperature. A photomicrograph of the surface near the (100) pole is shown as figure 12.

Electrolytic phenomena.– When a crystal of nickel was subjected to an alternating current of 1 ampere at 60 cycles in a cell containing 300 grams of hydrous nickel chloride, 30 grams of boric acid, and 300 grams of sodium chloride per liter, a faint pattern consisting of bright (100) regions connected by bright lines running through the (110) poles formed within 15 minutes. After 1 hour, when a beam of light was directed normal to the surface of the (100) pole, the (100) region became very bright and gave strong specular reflections, this fact indicating the development of facets parallel to the (100) faces. The surface of the sphere was badly pitted. The use of alternating current offers a simple method of determining the electrolytic preferentiality of a crystal.

Silver

The silver used had a listed purity of 99.9 percent silver. The melting point of the pure metal is 960°. (See reference 2.)

BODY-CENTERED CUBIC STRUCTURE

Chromium

The chromium used had a listed purity of 98.5 percent chromium. The melting point of the pure metal is 1800°.

Growth.– Chromium was purchased in the form of large irregular chunks, roughly 1 inch in diameter, which contained a few large crystals. Because of its extreme hardness and brittleness, it is exceedingly difficult to machine. Chromium cleaves readily along the (100) planes; this may be easily seen as small lines on the surface of the lumps. Accordingly, the lumps were converted into spheres by sawing and grinding. An irregular lump was held in a vise, and small grooves were sawed with a hack saw along the boundaries of a grain and parallel to the cleavage planes of this grain. When a small chisel was inserted in the grooves and rapped with a hammer, the desired grain sheared from the aggregate. This rectangular block was centered in a four-jaw chuck on a lathe, and a small shaft was ground on one end with the aid of a tool post grinder. Because of brittleness great care must be taken in grinding, and one cut should not exceed 0.002 inch. The shaft was then held in a collet and the head ground in the approximate shape of a sphere. It was then converted more nearly into the spherical shape by careful hand-grinding against a bench grinder. The sphere was completed by mounting the shaft in the lathe collet and carefully polishing all rough points with coarse emery cloth. The shape of the final crystal

was not a perfect sphere but it was sufficiently spherical to indicate clearly the symmetry of any pattern formed.

Polishing.– The crystals were mechanically polished with numbers 1 to 000 emery papers, and bright surfaces were obtained by electrolytic polishing in 70-weight-percent sulphuric acid. A few small irregularities, probably due to some impurity, remained on the surface, but the polishing was satisfactory for most of the experiments. The cell consisted of a 250-milliliter beaker containing a cylindrical aluminum cathode. A current density of 10 amperes per square decimeter at a potential of 25 volts was used and the bath was stirred vigorously. At the polishing point a viscous, dark-orange layer, which was soluble in cold water, formed on the surface. The crystal was removed from the polishing bath before cutting off the current. The final surface was marred by a number of fine cracks parallel to the (100) plane which were formed during the growth or grinding operations. Evidence that the strained layer had been removed was obtained by the appearance of a sharply defined etch pattern when the current density was lowered.

Oxidation.– When a crystal was heated in air at 400° for 3 to 10 hours or at 550° for about 10 minutes, striking interference colors were obtained, but no pattern could be identified. At any one time the color was approximately the same over the entire surface, but the color changed with time from straw to brown to blue to purple. Since chromium is of special interest because of its ability to become passive and since it is the only one of the metals forming oxides with bright interference colors and no pattern indicative of preferential oxidation, this experiment was repeated in various forms about 20 times with the same general result. It should be pointed out that the oxide film which forms on chromium on exposure to air cannot be reduced by heating in hydrogen at 550°, as is the case with copper, nickel, and iron.

Mineral oil.– No visible change in the surface or detectable weight loss was observed after a crystal was alternately exposed to air and immersed in mineral oil at 200° for 24 hours.

Oiliness agents.– When a crystal was alternately exposed to air and immersed in stearic acid at 200° for 24 hours, in one instance the weight loss was 0.0056 gram and in another 0.0019 gram, an average of 0.0037 gram (0.050 g/sq dm). The inability to reproduce etching results accurately was characteristic of chromium. From examination of the surface it appeared that all the etching took place near the lower end of the shaft where the aluminum supporting wire was attached to the crystal during both the polishing and etching. In order to determine whether this etching was influenced by galvanic action between the two different metals, etching experiments were carried out with silver and gold supporting wires and also with a glass supporting rod. Losses in weight of the same order of magnitude were obtained and the etching was localized at the end of the shaft. Thus it was concluded that the etching in this case was not influenced appreciably by galvanic action. It is believed that the localization of the etching at the bottom of the shaft was due to the following cause. In electrolytic polishing of chromium it is necessary to wrap the supporting wire tightly to the shaft in order to obtain good electrical contact. If this is not done, contact is broken apparently by a passive or oxide film formed on

the aluminum supporting wire by the action of the electrolytic polishing. No electrolytic polishing takes place and apparently no passive film forms at the points of contact between wire and shaft. Therefore when the crystal is heated in stearic acid, only this small region is attacked. It is thought that this may also be the explanation for the lack of agreement between the aforementioned two weight measurements. In order to test the protective action of the oxide film, a crystal on which a purple oxide film had formed because of previous heating in air was heated by alternate immersion in stearic acid at 200° for 48 hours. The oxide was not appreciably attacked, as shown by no weight loss and by an increase in the depth of the purple color. If a copper crystal containing a colored oxide film is heated in stearic acid, the oxide film is soon removed. The effect on etching of destroying the passive oxide film prior to heating in stearic acid was tested. A highly polished crystal was immersed in hydrochloric acid. Rapid reaction took place, and a definite etch pattern was produced. This crystal was then heated by alternate immersion in stearic acid at 200° for 48 hours. The weight loss during this period was 0.0020 gram (0.035 g/sq dm). Because of the etch pattern previously produced by hydrochloric acid, it was impossible to tell whether the etching was localized on the shaft, but the weight loss was of the same order of magnitude as that previously obtained by etching a polished sphere in stearic acid. Thus, breaking up the passive film prior to heating in stearic acid seemed to have no effect on etching. The film apparently formed again immediately as would be expected. In order to summarize the action of stearic acid, it may be concluded that stearic acid did not attack chromium appreciably at 200° because of the protective action of a film of oxide. Heating in hydrogen up to 550° will not remove this film, as it will in the case of copper, nickel, and iron.

When a crystal was alternately exposed to air and immersed in oleic acid at 200° for 24 hours, the weight loss was 0.0017 gram (0.022 g/sq dm) and all etching took place near the point of contact between the chromium shaft and the aluminum supporting wire.

Chemical polishing agents.– No change in the surface or detectable weight loss was noted when a crystal was alternately exposed to air and immersed in tricresyl phosphate at 200° for 24 hours.

Commercial oils.– No change in the surface or detectable weight loss was noted when a crystal was alternately exposed to air and immersed in new aviation oil at 200° for 24 hours.

A slight gain of 0.0002 gram (0.007 g/sq dm) was obtained when a crystal was alternately exposed to air and immersed in used aviation oil at 200° for 24 hours. Very slight preferential etching was noted where the supporting aluminum wire touched the shaft.

Amines.– No weight loss was noted when a crystal was alternately exposed to air and immersed in dodecylamine at 200° for 24 hours. A slight tan color was apparent on the surface.

Rearrangement due to action of hot gases.– No apparent reaction took place when a crystal was heated for 5 hours in a 7:1 mixture of hydrogen and oxygen at 400° to 460°.

Passivity.– When an electrolytically polished crystal was immersed in concentrated sulphuric acid, a striking etch pattern appeared almost immediately. An energetic evolution of hydrogen occurred but soon diminished with time. In several minutes the pattern almost disappeared, the surface assumed a dull gray appearance, the hydrogen evolution stopped, and the metal apparently became completely passive. Dipping in concentrated hydrochloric acid restored the activity. Re-immersion in the sulphuric acid restored the etch pattern until passivity set in and the pattern disappeared.

Iron

The iron used had a listed purity of 99.8 percent iron, 0.012 percent carbon, 0.017 percent manganese, and a trace of silicon. The melting point of the pure metal is 1535°.

Growth.– After many attempts, single crystals were grown by the strain-anneal method in Armco iron rods from which two spheres, about 1/2 inch in diameter, were machined. These crystals were satisfactory for the desired chemical tests, but the principles involved and the exact conditions necessary for the growth of these crystals have not yet been determined, although a definite attempt has been made to do so. Attempts by others to obtain and understand the growth of large crystals of iron have been summarized in reference 2. Additional experiments carried out in the present study, whereby the two single crystal spheres were obtained, are summarized as follows.

It should be remembered that, although small single crystals of iron, of the order of 1/4 inch by 1/2 inch by 1 inch and of variable shape have been grown by others from solid bars by using several different methods, no references have been found on the growth of crystals of the desired size, 1/2 inch to 5/8 inch in diameter.

By following the suggestion of Cioffi of Bell Telephone Laboratories that the strain produced in going from the gamma to the alpha phase at 910° was capable of causing grain growth with iron of the proper purity, a piece of Armco iron, 1/8 inch in diameter and 5/8 inch in length, was heated to 1450° over a period of 48 hours in hydrogen and then cooled over a period of 24 hours to room temperature. It was found to be a single crystal except for a cluster of four tiny crystallites on one side. An attempt was made to obtain similar results with larger Armco rods, 1/2 inch or greater in diameter, by using longer decarburizing and annealing times. Although large irregular grains were consistently produced, several grains of different orientation always met at the center of the rod. These grains had irregular boundaries in contrast with smooth boundaries generally characteristic of completed growth, but further heating below the transition

temperature produced no change. For the decarburization at 1450° and for other uses, a special molybdenum-wound furnace was constructed, in which both the windings and annealing chamber operated in hydrogen.

A sample of electrolytic iron, of 99.9 percent iron, was melted in an atmosphere of hydrogen in a crucible made of Norton cement, RM 922, to form a rod 1/2 inch in diameter. The bar was decarburized at 1400° and annealed at 870° for 4 days. The results were similar to those previously obtained. The same procedure was carried out with iron carbonyl powder containing 99.7 percent iron, but similar results were obtained.

A number of experiments were carried out with the decarburize-strain-anneal method, largely studied by Edwards and Pfeil (reference 6). Annealing and decarburizing temperatures from 750° to 1400° were employed and Armco iron was used. The best results were obtained by using a $\frac{1}{2}$-inch bar, decarburized at 950° for 10 hours in moist hydrogen, strained 3 percent, and annealed in hydrogen for 6 days. A thin layer of small crystals generally formed on the surface in this method, but the inside contained large crystals, generally occupying one-fourth to three-fourths of the entire cross section. In one case a crystal formed completely across the bar and 3/4 inch along the bar. It was from this bar that the larger sphere used in these experiments was cut. Unsuccessful attempts were made to repeat this experiment.

Since additional iron crystals are desired for further experiments because of the importance of the metal, these experiments on the growth of iron are being continued. High-temperature furnaces and a mechanical stretching machine are now available in this laboratory. This should now facilitate the study of crystal growth by this particular method. The effect of grain size, purity, amount of strain, temperature and time of decarburizing and annealing will be investigated further.

Machining.- The large crystals in the rods treated as in the foregoing section are located by etching in dilute nitric acid. Often adjoining grains are not held tightly together and may be broken apart by tapping with a small hammer. Generally the grains will withstand fairly strenuous machining operations. Even though a crystal may extend completely across the bar, it always extends for a greater length on one side of the bar than on another. The bar is, therefore, mounted eccentrically on the lathe so that the center of the desired crystal is located in the center line of the lathe. The rod must be etched in acid occasionally to relocate the boundaries of the crystal. The machining of iron in this form is similar to the machining of cast iron, the same tool angles, speeds, and depths of cutting having been found satisfactory.

Polishing.- The spheres were first mechanically polished by metallographic emery papers numbers 1 to 0000. Very bright and smooth surfaces were obtained by electrolytic polishing by using the method of Jacquet and Rocquet (reference 7). The cell consisted of a 250-milliliter beaker containing 125 milliliters of solution and a cylindrical aluminum cathode. The solution was stirred vigorously, and the cell was immersed in iced

water to maintain the temperature below 25°. The polishing solution consisted of 76.5 percent of acetic anhydride, 18.5 percent of 70-percent perchloric acid, and 5 percent of distilled water by volume. The current density was 4 to 6 amperes per square decimeter at a potential of 25 to 30 volts.

A few preliminary results on oxidation and etching of a sphere of iron containing several large crystals have been previously described in reference 2. These experiments have been repeated with the spheres containing one crystal only. The results are described in the following paragraphs.

Oxidation.- Very indistinct interference color patterns were obtained when a crystal was heated rapidly in hydrogen to 250° to 400° and oxidized in air at these temperatures. However, when the crystal was previously heated in hydrogen at 550° for 24 hours and then oxidized in oxygen at 240° for 3 hours, a very distinct and complex pattern was obtained, as shown by figure 4. It is difficult to describe this pattern, but important features were: a large blue square at the (100) pole surrounded by a narrow dark-purple band, broad violet diffuse lines connecting corners of the square at the (100) pole to the neighboring (111) poles, a very sharp and minute dark-blue triangle at the (111) pole, very sharp and narrow dark-brown lines connecting neighboring (111) poles, a small light-blue diamond at the (110) pole. The area between the square at the (100) pole and the (110) pole was a very light straw color and a region of low rate. The (100) and (111) regions appear to be regions of high rate.

Mineral oil.- Very faint preferential color films formed in 24 hours on alternate immersion at 200° in mineral oil and air, and no weight loss or visible etching was detectable. A faint but preferential etching occurred when a crystal was suspended above the liquid maintained at 200° for 24 hours, and the weight loss was 0.0002 gram (0.001 g/sq dm).

Oiliness agents.- When a crystal was alternately exposed to an atmosphere of tank hydrogen and immersed in stearic acid at 200°, a definite etch pattern giving specular reflections from the (100) and (110) regions appeared in 3 hours and remained until the completion of the experiment. No severe pitting was obtained, but the surface was preferentially roughened, the (111) regions remaining quite smooth. The weight loss after 24 hours was 0.0131 gram (0.385 g/sq dm).

When a crystal was completely immersed below the level of stearic acid at 200° for 24 hours, the weight loss was 0.0564 gram (1.15 g/sq dm). Striking reflections normal to the surface in the (110) regions were obtained, but no pitting was observed. When a crystal was alternately exposed to air and immersed in liquid at 200° for 24 hours, the weight loss was 0.3470 gram (10.02 g/sq dm). Within 5 minutes a very striking etch pattern similar to that produced by stearic acid in an atmosphere of hydrogen was obtained. Powerful reflections and severe pitting developed in 2 hours. At the end of 24 hours reflections normal to the surface in the (110) regions were still visible, and very severe pitting of the surface had occurred. Under

the microscope well-developed facets within the pits were visible. The surface surrounding the pits showed striking interference colors indicative of oxide. The presence of this oxide suggests that the pitting is due to galvanic action between the oxide-covered area as cathode and the pit as anode. In the beginning a pit may be started by an impurity or some local disturbance. It is significant that in experiments in atmospheres deficient in oxygen, such as those conducted in tank hydrogen or with the crystal below the liquid, little or no pitting was obtained.

When a crystal was alternately exposed to air and immersed in oleic acid at 200°, strong reflections normal to the surface in the (110) regions developed within 1 hour. Severe pitting occurred within 2 hours. After 8 hours the crystal was suspended below the liquid for an additional 11 hours, and the tendency to pit was greatly reduced although reflections from the (110) regions were still obtained. The weight loss at the end of 19 hours was 0.6373 gram (7.97 g/sq dm).

Chemical polishing agents.- When a crystal was alternately exposed to air and immersed in tricresyl phosphate at 200° for 24 hours, a slight film formed followed by slight preferential etching. The weight loss was 0.0004 gram (0.001 g/sq dm). Slight pitting took place.

Commercial oils.- A slight preferential color film was formed when a crystal was alternately exposed to air and immersed in new aviation oil at 200° for 24 hours. A barely detectable gain in weight was obtained.

When a crystal was alternately exposed to air and immersed in used aviation oil at 200° for 24 hours, very faint reflections were visible but no weight loss was detectable. The surface was covered with a thin brown lacquer which could be readily removed while hot by rubbing with tissue. A faint straw and brown interference color pattern could then be seen. When a crystal was suspended above the liquid at 200°, a slight lacquer formed and faint but definite reflections could be seen, but no weight loss was detected. When a crystal was alternately exposed to air and immersed in liquid at 300°, heavy irremovable lacquers formed in 30 to 40 minutes. Weight measurements were meaningless.

Amines.- When a crystal was alternately exposed to air and immersed in amines at 200°, an etch pattern, exhibiting specular reflections from the (110) regions, developed in 45 minutes. The weight loss after 24 hours was 0.0006 gram (0.002 g/sq dm). An interference color pattern similar to that obtained by oxidizing a crystal in air at 200° without previous annealing in hydrogen was obtained.

Wetting.- When a crystal was heated in stearic acid at 200° in an atmosphere of tank hydrogen, it remained completely wet when raised above the liquid.

When an iron crystal was suspended above the level of stearic acid after being alternately exposed to air and immersed in the liquid at 200° at the rate of 15 times per minute, the film covering the surface broke and rolled off the crystal. The action was so rapid that it was impossible

to tell whether it was preferential. However, when the crystal was immersed below the level of the liquid for 3 to 5 minutes and then raised above the liquid, a very striking wetting effect was obtained. The film turned dark brown in color within several seconds and broke at small circular regions at the (110) poles. The film receded from these positions and gave very striking, complicated, and symmetrical patterns as it moved, until drops finally took up their position at the (111) regions as shown by figure 13.

A crystal remained completely wet when raised above oleic acid at 200°.

Rearrangement due to action of hot gases.– When a crystal was heated in a 7:1 mixture of hydrogen and oxygen at 400° to 460°, no catalytic reaction was noted. The surface oxidized preferentially.

HEXAGONAL CLOSE-PACKED STRUCTURE

Cadmium

The cadmium used had a listed purity of 99.9 percent cadmium. The melting point of the pure metal is 321°.

Growth.– After about 15 unsuccessful attempts, a satisfactory single crystal of cadmium, 5/8 inch in diameter by about 8 inches in length and pointed at one end, was grown in an evacuated glass tube by lowering from an electric furnace at a rate of 3/8 inch per hour. The furnace was maintained at a temperature of about 370°, which is 50° above the melting point. Prior to melting, the glass tube containing the metal was evacuated in a second furnace maintained at 450°, and care was taken to remove all air bubbles, especially from the tip, before sealing from the pumps. This was done by carefully tilting and shaking the tube while the metal was kept molten over a gas flame. The tube was then returned to the melting furnace, sealed off from the pumps, and finally placed in the furnace from which it was lowered. Even with this precaution blowholes formed on the surface at solidification. Cadmium from several different sources, with listed purities of 99.8 percent cadmium or greater, was used. In most cases the several crystals which first formed at the bottom of the rod grew vertically and retained their cross-sectional area throughout the length of the rod. This effect was only found with cadmium. The temperature of the furnace should not be more than 50° above the melting point of the metal. No explanation has been found for the difference in behavior of cadmium from the several sources. All metal used was considered to be of a high purity. Unsuccessful attempts were made to grow cadmium crystals in the form of a sphere.

Machining.– Since cadmium has the hexagonal structure, it shears along the (0001) plane. It is not a brittle metal and does not cleave readily during ordinary machining like zinc, but, being a soft metal, it tends to

flow readily along the shear planes. When a rod with the (0001) planes running almost perpendicular to the axis was cut crossways with a thin abrasive wheel, a definite lump formed on the far side of the rod when it was cut half-way through. The same effect was obtained when the rod was pressed against a dull knife blade. Spheres were carefully machined from the rod by using a technique similar to that employed with the soft metal tin, described under BODY-CENTERED TETRAGONAL STRUCTURE.

Polishing.- The spheres were mechanically polished with metallographic emery papers numbers 1 to 0000, coated with a solution of paraffin in kerosene. No suitable method of electrolytically polishing cadmium could be found. A fair polish was obtained by vigorously agitating the crystal in concentrated nitric acid for 1 to 3 minutes. The crystal was supported by a platinum wire and after etching was rapidly removed from the acid and immersed immediately in a stream of water. The complete removal of the strained layer on the surface was determined by the sharpness of the pattern produced by etching in hydrochloric acid.

Oxidation.- Since cadmium oxide cannot be readily reduced by heating in hydrogen at a temperature below its melting point, the oxidation pattern obtained was not as distinct as those obtained with copper, nickel, and iron. When a crystal was heated in air at 200° for 19 hours, a pattern formed in 2 hours and increased in intensity until the end of the experiment. The pattern is shown as figure 5. The two large white spots in the center of the crystal are reflections from the source of illumination and should not be considered as part of the pattern. The pattern consisted of smooth and rough regions with a few natural colors showing in certain regions when the crystal was examined with a flashlight in a darkened room. No interference colors were visible when examined within a tube of white paper. A large hexagon-shaped region centered at the (0001) pole remained very smooth, and under the microscope at a magnification of 600 there appeared to be no change in the surface. Six irregular dark-brown regions, one opposite each side of the hexagon and showing as dark areas in the photographs, were the roughest regions. Radiating from each corner of the hexagon were six misty-blue lines. Faint specular reflections appeared from an entire hemisphere when a beam of light was directed at the surface at the (0001) pole. Under the microscope tiny black dots could be seen but these were not resolvable at a magnification of 600 and it is not known whether they were definite facets which might be responsible for the specular reflections.

Mineral oil.- When a crystal was alternately exposed to air and immersed in mineral oil at 200° for 24 hours, the weight loss was 0.0629 gram (0.97 g/sq dm). Within 2 hours a light-brown preferential oxide film formed on the surface, and soon thereafter preferential etching began. Strong reflections were obtained from the (0001) region when a beam of light was directed normal to the surface at this pole position, but in general the surface was not greatly roughened.

Oiliness agents.- When a crystal was alternately exposed to air and immersed in stearic acid at 100° for 24 hours, the weight loss was 0.1179 gram (1.81 g/sq dm) and the surface was etched preferentially

with the development of (0001) planes. Weak specular reflections were also obtained from several other minor planes. With the liquid at 200° and with the same method of immersion, the weight loss was 2.4295 grams (37.4 g/sq dm). The entire surface had a misty appearance and only very faint reflections were visible. When the crystal was suspended above the liquid, the film broke rapidly and settled in small drops on the surface. The drops oscillated vigorously on the surface in a manner similar to the behavior of stearic acid on lead, but it was impossible to identify any preferential arrangement.

When a crystal was alternately exposed to air and immersed in oleic acid at 200° for 24 hours, the weight loss was 2.001 grams (32.3 g/sq dm) and the appearance of the crystal was identical to that obtained with stearic acid. The crystal was completely wet by the liquid during the entire period.

Chemical polishing agents.– When a crystal was alternately exposed to air and immersed in tricresyl phosphate at 200° for 24 hours, a slight film first formed on the crystal and preferential etching took place later. The weight loss at the end of 24 hours was 0.0026 gram (0.043 g/sq dm).

Commercial oils.– With alternate exposure to air and immersion in new aviation oil at 200°, a faint and indistinct preferential color film formed. Faint reflections developed normal to the surface in the (0001) regions. The weight loss was 0.0004 gram (0.006 g/sq dm).

With alternate exposure to air and immersion in used aviation oil at 200° for 24 hours, preferential etching with the development of (0001) planes and the formation of a faint preferential lacquer took place. The weight loss was 0.0009 gram (0.013 g/sq dm).

Amines.– With alternate exposure to air and immersion in dodecylamine at 200° for 24 hours, a yellow film which could be partly wiped off with tissue formed. Preferential etching which developed the (0001) planes took place, and the weight loss was 0.0122 gram (0.204 g/sq dm).

Zinc

The zinc used had a listed purity of 99.99 percent zinc. The melting point of the pure metal is 419°.

Growth.- Since zinc single crystals shear very easily on machining, crystals in the form of a sphere, 5/8 inch in diameter with a shaft 5/16 inch in diameter by 1 inch in length extending from one side, were grown in a glass bulb. This was made by blowing a glass bulb of the desired size on the end of a 10-millimeter Pyrex tube, and sufficient metal was placed in the tube to form a shaft extending about 1 inch above the bulb. The tube was evacuated and sealed off from the pump after the metal had been melted and all possible air bubbles removed. The melt was lowered at the rate of about 1/2 inch per hour from the furnace maintained at a temperature of about 470°. At the time when the zinc crystals were grown, the practice, which was developed for tin, of attaching a small tip at the bottom of the bulb for the

development of a single nucleus, had not been adopted. Without the use of this tip only about one out of five attempts was successful. With very great care several spheres were also machined from a single crystal rod but growth in the spherical form as described was found to be preferable. The machining of zinc is similar in general to that of bismuth, described under RHOMBOHEDRAL STRUCTURE, except that greater care should be used and the cuts should be only about 0.003 inch deep.

Polishing.– The spheres were mechanically polished with emery papers numbers 1 to 0000, and paraffin in kerosene was used as a lubricant. They were electrolytically polished by the method of Vernon and Stroud (reference 8). The sphere was supported shaft upward by means of a number 18 B. & S. gauge zinc wire inserted through a hole in the shaft. The cell consisted of a 250-milliliter beaker containing a cylindrical zinc cathode. The solution was stirred vigorously to prevent pitting. Extremely bright surfaces were obtained at a current density of 50 amperes per square decimeter at a potential of 5 volts. A sharply defined electrolytic etch pattern showing the six-fold symmetry about the (0001) pole was visible at low current densities after the disturbed metal had been etched away.

Oxidation.– A definite interference color pattern formed within several hours and continued in intensity for 48 hours when a crystal was heated in air at 400°. The final pattern consisted of a yellow hexagon of about 9 milliliters in diameter located at the (0001) pole and yellowish-red circular regions of 5 millimeters in diameter located opposite each side of the hexagon and at positions 90° to the (0001) pole. Blue-green lines radiated from the corners of the hexagon, and a narrow purple border extended around the periphery of the yellow hexagon. It appeared that the region within the hexagon was one of low rate whereas the border surrounding the hexagon had a comparatively high rate. A photograph is shown as figure 6, but this does not do justice to the pattern except to show roughly the outline of the hexagon.

Mineral oil.– At 100° the weight loss with alternate immersion in an atmosphere of air was negligible after 24 hours. At 200° the weight loss with alternate immersion was negligible and with complete immersion it was very small (0.003 g/sq dm), but on being suspended immediately above the mineral oil the loss was quite appreciable, 0.0033 gram (0.033 g/sq dm) after 24 hours and 0.0127 gram (0.127 g/sq dm) after 48 hours. The crystal suspended above the liquid showed very pronounced corrosion and gave an etch pattern with specular reflections from (0001) facets when a beam of light was directed normal to the surface at that pole. It is interesting that the rate of attack by the volatile constituents of the oil in an atmosphere of air was greater than the attack with either alternate or complete immersion.

Oiliness agents.– Zinc was in general greatly attacked by stearic acid. At 100° very preferential etching occurred when a crystal was completely immersed below the liquid for 6 hours. Strong reflections were obtained when a beam of light was directed normal to the surface at the (0001) pole. A solid material gradually formed which when wiped off with tissue gave a striking figure with six-fold symmetry, as shown by figure 10.

Apparently the solid material was easily removed from the smooth regions but remained in the roughened regions with well-developed facets, showing up with a dull-gray color when examined within a paper tube. The weight loss in 6 hours was 0.0396 gram, which could be extrapolated to be 1.76 gram per square decimeter per day. At 200° a 12-gram sphere lost 0.5402 gram in 1 hour (7.72 g/sq dm). Faint reflections were obtained but the surface soon became covered with a solid material which was insoluble in any of the common organic solvents.

At 100° when a crystal was immersed below the level of oleic acid, an excellent pattern similar to that obtained in stearic acid developed in a few minutes. The pattern increased in intensity for 1 hour; then it rapidly became covered with a uniform dull-gray material which was probably zinc oleate and only slightly soluble in oleic acid. The weight loss in 24 hours was 0.1321 gram (1.65 g/sq dm). In an atmosphere of hydrogen purified by passage over hot copper the weight loss was reduced to about one-half of the loss in air but in all other respects the attack was similar to that in air. At 200° the attack with the crystal below the liquid was similar to that at 100°. The weight loss in 1 hour was 0.0552 gram or an extrapolated loss of 12 grams per square decimeter per day. A crystal suspended above the level of the liquid lost 0.1868 gram in 24 hours (1.55 g/sq dm). The attack was concentrated in the region nearest to the liquid and was preferential with face giving reflections from the (0001) and (1100) planes.

Chemical polishing agents.- In tricresyl phosphate at 100° a zinc crystal remained unaltered after exposure by alternate immersion in liquid and air for 24 hours. At 200° the surface became covered with a colored lacquer in several hours. Preferential etching with the development of (0001) planes then occurred. The weight loss in 24 hours was 0.0021 gram (0.0175 g/sq dm).

Commercial oils.- At 200° after 24 hours with both alternate immersion and suspension above new aviation oil the weight losses were negligible; with immersion below the liquid the loss was small, 0.0006 gram (0.004 g/sq dm), and very faint reflections were observed. At 300° below the level of the liquid for 24 hours the crystal became coated with a heavy black lacquer which was readily rubbed off; the result was a color pattern with six-fold symmetry about the (0001) pole. A weight-loss measurement in this case was meaningless since both etching and lacquer formation took place simultaneously. When a crystal was suspended above the liquid at 300° for 24 hours, definite preferential etching was visible and the weight loss was 0.0016 gram (0.013 g/sq dm).

At 100° after 24 hours with alternate immersion in used aviation oil a thin black film which was easily rubbed off formed without any change to the surface. At 200° after 24 hours with alternate immersion the weight loss was 0.0013 gram (0.013 g/sq dm); with complete immersion it was 0.0031 gram (0.028 g/sq dm); with suspension above the liquid it was 0.0025 gram (0.023 g/sq dm). The crystal heated by alternate immersion was covered with a black deposit which was easily wiped off from the entire surface. No reflections were obtained. The crystal immersed below

the liquid had a striking etch pattern with strong reflections having a six-fold symmetry at the (0001) pole.

Amines.– At 100° after alternate immersion in dodecylamine for 24 hours a crystal lost 0.005 gram (0.045 g/sq dm) and a preferential etch pattern with six-fold symmetry was obtained. At 200° after alternate immersion for 24 hours a crystal lost 0.0075 gram (0.048 g/sq dm) and a pattern similar to that obtained at 100° was formed. A crystal completely immersed first showed preferential etching but then became coated with an insoluble film. The weight loss was 0.0036 gram (0.033 g/sq dm). Since in these experiments the etching appeared to be rapid at the beginning of the experiment, it appeared that attack was limited by the formation of an insoluble film.

Electrodeposition.– Zinc was deposited on a zinc single crystal from a solution of 60 grams of zinc chloride, 84 grams of sodium cyanide, and 60 grams of sodium hydroxide per liter with a current density of 4 milliamperes per square decimeter. The deposition was preferential with plane for 8 to 10 hours as shown by preferential reflections from the (0001) and (1100) planes. These reflections appeared within 10 minutes of the start. After 10 hours the deposit became randomly oriented.

Evaporation.– A crystal was heated at 400° for $2\frac{1}{2}$ hours in a glass vessel evacuated by a Hyvac pump. Very powerful reflections were obtained when the light was directed normal to the surface at the (0001) pole, and weaker reflections were obtained from other regions when the light was directed normal to their surface. Figure 17 shows a photomicrograph of the surface at the (0001) pole. Condensation of zinc in a vacuum on the walls of a glass tube also resulted in the formation of globules showing well-developed faces.

RHOMBOHEDRAL STRUCTURE

Bismuth

The bismuth used had a listed purity of 99.8 percent bismuth. The melting point of the pure metal is 271°.

Growth.– Single crystals, about 1/2 inch in diameter by 4 inches in length and pointed at one end, were grown in an evacuated glass tube by the same method used for cadmium. The furnace was maintained at about 325°. Bismuth forms twin crystals very readily and a number of tries were required before a satisfactory crystal was obtained from which a sphere could be machined. When the crystal was removed from the glass tube, many slip lines which had formed on cooling could be seen on the surface. Attempts to grow a crystal in the spherical shape were unsuccessful.

Machining.– Although bismuth is quite soft, it is also remarkably brittle and easily broken. Spheres were machined with care from the single crystal rod by using a tool with a negative rake and taking cuts less than 0.004 inch.

Tools with a positive rake tend to dig in and break the crystal. Cutting oil is unnecessary. It was observed that machining produced patches on the surface which resembled etch-pits produced by preferential chemical action. Under the microscope the patches appeared as small pits having one side flat and the others rough. Apparently the flat side represented a preferred crystal plane from which small chunks had been sheared by the action of the tool. This effect indicates the common dependence of physical as well as chemical effects on crystal plane.

Polishing.- The spheres were machanically polished with emery papers numbers 0 to 000. Care was taken not to press the papers too tightly against the sphere in order not to shear the sphere from its shaft. It was necessary to develop a method of electrolytic polishing for bismuth. The electrolyte was a mixture of 940 milliliters of saturated potassium bromide solution and 60 milliliters of concentrated hydrochloric acid. The cell consisted of a cylindrical lead cathode and a glass stirrer in a 250-milliliter beaker. The crystal was supported shaft upward by means of a number 22 B. & S. gauge platinum wire which did not touch the liquid. Bright and smooth surfaces were obtained at a current density of approximately 100 amperes per square decimeter at a potential of 7 to 8 volts. Polishing began within several minutes. The brightest surface was obtained by removing the crystal from the cell without breaking the current. The crystal was washed in a solution of saturated potassium bromide solution in order to remove any bismuth oxychloride or oxybromide. A sharply defined etch pattern showing six-fold symmetry about the (0001) pole was visible at low current densities after all of the disturbed layer had been removed.

Oxidation.- When a crystal was heated in air at 230° for 18 hours, a pattern of specular reflections was obtained. When a beam of light was directed normal to the surface at the (0001) pole, reflections from three narrow bands running at 120° to each other and extending from the (0001) pole could be seen. Reflections from the center of a band were also obtained when the light was directed normal to the surface at a position 45° from the (0001) pole along the band. When the pattern was viewed within a cone of paper, the areas exhibiting these specular reflections had a dark-brown appearance.

Mineral oil.- When a crystal was alternately exposed to air and immersed in mineral oil at 200° for 24 hours, a pattern of specular reflections identical to that described in the foregoing section was obtained. The weight loss was very slight, 0.0002 gram (0.003 g/sq dm).

Oiliness agents.- When a crystal was alternately exposed to hydrogen and immersed in stearic acid at 200° for 24 hours, a very slight preferential etching took place and the weight loss was 0.0009 gram (0.018 g/sq dm).

On alternate immersion in stearic acid at 100° for 24 hours, deep pitting occurred on various parts of the surface, and the weight loss was 0.1633 gram (2.34 g/sq dm). Some of the pits were as deep as 1 millimeter and powerful reflections were obtained from the sides of the pits. At 200° no appreciable pitting was observed, and a striking etch pattern

similar to that obtained on oxidation developed in several minutes. Three arms making angles of 120° with each other radiated from the (0001) pole. These regions were very rough and the regions between the arms were moderately rough but exhibited no specular reflections. A triangle around the (0001) pole was very smooth. The loss in weight in 24 hours was 1.555 grams (33.8 g/sq dm). When the crystal was suspended above the level of the liquid, the film broke slowly, moved over the surface, and then became very viscous. No preferential wetting could be detected. In an atmosphere of hydrogen the surface remained completely wet.

Commercial oils.– After alternate exposure to air and immersion in new aviation oil at 200° for 24 hours, a slight nonpreferential tan color formed on the surface, and no weight loss was detectable.

After alternate exposure to air and immersion in used aviation oil at 200° for 24 hours, definite preferential etching occurred and the weight loss was 0.0004 gram (0.005 g/sq dm).

BODY-CENTERED TETRAGONAL STRUCTURE

Tin

The tin used had a listed purity of 99.97 percent tin. The melting point of the pure metal is 232°.

Growth.– Single crystals were grown both directly in the spherical form and also in rods which were machined with care into spheres. Because of the ease with which the mechanically strained crystals recrystallized on heating, the former method was preferable. The method previously described for growing zinc crystals in the spherical form was used with the addition of a small tip sealed onto the bottom of the bulb to promote the formation of a single nucleus. This tip was subsequently cut from the crystal. Considerable care was required in sealing one of these small tips to the glass bulb without destroying its spherical shape over a considerable portion of the surface. Etching experiments are greatly facilitated by the spherical shape. In growing the crystals in both rod and spherical form the melt was lowered from the furnace at the rate of about 1/2 inch per hour. The temperature of the furnace was about 280°.

Machining.– In contrast with bismuth, which exhibited a tendency to be torn off in small chunks or flakes so that a rough surface with small pits remained, tin appeared to be plastically smeared over the surface so that an amorphous layer with a high polish and smooth surface resulted. The metal flowed off in a continuous strip with the tools used. In order to remove the chip without pushing it ahead of the tool and smearing it on the surface, an extreme positive rake and sharp edge were ground on the tool. Carbon steel is preferable and the tool is not stoned after grinding on a fine wheel. The rake angles are best obtained by grinding a groove along the top face of the tool parallel to the cutting edge. This groove becomes the cutting edge and the chips come off in a

helix due to the curvature of the edge. The clearance angle was about 8°; smaller angles caused the tool to rub against the work and produce excessive distortion. The tool should have only a small nose radius, and the lathe should be operated at a fairly high speed with a very slow feed of the tool into the work. No cutting oil was necessary.

Polishing.– The spheres were mechanically polished with emery papers numbers 1 to 0000 and paraffin dissolved in kerosene was used as a lubricant. The lubricant reduced heating and distortion of the metal surface. Spotted and very inferior surfaces were obtained by the electrolytic polishing method of Jacquet (reference 9). Fair surfaces were obtained in 35-weight-percent sulphuric acid at a current density of 13 amperes per square decimeter and a potential of 30 volts. The cell consisted of a 250-milliliter beaker with cylindrical aluminum cathode and glass stirrer. The sphere was supported shaft upward by means of a strip of tin foil inserted through a hole in the shaft. At the polishing point a thick tan film appeared on the anode surface. The anode was removed from the electrolyte without breaking the current, and the film was washed off by swabbing with a piece of absorbent cotton held beneath a stream of water.

Oxidation.– No conditions could be found under which a tin crystal would give a definite interference color pattern when heated in air. When a crystal was heated at 210° in air, interference colors developed in 24 hours or longer but no definite pattern was obtained. In several experiments the (100) regions had the most advanced colors, or greatest rates, but the results could not always be duplicated.

Mineral oil.– At 100° after alternate immersion in mineral oil for 24 hours, a crystal remained very bright and unattacked. At 200° for 24 hours the losses were: for alternate immersion, 0.0006 gram (0.008 g/sq dm); for suspension above liquid, negligible; and for complete immersion, 0.0004 gram (0.006 g/sq dm). Moderately strong reflections were obtained from the (100) regions when a beam of light was directed normal to the (100) poles in the cases in which weight losses were incurred.

Oiliness agents.– At 100° after alternate immersion in stearic acid for 24 hours, a crystal lost 0.0437 gram (0.49 g/sq dm), and preferential etching occurred within about 30 minutes after the experiment was begun. At 200° with alternate immersion an etch pattern of smooth and rough areas formed at the beginning but became less distinct with time except for strong specular reflections from the (100) regions. At the end of 24 hours the weight loss was very great, 3.0058 grams (35.4 g/sq dm). When this experiment was carried out in an atmosphere of hydrogen purified by passage over hot copper, the crystal lost 0.0910 gram (1.25 g/sq dm), and an etch pattern with striking specular reflections was obtained.

At 100° with alternate immersion in oleic acid a distinct pattern formed in 2 hours. When a beam of light was directed normal to the (100) region, striking reflections which increased in intensity until the completion of the experiment in 24 hours were obtained. The weight loss was 0.0108 gram (0.123 g/sq dm).

Chemical polishing agents.– When a crystal was alternately immersed in tricresyl phosphate at 100° for 24 hours, a faint mistiness appeared on the surface and the weight loss was negligible.

Commercial oils.– At 100° with alternate immersion in new aviation oil for 24 hours no weight loss was detectable. At 200° with alternate immersion interference colors formed within 16 hours and at 24 hours a pattern was obtained but the active regions could not be identified. The weight losses under the following conditions were small: for alternate immersion, 0.0002 gram (0.003 g/sq dm); for immersion below liquid, 0.0002 gram (0.003 g/sq dm); and for suspension above liquid, 0.0006 gram (0.008 g/sq dm). The latter crystal gave strong specular reflections from (100) regions.

At 100° with alternate immersion in used aviation oil the loss was negligible after 24 hours. At 200° with alternate immersion a pattern of specular reflections developed soon after starting. A lacquer formed on the surface preferentially but the active regions could not be identified. The weight loss in 24 hours was 0.0012 gram (0.012 g/sq dm).

FACE-CENTERED TETRAGONAL STRUCTURE

Indium

The indium used had a listed purity of 99.9 percent indium. The melting point of the pure metal is 156°.

Growth.– Since indium is too soft and ductile to be machined and recrystallizes under a slight amount of mechanical strain, single crystals in the form of a sphere 5/8 inch in diameter with a shaft 5/16 inch in diameter by 1 inch in length were grown in glass bulbs by the same method used for zinc. The furnace was maintained at about 200°. Care was required in removing the crystal from the glass bulb. The bulb was cracked by lightly tapping with a small hammer, and fragments of glass were carefully removed with the aid of the finger nail. Small crystals grew wherever the surface was scratched, and a cluster of minute crystals could be seen at the point where the bulb was struck with the hammer. The fact that the sphere was a single crystal could be determined by the pattern formed on etching with concentrated hydrochloric acid or by alternate etching in hydrochloric acid and dilute nitric acid.

Polishing.– Indium cannot be mechanically polished at room temperature without recrystallizing. A fairly bright but none too smooth surface was obtained by agitating the crystal for several seconds in concentrated nitric acid.

Etching.– Alternate exposure to air and immersion in liquid at 100° for 24 hours caused no change in the surface or detectable weight loss

with the following liquids: mineral oil, stearic acid, oleic acid, tricresyl phosphate, new aviation oil, used aviation oil, and dodecylamine. The crystal remained completely wetted in all the oils.

ELECTRODEPOSITION ON A SINGLE CRYSTAL OF COPPER

Copper on Copper

Experiments have been previously carried out in this laboratory on the deposition of copper on a single crystal of copper. They will be briefly described to serve as a starting point in considering the deposition of various metals on a crystal of copper. The electrolyte consisted of 200 grams of hydrous copper sulphate and 48 grams of sulphuric acid per liter of solution. The copper crystal was placed in the center of a hollow copper sphere about 6 inches in diameter, which served as cathode in order that the spacing between electrodes would be the same over the entire surface of the crystal. At a low current density of 0.2 ampere per square decimeter after 450 hours, the spherical crystal had been converted to a polyhedron. A plane surface, about 5 millimeters in diameter, had formed at each of the (111) poles. These flat surfaces were connected by striking step-like bands consisting of facets parallel to (111) planes. Four roughly flat surfaces approximately parallel to the (210) planes formed adjacent to each (100) pole. Directly at the (100) pole the surface was rough. At 2 amperes per square decimeter after 5 hours with a new crystal, the deposit at the (111) region was still single-crystalline and had followed the orientation of the underlying crystal sphere. In the other regions the deposit had become polycrystalline with random orientation. At a current density of 8 amperes per square decimeter the entire surface became covered with small randomly oriented crystals within 15 minutes.

Lead on Copper

Lead was deposited on a single crystal of copper at a current density of 0.2 ampere per square decimeter from a solution of 60 grams of lead acetate and 200 grams of sodium hydroxide per liter. At the beginning the lead deposited exclusively in the (111) areas and slowly spread toward the (100) and (110) poles. In 3 hours weak reflections could be seen from the (111) areas when light was directed normal to the surface at these positions. The pattern after 17 hours was almost identical with that formed at the beginning, the deposit being concentrated in the (111) regions with a slight deposit in the (110) areas. Under the microscope the deposit appeared compact and continuous in the (111) areas, whereas large openings in the deposit exposing bare copper could be seen in the other areas. At a current density of 2 amperes per square decimeter small crystallites appeared over the entire surface, exhibiting strong reflections when light was directed normal to the surface at the (100) pole.

Nickel on Copper

Similar results were obtained when nickel was deposited on copper from two different solutions: one, 120 grams of nickel sulphate, 22.4 grams of ammonium chloride, and 30 grams of boric acid per liter with the hydrogen-ion concentration adjusted to 6 with ammonium hydroxide; and the other, 2.75 grams of nickel chloride with 6 molecules of water per molecule of nickel chloride and 30 grams of boric acid. At current densities of 0.1 to 10 amperes per square decimeter the deposit at first formed exclusively on large triangular regions at the (111) poles and then spread rapidly until the corners of neighboring triangles touched at the (110) pole positions. Little or no deposit formed at large circular regions at the (100) poles. When light was directed normal to the surface at the (311) pole, reflections were obtained from small regions between the (311) and (100) poles. These reflections decreased in brilliance and finally disappeared completely, the final deposit exhibiting no reflections.

Cadmium on Copper

Cadmium was deposited on a single crystal of copper at a current density of 2.5 amperes per square decimeter from a bath consisting of 26 grams of cadmium oxide and 109 grams of sodium cyanide per liter of solution. In 5 minutes specular reflections were obtained from a circular band around the (111) pole, and in 10 additional minutes the deposit grew toward the center until specular reflections were obtained from a hexagonal-shaped area the center of which was located at the (111) pole. When light was directed normal to the surface at the (100) pole, specular reflections were obtained from a cross located at this pole with each arm of the cross directed toward a (111) pole. After 17 hours when the light was directed normal to the surface at a (111) pole, reflections were obtained from a hexagonal-shaped area at that pole and from the three similarly shaped (111) areas adjacent to the first (111) pole. When a light was directed normal to the surface at the (100) pole, reflections were obtained from a small cross located at this pole and from the four rectangular (110) areas adjacent to this (100) pole. When the deposit was etched in concentrated hydrochloric acid, the pattern of specular reflections remained until all the cadmium was dissolved.

Zinc on Copper

Zinc was deposited on a copper crystal at a current density of 1 ampere per square decimeter from a solution of 24 grams of zinc chloride, 34 grams of sodium cyanide, and 20 grams of sodium hydroxide per liter. The anode consisted of a cylindrical sheet of zinc placed on the periphery of a 150-milliliter beaker. A uniform gray color appeared on the copper surface immediately, and within 1 minute a pattern could be seen consisting of a circular band 1 millimeter in diameter around the (100) pole, a four-leaf clover at the (100) pole, very narrow sharply defined lines connecting neighboring (100) pole, and foggy areas at the (210) pole. After 2 minutes

when a beam of light was directed normal to the surface at the (111) pole, strong specular reflections could be seen from areas of an approximately triangular shape located at these positions. After 30 minutes a striking pattern was obtained consisting of specular reflections from a square at the (100) pole; from one leaf of the four-leaf-clover pattern located at the (100) pole when a beam of light was directed normal to the surface at the (311) pole; and from a triangular area at the (111) pole when a beam of light was directed normal to the surface at this pole, the strongest reflections coming from six equally spaced lines radiating from the (111) pole to the boundary of the triangular area. The regions of specular reflection were very sharply defined, the boundary between two regions having the appearance of a grain boundary.

Indium on Copper

Indium was deposited on a copper crystal at a current density of 0.2 ampere per square decimeter from an electrolyte consisting of 18 grams of indium as indium chloride, 30 grams of dextrose, 160 grams of potassium cyanide, and 40 grams of potassium hydroxide per liter of solution. The anode consisted of a carbon rod about 1 inch in diameter, and the liquid was stirred at a moderate speed. The indium deposited preferentially, going first on each of the (111) regions and on two of the six (100) regions. The deposit slowly formed over the entire surface, and specular reflections developed in the (111) and (100) areas. At a current density of 2 amperes per square decimeter the deposit formed over the entire surface, and within 5 minutes reflections were obtained from the (111) and (100) regions when a beam of light was directed normal to the surface at these poles. These reflections were obtained until the end of the experiment in 2 hours.

ELECTRODEPOSITION ON A SINGLE CRYSTAL OF LEAD

Indium on Lead

Indium showed a strong tendency to form oriented deposits. Indium was deposited on lead at current densities ranging from 1.6 amperes to 150 amperes per square decimeter from the same solution as used in the aforementioned experiment. At low current densities indium plates initially on the (100) and (111) regions. At current densities as high as 150 amperes per square decimeter specular reflections were obtained from the (100) and the (111) regions when a beam of light was directed normal to the surface at these positions. At a current density of 30 to 35 amperes per square decimeter, gaseous evolution occurred. At 1.6 amperes per square decimeter powerful reflections were obtained from the (100) and (111) regions when a beam of light was directed normal to the surface at these positions. (See fig. 16.) The reflecting areas spread until after 2 hours reflections were obtained from (100) and (111) planes over entire hemispheres. The current density was then raised to 30 amperes per square decimeter and the entire surface became covered with a heavy milky deposit. No reflections were obtained from the surface. When the current density was decreased to 10 amperes per square decimeter and the crystal was agitated below the level of the liquid, the white film readily scaled off and reflections again developed in the (100) and (111) regions. Similar results were

obtained several times when the current density was varied between 10 and 30 amperes per square decimeter.

ELECTRODEPOSITION ON A SINGLE CRYSTAL OF SILVER

Copper on Silver

Copper was deposited on a single crystal of silver at a current density of 2.5 amperes per square decimeter from a solution of 210 grams of hydrous copper sulphate and 30 grams of sulphuric acid per liter. The copper deposited over the entire surface but soon developed specular reflections from the (111) and (100) regions when a beam of light was directed normal to the surface at these pole positions. After 4 days the entire surface appeared to be a single crystal. Reflections were still obtained from the (111) and (100) regions, and the shape of the crystal was approaching a polyhedron as formerly obtained when copper was deposited on a crystal of copper. After slight mechanical and electrolytic polishing, the crystal was alternately exposed to air and immersed in stearic acid at 200° for 17 hours. A perfect stearic acid etch pattern appeared in several hours and preferential wetting of the (110) regions was noted at the end of 17 hours, this result confirming the single-crystal nature of copper deposit.

Nickel on Silver

Nickel was deposited on a single crystal of silver at a current density of 2.5 amperes per square decimeter from a solution of 120 grams of nickel sulphate, 22.4 grams of ammonium chloride, and 30 grams of boric acid per liter. The nickel appeared to deposit exclusively on the (111) regions. After 1 hour specular reflections were obtained from the (311) area but soon disappeared, and the entire surface had a matte appearance with only slight evidence of any preferential deposit. Gas bubbles adhered to and badly pitted the surface. The electroplating of nickel onto copper and that on silver crystals were quite similar.

Lead on Silver

Lead was deposited on silver at current densities up to 2 amperes per square decimeter from a solution of 70 grams of lead acetate and 200 grams of sodium hydroxide per liter. The lead deposited in tiny crystallites randomly scattered over the surface. Occasionally reflections developed normal to the surface in the (111), (100), and (311) regions. The deposits near the pole positions, as judged by rubbing with tissue, were more adherent than deposits in other regions where no reflections were obtained.

ELECTROLYTIC REPLACEMENT OF COPPER BY OTHER METALS FROM A SOLUTION OF COPPER STEARATE IN STEARIC ACID

When strips of bismuth, cadmium, cobalt, iron, nickel, tin, and zinc were heated at 200° for about 3 hours in old stearic acid in which a copper crystal had been previously heated for about 24 hours, a red film of copper deposited on the strips. Copper failed to deposit on specimens of aluminum and chromium, metals which are conspicuous for their passivity.

DISCUSSION

With one or two exceptions, such as the oxidation of chromium, all reactions which were studied, if they took place at all, were found to vary in rate with crystal plane. This variation in rate means that one metal cannot be thought of as possessing one surface property with respect to a particular process but must be thought of as having a number of properties, one for each important plane, for any one process under any one set of conditions. This in effect is equivalent to multiplying greatly the number of metals at our disposal. At first thought it appears that this discovery would complicate surface processes and render more difficult than ever a complete understanding of surface events, but actually it simplifies the problem in specifying what the complications are and in offering a new point of view for future study. The existence of these variations with crystal plane explains in part the difficulty of interpreting results with polycrystalline surfaces.

There are several factors which may mask the effect of this variation in rate with plane. The formation of an insoluble protective film may do this, and, in the case of rapid reactions with strong reagents, the peaks which tend to form because of preferential action will be etched away because of rapid diffusion of the reaction products, whereas reaction in the valleys will be much slower because of a low rate of diffusion. This tends to keep the surface smooth, as in the case of electrolytic polishing and chemical polishing with some concentrated acids.

The metals used in these experiments may in general be considered of high purity although they are in no sense spectroscopically pure. The reactivities of commercial metals will not necessarily be the same as those used in this study, but it is believed that the results obtained give a fair picture of the relative properties of metals as ordinarily used. Impure metals will probably have a greater reactivity than pure ones. In order to reduce greatly the number of experiments, most of them were carried out at 200° only. This was found to give the essential information. At 100° similar results were obtained at a reduced rate and at 300° the oils rapidly oxidized and decomposed.

PRESENT THEORY OF INFLUENCE OF CRYSTAL PLANE ON SURFACE REACTIONS AND ATTEMPTS TO CLASSIFY RESULTS

No two reaction patterns are alike, and hence it cannot be expected that any simple explanation or correlation of the results will be possible. In fact the various patterns are as individualistic as finger prints, and, if conditions were accurately controlled, the patterns formed might be used as a means of identifying a particular reaction. In spite of the individuality of each pattern, however, in the case of oxidation, the simplest of the processes studied, there are certain similarities among the patterns. Before discussing them, the energy relations between the various faces should be considered.

Since the arrangement of atoms in a surface varies with the crystal plane, the free energy of a solid surface in a vacuum should vary with plane. The free energy of a surface should also depend on the medium in which it exists. A few calculations have been made of the free surface energy of ionic crystals (references 10 and 11) and of tungsten (reference 12). (The surface energies of the different faces of tungsten given are relative values.) The magnitude of the surface energy was found to depend strongly on the crystal plane exposed, the ratio of the energies between two faces being in some cases as high as a factor of five. Since the surface energy varies with plane, the surface-energy changes during reaction would be expected to vary with plane. Attempts have been made to determine experimentally the free energy of a solid surface by measuring the surface tension, but all methods of experiments so far used are open to criticism (reference 13). Contact potentials have been found experimentally to vary with face (reference 14), but there is uncertainty in the exact nature of the surface in such measurements.

In many cases the time required to establish equilibrium is so long that the form having the lowest energy is not reached in practice, and the energy of activation must be considered. There are few theoretical calculations of the energy of activation for surface processes. In the adsorption of hydrogen on nickel the energy of activation has been shown mathematically to be a minimum for the (110) plane (references 15 and 16) and therefore the rate of adsorption should be greatest on this plane. In agreement it has been found experimentally that the rate of the catalytic reaction between hydrogen and ethylene on nickel films is greatest when the (110) plane of nickel is parallel to the surface (reference 17). Thus from meager calculations of energy relationships it is to be expected that the free-energy change, which determines the equilibrium, and the energy of activation, which determines the rate, will vary with crystal plane.

In the case of oxidation of a metal surface there are no theoretical treatments available of the energy of activation for adsorption of oxygen on definite crystal planes. Furthermore, adsorption is only the preliminary and not necessarily the controlling step. Diffusion becomes the limiting step as the thickness of the oxide layer increases, and in most cases of

oxidation the metal is thought to diffuse outward through the oxide layer (reference 18). Since in quantum-mechanical treatments of chemical reactions the internuclear distance between atoms is taken into consideration, it seems reasonable, as in the case of adsorption of hydrogen or nickel, that the adsorption of oxygen on a metal surface and the subsequent processes of diffusion would vary, the variation depending on the orientation of the crystal. But no theoretical information is yet available to indicate on a quantitative basis the planes and the directions that might be expected to be the most favorable. Because of lack of specific information on this subject, some simpler basis of interpreting the results must be used.

During the initial stages of oxidation it might be expected, as a first approximation, that the planes having the greatest density of atoms, or the least residual affinity, would be the least reactive. In copper the planes with the greatest density are, in decreasing order: (111), (100), (110), (311), (331), (210), and so forth. Those at the beginning of the list would be expected to be the least reactive and those near the end the more reactive. The relative rates of oxidation in air at 200° and atmospheric pressure as determined in these studies, the face at the beginning of the list having the lowest rate and that at the end the highest, were: (311) regions, (110) regions, (111) regions, boundary lines between (311) and (110) regions, boundary lines between two (311) regions, (210) regions, and (100) regions. By omitting the (100) which is completely out of order, a very rough agreement is obtained in this case with copper. The arrangement of the atoms in the surface, as well as the number per unit area, probably plays an important part in controlling the rate of reaction. In reference to physical properties, it is interesting that slip actually takes place along the plane of greatest density which has the least affinity between planes.

Thus no theoretical studies have been made which will enable us to predict the relative rates of oxidation on the various planes, and simple energy concepts based on the spacing of the atoms are of little value. A more successful basis for correlating the results of oxidation has been the physical structure in which the metals crystallize. The face-centered cubic metals should be divided into two groups, those the oxides of which can be readily reduced by heating the metals below their melting points in hydrogen and those the oxides of which cannot be so reduced. It is interesting that the metals of the first type, copper and nickel, give very sharply defined patterns of the same general type, as shown by figures 1 and 2, respectively. In order to obtain visible color films, it was necessary to heat the metals in air at different temperatures, and this would account for slight differences in the patterns. In the case of aluminum and lead, protective oxides of which cannot readily be removed, the patterns were not sharply defined but resembled those of copper and nickel in one respect. The cube faces appeared to be the most active, although the identification of the active regions is not always certain on surfaces which form protective oxide films. No interference colors were obtained on aluminum, the pattern consisting of some bright and some

dull regions. The other metals of the face-centered cubic system, silver and gold, were unreactive with oxygen.

In the body-centered cubic class, crystals of chromium and iron were studied. Iron gave a sharply defined and complicated pattern which was very different from the general type obtained on the face-centered metals, with the exception that the (100) face had a high rate. When chromium was heated in air at 400°, color films with no definite pattern were obtained, this result indicating that under the conditions the rate did not vary with plane. No completely satisfactory explanation has been found for the facts that chromium gave no pattern and other metals, oxides of which cannot readily be reduced below the melting point, gave only relatively indistinct patterns, as compared with metals, oxides of which can be reduced. It is known that these oxides which cannot be readily reduced are in general protective and therefore the diffusion through them is slow, but it is difficult to see how this could account for the failure to react preferentially with plane, unless diffusion were the limiting factor. But even in this case it would be expected that diffusion would vary with plane. The chromium used was only 98.5 percent chromium.

In the case of two metals, cadmium and zinc, with the hexagonal close-packed lattice, sharply defined patterns were not obtained, but the general hexagonal shape of each can be seen in figures 5 and 6. The regions of high and low activity are also the same, the (0001) plane which has the greatest density having the lowest rate. Each of the other metals studied, bismuth, tin, and indium, have different lattice spacings, and therefore their oxide patterns cannot be compared with those of cadmium and zinc.

Although this classification of patterns, or relative rates of oxidation, according to lattice spacing has not been perfect, it has been about as successful as would be expected. Such a classification simply means that there are structural factors which relate the relative rates for the different faces on any one crystal system. For example, the rate of oxidation of metals with the same lattice spacing, under a given set of conditions as regards temperature and pressure, may be expressed as being proportional to two sets of constants R which is characteristic of the process and f which is characteristic of the face or atomic arrangement. Thus, for copper,

Rate of formation $Cu_2O_{(100)}$ is proportional to $R_{(Cu_2O)} \times f_{(100)}$

Rate of formation $Cu_2O_{(111)}$ is proportional to $R_{(Cu_2O)} \times f_{(111)}$

For nickel,
Rate of formation $NiO_{(100)}$ is proportional to $R_{(NiO)} \times f_{(100)}$

Rate of formation $NiO_{(111)}$ is proportional to $R_{(NiO)} \times f_{(111)}$

Thus the factors $f_{(100)}$ and $f_{(111)}$ are roughly the same for copper and nickel. Another set of factors should be the same for cadmium and zinc. This suggestion should be considered as preliminary and must be

confirmed by further study. There are also other influences which may account for the similarity between copper and nickel and between cadmium and zinc. The lattice constants for copper and nickel are approximately the same, 3.60 and 3.51 A, respectively. The atomic diameters are 2.55 and 2.49, respectively, and the ratios of volume of oxide to volume of metal are 1.71 and 1.64, respectively. The lattice constants for aluminum and lead, on the other hand, are 4.04 and 4.94 A, respectively. The c/a ratios (ratio of lattice constants) for cadmium and zinc are very close, being 1.88 and 1.85, respectively. Unquestionably all these factors, as well as many others, play some part in the oxidation process, but an approach to an understanding of the mechanism of oxidation through a study of the atomic spacing in the surface offers interesting possibilities.

The possibility that the interference colors might be caused by an unequal expansion of the oxide film forming on the sphere was considered, but it is not believed that an effect of the magnitude obtained could be produced by any such process. Furthermore, the same colors were obtained on large flat surfaces filed on a sphere of copper as were obtained on the corresponding small curved areas on the surface of the sphere. The relative thicknesses of the films on copper as determined by the interference colors were checked approximately by the quantity of electricity required to reduce the oxide films electrolytically by using a drop of ammonium chloride as the electrolyte.

An explanation of passivity of ferrous alloys has recently been given by Uhlig (reference 19) in terms of electron configuration of the metal. It is concerned especially with the transition elements, chromium, iron, nickel, cobalt, molybdenum, and tungsten, which contain incompleted electron shells. For example, iron alloyed with chromium becomes passive by sharing electrons with chromium. Since there are five vacancies in the third shell for chromium and the sharing of one extra electron per iron atom renders iron passive, one chromium atom is able to share five electrons and can, therefore, passivate five iron atoms. This corresponds to an atomic ratio of chromium to iron of 1:5 or 15.7 percent of chromium by weight. In practice 12 percent of chromium is found to be necessary to passivate iron. Iron may become passive either by alloying or by surface adsorption. In the case of oxygen adsorbed on iron, the iron shares two electrons with oxygen and therefore becomes less reactive. A distinction is drawn between chemical passivity resulting from this sharing of electrons and mechanical passivity due to a layer of oxide or other material which protects the surface by limiting the accessibility of the underlying metal to the corrosive gas or liquid. This distinction does not seem necessary since both effects must be different manifestations of the altered activity of the metal atoms, but at least a mechanically protective layer is not necessarily required for passivity. The significant point for this discussion is that a kind of "Law of Definite Proportions" in terms of electron configuration is established for surface passivity of alloys. Hume-Rothery (reference 20) has also established an "Electron-Atom Rule" for the formation of phases in substitutional alloys. These concepts suggest that surface reactions might be explained, in part at least, by a consideration of electron configuration. If so, the question must be asked as to what is the influence of crystal plane on electron configuration. If an oxide forms

on a metal surface, the number and location of atoms of oxygen which surround a metal atom in the surface will vary with plane, and hence the spatial possibilities whereby two different atoms on a surface can share electrons will vary with plane. Even in the case of a gas adsorbed on a metal, the low-voltage electron diffraction experiments of Davisson and Germer (reference 21) with a single crystal of nickel indicated that the adsorbed atoms occupied definite and restricted positions on the surface lattice. The adsorbed gas seemed to have a kind of crystal structure, the adsorbed particles occupying every other open space in a (111) face of nickel.

Thus in the case of the formation on the surface of either an adsorbed layer or a definite chemical compound, the variation in chemical activity with plane might be explained by the variation in the possibilities for sharing electrons. In a sense this is equivalent to the statement that the chemical activity varies with plane, but it opens up a different point of view. If the spatial arrangements of atoms on the various faces for possible surface compounds can be determined experimentally and the possibilities for electron sharing arrived at in a manner somewhat analogous to the rules suggested by Uhlig for surface passivity and by Hume-Rothery for substitutional alloys, it might be possible to predict in advance those faces which would be most reactive for simple surface reactions. A kind of Law of Definite Proportions for simple surface reactions based on sharing of electrons on different faces, especially for the transition metals, might be found. Furthermore the electrochemical series lists the metals in decreasing tendency to lose electrons and indicates in general the manner in which elements replace one another from solution. It is interesting that in these studies the electrochemical replacement of one metal by another in aqueous solution was found to vary greatly with plane, as shown by figures 14 and 15; this result indicates that the tendency to gain or lose electrons varies with plane. It seems reasonable that the tendency to share electrons would also vary with plane.

Sufficient information on the spatial relationships in oxide films has not been obtained at the present time to test the possibilities for electron sharing on various crystal faces. The following information is required. The type of oxide formed on the various faces must be determined. For example, in the case of copper it must be determined whether the oxide is cuprous or cupric. The former is thought to form in thin films. The orientation of the oxide with respect to the underlying copper lattice must be determined for the different faces. Then the rates of formation of the oxide on the different faces must be determined quantitatively. At this point, when mention is made of the importance of electron configuration in surface processes, the need for a fundamental study of the electrochemical properties of single crystals in general should be emphasized. It is probable that all chemical reactions are dependent on the electrochemical properties of the individual crystals.

In the corrosion of metal surfaces by lubricating oils, oxidation is a controlling process, and this question of the orientation of the oxide with respect to the underlying lattice is of the greatest importance. In spite of the fact that oxygen accelerates greatly the attack by liquids,

the plane of greatest rate of oxidation is not necessarily the plane most rapidly attacked by liquid. Furthermore a (111) plane may be developed in a (100) region and not in a (111) region; this indicates the necessity for a certain critical angle between the geometrical surface and a particular plane. This emphasizes the importance of studying surface reactions from the viewpoint of the orientation of the metal surface, the orientation of the oxide formed on the surface with respect to the underlying metal lattice, and the orientation of the reacting liquid molecule with respect to the oxide. The single crystal method of study with the aid of electron diffraction offers special opportunities for such studies. (A further analysis of anisotropic oxidation of metallic single crystals is given in the appendix.)

In attempting to classify etching results according to lattice spacing, only a few statements can be made. In the case of etching by stearic acid, copper and nickel, two metals of the face-centered cubic lattice, had patterns which were in general similar, as can be seen in figures 8 and 9, respectively. Other metals of this lattice could not be compared since aluminum, gold, and silver were largely unreactive and lead was greatly etched, but the reaction was not very preferential with plane. In the case of iron and chromium, which have the body-centered cubic lattice and are known to become passive under certain conditions, the attack by acids was not uniform and pitting occurred on iron. With cadmium and zinc, of hexagonal close-packed lattice, the (0001) planes which have the greatest density were generally developed on etching.

In general the rate of reaction of the following metals, if reaction took place at all, varied markedly with plane: aluminum, copper, gold, nickel, silver, iron, zinc, and bismuth. The rates of the following metals varied only slightly with plane: lead, chromium, cadmium, tin, and indium.

The following general statements can be made about the etching properties of the metals. With the exception of iron, all metals which were appreciably attacked by stearic acid were also attacked by used aviation oil. The metals such as copper, iron, and bismuth which formed thick oxide films in short intervals of time in air at 200° formed heavy adherent lacquers in used aviation oil and air at this temperature. All metals investigated showed greatly reduced weight losses in stearic acid in an atmosphere of hydrogen as compared with etching at 200° in an atmosphere of air. The etching of an aluminum crystal generally inert in stearic acid at 200° was greatly accelerated by contact with the electropositive metal bismuth.

In attempting to classify the results of wetting by stearic acid at 200°, a few general conclusions may be drawn: (1) Wetting on special crystal faces only occurred with copper, nickel, and iron, three metals the rates of oxidation in air of which vary greatly with plane. These metals are attacked by the acid at a moderate rate. Although roughness of the surface can undoubtedly influence wetting, it did not appear to be the controlling factor in these results. With nickel and iron the drops adhered to the (111) regions the roughness of which was very slight and apparently of the same degree as that on the remaining surface. With copper after etching

for a considerably long time, the drops adhered to the (110) regions which were strikingly rougher than the other regions, but when a freshly polished crystal was placed in old acid in an atmosphere of air, the drops formed at (111) regions which were smooth. These three crystals remained completely wet in an atmosphere of hydrogen, this fact indicating again the importance of oxidation. (2) Complete wetting on all faces occurred with aluminum, chromium, gold, silver, tin, and indium, metals which are not appreciably attacked by the acid and which are either not oxidized or form a thin protective oxide film. (3) No wetting but formation of irregular unstable drops occurred with lead and cadmium, which are greatly attacked by acid but oxidation patterns of which are not very distinct. Zinc and bismuth rapidly formed viscous reaction products which prevented movement of the liquid. (4) All the metals remained completely wet in an atmosphere of hydrogen. The significance of these results on wetting will be discussed further under IMPORTANCE OF RESULTS TO PRACTICAL PROBLEMS OF LUBRICATION, FRICTION, AND WEAR.

Electroplating is conspicuous for the addition agents, intermediate deposits, and special conditions which are required for adherent deposits of the proper physical texture. The fitting of the depositing atom into the proper lattice is a very important factor in controlling the nature of the deposit. In hopes of obtaining information on the effect of lattice structure on the deposition of one metal on another, especially in connection with the manufacture of bearings and cylinder walls in engines, a few experiments were conducted on the deposition of one metal on a single crystal of another. A large amount of information can be obtained from the patterns produced on single crystals, although electron diffraction measurements would give much additional information. In attempting to interpret the results, emphasis is placed on the atomic spacings of the two metals. The results of several experiments involving important metals will be considered.

In the case of depositing lead on a single crystal of copper, the deposit was conspicuous for its tendency to form isolated crystallites. Large bare spots of copper could be seen in many areas. This may be explained by the fact that the lattice constants a for copper and lead are 3.61 A and 4.94 A, respectively. In order for the lead to fit onto the copper lattice, the lattice of the lead would be distorted 27 percent. This would certainly serve as a barrier to the formation of a dense deposit of lead.

In the case of depositing zinc on copper, it appeared from the reflections obtained that the zinc followed the orientation of the underlying copper in each octant. This may be explained as follows. Each atom on a (111) plane of a face-centered cubic lattice has six neighbors equally removed by 2.55 A. Each atom on the (0001) basal hexagonal plane of zinc has six neighbors equally removed by 2.66 A. Thus a layer of zinc atoms with the structure of the basal hexagonal plane could fit onto the (111) plane of copper with a distortion of only 4 percent. If zinc were deposited on the (100) plane of copper, with the c-axis of zinc oriented parallel to the cube-face diagonals of copper, a distortion of 3.2 percent in the lattice constant c and 4 percent in the lattice constant a would result.

With the same reasoning cadmium would be distorted 16 percent on the (111) plane of copper, 10 percent in the c-lattice distance, and 16 percent in the a-lattice distance on the (100) plane of copper.

Electrodeposited indium exhibited a great tendency to be oriented on single crystals of lead. Face-centered tetragonal indium is only slightly distorted from a face-centered cubic structure, the lattice constants being for a, 4.58 A and for c, 4.94 A. The lattice constant a of lead is 4.94 A. Since the interatomic distances of lead and indium are so nearly the same, it is easy to see why orientation of deposited indium readily occurs on lead.

Not all the results can be interpreted by reasoning such as in the preceding discussion. Although the lattice constants and weights of copper and nickel are approximately the same, nickel did not form highly oriented deposits or large grains when plated on a copper crystal. It has been proposed that very small traces of iron can greatly affect nickel deposits. No plating baths for nickel have been developed which will give deposits containing large grains (reference 22).

The results obtained in depositing metal on a single crystal of its own kind and of other kinds indicate in general that the rate of deposition varies with crystal plane. In extreme cases the metal may deposit greatly on one face and hardly at all on another. It has been impossible to make a careful study of all the factors involved but it appears that an approximate equality of lattice constants in one or more dimensions will control in varying degrees the nature of the deposit.

IMPORTANCE OF RESULTS TO PRACTICAL PROBLEMS OF LUBRICATION, FRICTION, AND WEAR

These studies have not been limited strictly to the corrosion of metals by oils but have included any process which might be important to lubrication and which lent itself to this method of study. Since the relationship of some of the results to lubrication may not be clear at first sight, their possible importance to aircraft engines will be discussed. One of the advantages of this method of study is that it makes possible the relation of many apparently unrelated surface processes. For example, it makes possible the study of the relation of oxidation to corrosion, to wetting, and to friction and wear.

Oxidation and Corrosion

Oxidation is one of the most important factors in lubricated machinery. It is appreciated that the harmful effect of oxygen in promoting destruction of oil and in accelerating corrosion has long been known in a general sort of way, but it is believed that the full significance of the effect on corrosion has not been appreciated and very little about the

mechanism of the process is known. There are amazingly few references to the subject in the literature, and in the latest of these (reference 23) the statement is made: "The important role of oxygen in the corrosion of bearing metals by lubricating oils has largely been overlooked until recently."

When two dry metals are brought together, the pure metals do not come in contact but are separated by a layer of oxide. If the metals are rubbed together, the oxide layer may be pierced, but it will re-form again instantaneously. When a drop of lubricant is placed on a metal surface, the lubricant does not come in contact with the metal but rests on a layer of oxide. If the lubricant is corrosive, it may attack the oxide, but the oxide will continually re-form or at least oxygen will enter into the reaction. Kinetic friction between dry metals has been shown to vary by a factor of 20, the result depending on whether the metals have been thoroughly degassed (reference 24). Static friction between two pieces of copper heated in hydrogen has been found to be roughly 30 times that obtained in air (reference 1). Furthermore Dayton (reference 25) has emphasized that flakes of oxide may be torn away from the bearing surface and act as an abrasive which increases wear. The fact that the rate of this oxidation varies greatly with plane, in the case of copper by a factor of at least 5, is of tremendous importance to both the theory and practice of bearing surfaces. In regard to flakes of oxide, when a copper crystal is heated at a sufficiently high temperature to form thick films of oxide, large flakes of oxide may be easily detached from the surface in some regions by rubbing with a tissue, whereas no flakes can be removed from others. Incidentally the action of nitrogen from the air on iron may also be important, and at present so little is known about this that there is still some question as to whether oxygen or nitrogen produces fatigue failure under certain conditions (reference 26).

Etching or corrosion by organic liquids must also be considered in relation to oxidation of surfaces. In the first place, the extent and the nature of corrosion is controlled by the oxidation process. Metals below hydrogen in the electromotive series were not appreciably attacked by lubricants, new or old, in an atmosphere of hydrogen, and the corrosion of metals above hydrogen in the series in an atmosphere of hydrogen was reduced to 1/20 to 1/300 of the values obtained in air. The importance of the structure and orientation of this oxide has been emphasized previously in this report. Etching, if it takes place at all, regardless of whether it takes place in hydrogen or air, varies with plane, the presence of oxygen serving to determine the nature and extent of etching. This variation in rate with plane means that some planes on the surface will be smooth and others will be very rough. Not only will an appreciable amount of metal be removed by simple chemical attack, but this roughness should also increase friction leading to additional loss of metal. This effect of preferential roughness due to etching will not be prevented by the formation of an amorphous-like layer, for, although such a layer will form on the softer of the two metals, no such layer will form on the harder of the two. The roughened areas of the harder metal will cut like a file into the softer. This effect has been demonstrated by rubbing a single

crystal of copper against a sheet of lead in the presence of hot stearic acid. Rubbing two metals of equal hardness together will produce an amorphous layer on each, but when a copper crystal is rubbed against lead, the pattern of rough and smooth regions forms on copper just as if the lead were not present.

Wetting

The practical usefulness of a lubricant depends on its ability to adhere to the metal surface. This adherence ranges from its ability to wet the surface on standing to its ability to cling to the surface under great pressure. Information on any factors which control the adherence of either addition agents with polar groups or straight chain hydrocarbons is badly needed both in understanding the mechanics of lubrication and in improving lubrication practice. The fact that some liquids wet only certain planes on the metals copper, nickel, and iron emphasizes the importance of the structure of the metal on the wetting process. The dependence of this preferred wetting on the presence of oxygen emphasizes the importance of the oxide film, or at least some oxygen-complex, in controlling wetting phenomena. Therefore, if it is desired to improve the wetting properties of lubricants, attention must be paid to the spacing of atoms in the surface and to the chemical nature of the surrounding gas. Hitherto these two factors have been almost completely neglected in this very important field. Obviously there are many questions which still remain to be answered. These wetting results have been obtained only with the highly polar molecules, stearic, myristic, and palmitic acids and tricresyl phosphate, but in the case of stearic acid in mineral oil with copper preferred wetting was obtained with mixtures containing up to 50 percent mineral oil; this indicates the strong influence which the adsorption of the acid-product had on wetting by mineral oil. The nature of the organic product which is responsible for this preferred wetting is not known. Eastman stearic acid of a high purity gave preferred wetting on heating with copper. The experiment with the mixture of stearic acid and mineral oil suggests that some compound is formed which is oleophobic on some planes and not on others. Although a small percentage of polar compounds is probably formed in time in commercial aviation oil and in mineral oil, no preferred wetting was obtained with either one of these materials when heated alone with copper. Either the concentration of polar molecules was not sufficiently great or the proper molecule was not developed, but these preferred-wetting results suggest that the adsorption of polar compounds in a commercial oil might vary with plane and hence the adherence of an oiliness agent might so vary. The question is raised as to the relation between wetting, orientation of molecules, and corrosion. Electron diffraction should give information on the variation of orientation with plane, and the measurement of contact angles should give information on the variation of energy of adhesion. The importance to practical lubrication of these results on wetting is believed to be great. Both the structure of the metal surface and the nature of the surrounding atmosphere have been shown to play controlling parts.

Rearrangement

In addition to oxidation, corrosion, and wetting, there is another interesting surface process which has not been investigated in any detail in these studies, but which was first discovered by this method of study and which may be of some importance to aircraft engines. It should be of great importance to the behavior of metals under the high temperatures encountered in jet propulsion. It has long been known that metals disintegrate under the action of hot gases. Beilby (reference 27) gave many interesting examples. But it was shown in these studies that some catalytic reactions between hot gases produced definite rearrangements on the surface of metals which varied with plane and which were highly characteristic of the reaction. Since on some planes the surface became quite rough and on others it remained smooth, the friction and wear between rubbing parts exposed to the action of hot gases should be dependent on the faces exposed in the surface of a polycrystalline metal. Valves and cylinder walls are examples of parts which might be affected by this action. A definite amount of evaporation of metal also takes place during these reactions. The number of gases investigated was not large but the results, it is believed, were significant and should be investigated further from the standpoint of friction and wear as well as from that of the mechanism of fatigue and contact catalysis.

Electrochemical Properties

The variation of electrochemical properties with crystal plane is important to lubricated machinery both in the manufacture of bearings by electroplating and in controlling the chemical properties of the rubbing surfaces. Industrial electroplating is largely an art based on empirical facts as shown by the intermediate deposits and addition agents which are necessary to obtain satisfactory adherence. The general importance in electroplating of the surface structure of the underlying metal has been shown in the present studies by the fact that the rate of deposition of metal both on metal of its own kind and on metal of other kinds varies with plane. The rate of formation of crystal nuclei also varies with plane. In connection with the silver-lead-indium bearing, it was found that the rate of deposition of indium on both lead and copper crystals varied with plane. For good adherence and rapid plating the depositing metal must fit into the proper lattice, the nature of which for any one metal is determined by the plane exposed. This suggests that by selecting the right face for the deposition of one metal on another, intermediate deposits and addition agents in some cases might be unnecessary. The effect of addition agents in influencing orientation of deposits has been interestingly shown in reference 28. In the deposition of polycrystalline copper it was found that the addition of thiourea produced a bright and smooth surface. Examination with X-rays showed that the surface crystals were simply oriented with the (100) planes parallel to the surface.

Other electrochemical processes important to lubricated machinery are electrolytic replacement and galvanic action. The possible importance of the former was illustrated by the fact that when a copper crystal was

rubbed against a lead sheet in hot stearic acid, copper deposited from solution on the lead sheet and resulted in copper rubbing against copper. The importance of galvanic action is illustrated by the fact that the corrosion of aluminum by hot stearic acid was greatly accelerated by contact with bismuth. The pitting of iron by corrosion is generally explained by galvanic action due to small cells produced by formation of isolated films of oxide. All these electrochemical processes have been found to vary greatly with plane, and it is believed that the electrochemical properties of the individual crystals are of fundamental importance to the plating of bearings and cylinder walls and to the corrosion and wear of lubricated parts. A fundamental study of the electrochemical properties of these unit crystals, without immediate regard for practical problems, is at present badly needed for a proper understanding of all surface phenomena. The contact potential is the fundamental property which probably controls all electrochemical processes, although the experimental difficulties of measuring potentials on surfaces of known configuration and chemical composition should be appreciated.

CONCLUSIONS

It has been shown that the rate of a number of chemical and electrochemical reactions with a large number of metals varied with crystal plane. The general order of magnitude of these variations was determined in order to evaluate their general importance and to indicate for practical application the planes which had high rates of oxidation and those which had low ones. The rates varied with plane in different degrees. For example, in the wetting of copper by stearic acid in air one plane was completely wet and others were dry, in the oxidation of copper the rates on two planes differed by a factor of 5, and in the oxidation of chromium no variation with plane was detected. However, in the few cases where no variation was detected, such as the oxidation of chromium, it is believed that a protective film was formed by which reaction in the more active regions was retarded. The influence of the surrounding atmosphere on the rate of chemical reaction, especially in the important processes of corrosion and wetting, was found to be great.

The importance of these results, as regards an understanding of the chemistry of the oil-metal interface, lies in the experimental proof that a particular metal surface cannot be thought of as having one characteristic property for a particular process but that it has a large number of properties, one for each crystal face exposed. Measurements ordinarily made on polycrystalline surfaces are composite quantities and are generally of little value for purposes of interpretation. The importance of these chemical results as regards their practical application is that they suggest that a control of chemical activity at the surface could be obtained by a control of the orientation of the surface crystals.

In addition to the obvious importance of the variation in corrosion and wetting with plane, the experiments especially showed that invisible

films of oxide greatly affected both chemical and physical processes. These oxide films have generally been considered as unavoidable, and little attention has been paid to their real significance. The role of these films is further complicated by the fact that their rate of formation varies with plane.

The question of whether an oriented surface is possible or desirable should be discussed. The results of these studies at the present time do not indicate whether an oriented single crystal or a polycrystalline surface in which the individual crystals are oriented is desirable or possible on a commercial scale. Corrosion might be reduced by controlling the plane exposed and the nature of the surrounding atmosphere. The tendency of certain oils to wet metals might be improved by a control of plane and other individual effects might be produced, but these are only a few of the factors controlling lubrication. The possibilities for the practical use of oriented surfaces look promising, but only further study can determine exactly what these uses will be.

A simple but significant viewpoint can be offered concerning the chemistry of the oil-metal interface. In considering the surface of metals in an engine, it should be kept in mind that solids, liquids, and gases are all simultaneously involved. The chemical interaction between these three forms of matter plays a more important role than is generally appreciated, and many of the difficulties commonly attributed to mechanical causes have their origin in chemical processes. If the nature of the crystalline metal is kept in mind, the great importance of the atomic spacing in the surface becomes apparent. The importance of this spacing has shown itself in the present studies by the variation in rate of many processes with crystal plane. If the surrounding atmosphere and the fact that it contains oxygen, one of the most active of molecules, and in some cases water vapor, hydrobromic acid, nitrogen oxides, and other constituents, are kept in mind, the importance of unobserved films forming on the surface which will completely alter the properties of the surface will be realized. Furthermore, the rate of reaction between the surface and many of these gases, especially oxygen, varies greatly with plane. As for the liquid, its structure and chemical nature have received more attention in lubrication studies than has the structure of the metal or the chemical nature of the gas, and it is sufficient to note at this point that the adsorbed or reacting liquid must in many cases fit structurally into the complex formed by the metal-gas reaction. The structural relationships between solid, liquid, and gas must be continually kept in mind. This study specifically gives information on the chemical importance of the structure of the metal surface.

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Charlottesville, Va., November 23, 1945

APPENDIX

FURTHER ANALYSIS OF ANISOTROPIC OXIDATION OF METALLIC SINGLE CRYSTALS

An attempt was made under PRESENT THEORY OF INFLUENCE OF CRYSTAL PLANE ON SURFACE REACTIONS AND ATTEMPTS TO CLASSIFY RESULTS to correlate and analyze the results obtained on the oxidation of metal crystals. Although it is believed that a satisfactory understanding of the variations in rate with plane is not possible until additional experimental information is obtained, an attempt has been made to interpret the results further in terms of possible steps which can take place at the surface. This analysis suggests certain possibilities of mechanism and offers a viewpoint by which future studies may be guided.

There are a number of conceivable mechanisms whereby oxidation of a metal surface may take place. Furthermore the controlling steps at the beginning of oxidation may be different from those which control the process after an oxide film of appreciable thickness has formed. When the oxidation film is continuous and has an appreciable thickness, Wagner and co-workers (reference 18) have proposed that the process of oxidation takes place largely by the diffusion of metal ions and electrons outward to react with adsorbed oxygen particles. Of the possible diffusing elements, electrons, copper atoms, cuprous ions, oxygen atoms, and oxygen ions, the electrons and cuprous ions are the smallest and therefore would tend to diffuse the most rapidly. Goldschmidt (reference 29) gives 0.96 A and 1.32 A for the radii of cuprous ions and oxygen ions, respectively. Cuprous oxide which exhibits electrical conductivity is known to form thin films under mild oxidizing conditions. It would also be expected that a slight diffusion of oxygen ions or atoms would take place through the oxide film since oxygen is known to diffuse at measureable rates through metals such as copper, nickel, and iron at high temperatures (reference 30).

With the assumption that the oxidation for copper takes place largely by diffusion of electrons and cuprous ions outward, the over-all process may be divided into the following steps:

1. Action of oxygen
   (a) Adsorption of oxygen on oxide layer
   (b) Pick-up of electrons
   (c) Reaction of oxygen ions with cuprous ions

2. Action of electrons
   (a) Transfer from metal to oxide
   (b) Diffusion through oxide
   (c) Transfer from oxide to region of adsorbed gas
   (d) Pick-up of electrons by adsorbed gas

3. Action of cuprous ions
   (a) Transfer from metal to oxide
   (b) Diffusion through oxide
   (c) Transfer from oxide to region of adsorbed gas
   (d) Reaction of cuprous ion with oxygen ion

These possible steps will now be considered, and an attempt will be made to select the rate controlling processes and to interpret the variation in the rate of over-all oxidation with crystal plane.

ACTION OF OXYGEN

It has previously been pointed out that from meager calculations step (a) (the adsorption of oxygen) would be expected to vary with plane. At the very start of the reaction adsorption would be expected to be the controlling process, but, after a film of appreciable thickness has formed, adsorption at 200° and atmospheric pressure would be relatively rapid and would not be the controlling process. No specific information is available on step (b) (the pick-up of electrons by adsorbed gas) but experiments on the decrease of thermionic emission by adsorbed gas (reference 31) indicate that some of the adsorbed particles exist as ions, so that the pick-up of electrons may be considered to be part of the adsorption process. Step (c) (the reaction between oxygen ions and cuprous ions) should take place rapidly and without variation in rate with plane, once the ions are brought into proximity.

ACTION OF ELECTRONS

Evidence from several sources suggests that the over-all rate of electron transfer from metal to adsorbed oxygen atoms may be the controlling process in oxidation. First, Mott (references 32 and 33) proposed that the rate controlling process in the oxidation of metals which form protective oxides is the rate of electron tunneling to the adsorbed oxygen atoms. He cites in evidence that aluminum forms oxide films of a limited thickness of 40 A in air, but when oxygen ions are supplied to the surface by anodic oxidation, film thicknesses of 10,000 A may be readily obtained. Second, McAdam and Geil (reference 34) noted that the oxidation rate of steels was accelerated when the steel specimens were placed in contact with a silver plate. Presumably an electrochemical cell was set up which aided the electron transfer in the oxidation of iron. Analogous phenomena occur in solution. The solution of electropositive aluminum in hydrochloric acid is greatly accelerated when the metal is placed in contact with electronegative gold. Third, as previously discussed, Uhlig (reference 19) has explained certain cases of passivity in terms of the transfer and sharing of electrons between metal and oxygen. Fourth, the results on atmospheric tarnishing at room temperature of copper single crystals reported in reference 1 suggest that electron migration is the

controlling process. Sunlight accelerated the rate of atmospheric tarnishing and increased the variation in rate with crystal plane. When the ultraviolet light, which influences electron transfer, was filtered out, the rate of tarnishing was appreciably reduced.

As regards the various steps taken by the electrons, step (a) (the transfer of electrons from metal to oxide) and step (c) (the transfer across the oxide-adsorbed gas interface) are probably the rate controlling ones until the films become quite thick, when step (b) (diffusion of electrons) probably becomes the controlling process. Cuprous oxide is slightly conducting, and it would be expected that electrons would diffuse through it with an appreciable rate. The conductivity, and therefore the diffusion, would not be expected to vary with crystal direction for cubic crystals (reference 35). Very little information on these individual electron steps is available, and it is therefore impossible to identify the rate controlling step under any one set of conditions. It is only possible to reason from over-all electron processes on metal surfaces. Both thermionic and photoelectric emissions are strongly influenced by the chemical nature of the adsorbed gas. Oxygen lowers the emissions tremendously. This fact would suggest that steps (a) and (c) are the limiting ones. As regards the variation in rate of oxidation with crystal plane, electron processes on metal surfaces have been shown to vary greatly with plane. Thus it would be expected that the electron processes involved in oxidation, with the exception of diffusion, would vary with plane. Martin (reference 36) has shown that the work functions in thermionic emissions from tungsten varied with crystal plane as well as with the nature of adsorbed particles. Farnsworth and co-workers (references 14 and 37) found that contact potentials varied with plane.

The possibility that electron processes may be the controlling factor in oxidation of metal surfaces emphasizes the desirability of quantitative measurement and correlation of the rates of oxidation, contact potentials, photoelectric and thermionic emissions, and electrodeposition processes on various faces of metal crystals.

ACTION OF CUPROUS IONS

Step (a) (the transfer of cuprous ions from metal to oxide) might be expected to be the controlling process at the start but it would not be expected to be a very slow one since the oxide has an appreciable solubility in the metal. This fact suggests that the metal ions would not be greatly out of their environment when in the oxide and therefore there would be no great barrier to overcome in passing into the oxide. Since the surface free energy of metal surfaces has been shown to vary with plane, it might be expected that the tendency for cuprous ions to leave the metal and enter the oxide would vary with plane.

Of the possible steps taken by cuprous ions, step (b) (the diffusion through the oxide) would be expected to be the controlling process as the

oxide film gets thicker. Barrer (reference 38) cites a number of instances of anisotropic diffusion for noncubic lattices, but he states that he does not believe that the rate of diffusion is anisotropic in metals of the cubic lattice. However, the experimental difficulties of measuring diffusion along definite crystal directions are great, and no reliable experimental results are available. Tammann and Arntz (reference 39) found that mercury drops spread at different rates on different faces of a clean copper crystal, but different thicknesses of oxide might have been responsible.

The following interpretation of variation in rate of oxidation with plane in terms of possible variation in rates of diffusion is given.

The process of diffusion through metals or salts may be thought to occur in one of two manners: (1) The diffusing element may move by a series of jumps into vacancies in the lattices, or (2) The diffusing element may move through the interstices of the lattice. In the oxidation of copper, nickel, and iron it appears that the diffusion of metal ions through the oxide film occurs largely through the interstices in the lattice. In determining possible openings in the lattice for diffusion, it is necessary to know the orientation of the oxide with respect to the underlying metal. Only incomplete information is available.

Mehl, McCandless and Rhines (reference 40) found that the cuprous oxide lattice was oriented in the same way as the underlying copper lattice, but Moore (reference 41) found continuation of the orientation and direction on the (110) and (111) planes and found on the (100) plane the orientation (111) Cu_2O (100) Cu and (110) Cu_2O (100) Cu. Iron crystals heated in H_2 and water at 700° C form ferrous oxide and the oxide is oriented with the (100) planes of the oxide and iron parallel, but the (110) direction in the oxide lies parallel to the (100) direction of iron (reference 40).

Cruzan and Miley (reference 42) have shown that the thin oxide films on copper are largely cuprous oxide. Bound and Richards (reference 43) found that at high temperatures the oxide films on nickel are cubic (sodium-chloride-type) nickel oxide. The structure of thin oxide films on iron is dependent on the purity of the iron, initial surface smoothness and structure, and the temperature (references 44 and 45). Because of lack of data for this investigation it will be assumed that the initial controlling oxide film is ferrous oxide in a sodium-chloride-type structure.

As can be seen from a comparison of figures 1 and 21 and figures 2 and 18 the shape of the interstices in oxide is mirrored in the shape of the oxidation patterns around the (100) planes of copper and nickel. Figures 1 and 2 should be rotated through 45° in the plane of the paper to coincide with the orientation of figures 18 and 21. In both cases the arms from the corners of the square radiate toward a (110) pole position. If the oxide on iron is ferrous oxide and the oxide is oriented as found by Mehl, McCandless and Rhines, figure 18 coincides with the relative iron orientation as shown in figure 4. Thus the corners of the square are directed toward (111) poles rather than toward (110) pole positions.

In the case of copper, fair correlation is obtained between the channels of interstitial space in the oxide and the rate of oxidation on the different crystal faces when a lattice of uniform spheres is assembled in a manner similar to the assumed structure of cuprous oxide. It may be argued that the holes do not represent empty space, but they probably do represent regions of low electron density and mass density.

The relative rates of copper oxidation on the different faces in order of decreasing rates are: (100) and (210), lines between (311) and (110), (111), (110), and (311) regions. The regions of high rate, (100) and (210), are regions of interstitial passageways in the oxide. Although the (110) pole regions have very large channels and are regions of low rate, the regions immediately surrounding the (110) have a high rate. Regions of low rate, such as the (311) and (111), are regions having very minute channels. The only correlation for the lines between (311) and (311) and (311) and (110), is the fact that with the exception of the (100) region, if a polyhedron is prepared with sides parallel to the regions of low oxidation rate, all the regions of high rate occur as corners or edges.

In the case of nickel, as can be seen from figures 18 and 19, interstitial channels run all the way through the oxide in directions perpendicular to (100) and (110) planes and in thin films in directions making finite angles with the (100) and (110) directions. However, perpendicular to (311) and (111) planes (fig. 20) no semblances of channels are visible. Nickel single crystals oxidized in oxygen at 400° C exhibited high rates of oxidation on (100) and (110) planes and low rates on (111) and (311) planes. Thus in the oxidation of nickel single crystals there is excellent correlation between the rate of oxidation and the presence of direct channels in the oxide.

In the case of iron, interstitial channels are present in the (100) area and it is a region of high rate. Because of lack of knowledge concerning the orientation at the (111) pole, it is impossible to attempt a correlation between channels and high oxidation rate. The fine lines running from neighboring (111) poles and forming a square around the (100) poles are regions of moderately high rate. These lines of high rate may be due to discontinuity in the oxide orientation, since the type of orientation around each (100) pole would not permit a monocrystalline oxide over the entire spherical surface.

Thus it would appear from this consideration that, with oxide films of appreciable thickness, the rate controlling steps are: (1) The transfer of electrons from metal out to the neighborhood of the adsorbed oxygen, and/or (2) The diffusion of copper ions through the oxide lattice. It is impossible with the present knowledge to state which of these is the more important. It would also be expected that both processes would vary with crystal plane. The importance of this analysis is to emphasize the necessity for a correlation of many apparently unrelated surface phenomena before any one of them can be thoroughly understood.

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TABLE I.– OXIDATION OF METAL SINGLE CRYSTALS IN AIR

Metal	Crystal system	Remarks	Active regions	Inactive regions
Aluminum	Face-centered cubic	No color film: preferential roughening in 1 to 2 days at 550°; pattern easily seen when viewed with flashlight	(100)	(111)
Copper	Face-centered cubic	Striking preferential color film; very sharp and complex pattern in several minutes at 200°	(100) (210)	(311) (111)
Gold	Face-centered cubic	No change at 200° to 550°		
Lead	Face-centered cubic	Preferential color films in several minutes at 200°	(100) (311)	(111) (210)
Nickel	Face-centered cubic	Preferential color films; very sharp pattern in several hours at 550°	(100) (110)	(111)
Silver	Face-centered cubic	(111) facets developed in 24 to 48 hours at 500°; preferential color films form in 30 hours in presence of mineral oil and air at 200°	In Mineral (100)	Oil and Air (111)
Chromium	Body-centered cubic	Color films in several hours at 400°; no preferentiality with chromium of 98.5 percent purity		
Iron	Body-centered cubic	Preferential color films form in oxygen in 1 hour at 240°; very sharp and striking pattern	(100) (111)	Region between (100) and (110)
Cadmium	Hexagonal close-packed	Preferential roughening and color in direct beam of flashlight	Six areas 45° to (0001)	(0001)
Magnesium	Hexagonal close-packed			
Zinc	Hexagonal close-packed	Preferential color films in 24 to 48 hours at 400°	Hexagonal ring centered at (0001)	(0001)
Bismuth	Rhombohedral	Preferential roughening in 12 to 24 hours at 230°; specular reflections from a 3-arm area normal to (0001); faint color		
Tin	Body-centered tetragonal	Color films form readily at 210° on roughened surfaces but not on smooth surfaces; investigation incomplete		
Indium	Face-centered tetragonal	No color films at 100°		

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TABLE II.- ETCHING OF POLISHED METAL SINGLE CRYSTALS BY OILS AT 200° (ALTERNATE IMMERSION)

[Weight losses in g/dm^2/day]

Metal	Mineral oil and air	Used aviation oil and air	Stearic acid and air	Stearic acid and hydrogen
Aluminum	0.000	0.000	0.000	0.000
Copper	0.03 Preferential oxidation followed by preferential etching	0.18 to 0.77 Preferential lacquer and preferential etching	5.47 Preferential roughening	0.000
Gold	0.003 Color film forms on the surface	0.000	0.000	
Lead	0.29 Preferential etching and preferential scaling	0.53	60.24 Preferential increases as rate decreases	0.93; tank 0.22; purified
Nickel	0.000	Slight gain	0.124 Preferential attack but not uniform	0.045; tank 0.003; purified
Silver	0.02 Preferential color film followed by preferential scaling	0.000	0.001 Very faint pattern	0.000
Chromium	0.000	0.007 Preferential but not uniform attack	0.050 Preferential but not uniform attack	
Iron	Slight gain Preferential oxidation	0.000 Preferential lacquer	10.02 Preferential; very severe pitting	0.385 Preferential and uniform attack
Cadmium	0.97 Very preferential	0.013	37.4 Preferential at lower rates	
Magnesium				
Zinc	0.000	0.013	185 Very preferential at lower rates	Etching rate decreases by 50 percent at 100°
Bismuth	0.003 Preferential oxidation	0.005 Preferential lacquer and etching	33.8 Very preferential etching	0.018; tank preferential
Tin	0.008 Preferential etching	0.012 Preferential etching	35.4 Preferential etching	1.25 Preferential etching
Indium 100°	0.000	Slight gain	0.000	

TABLE III.– WETTING BY STEARIC ACID AT 200° C

Metal	In air	In hydrogen
Aluminum	Completely wet	Completely wet
Copper	Preferentially wets rough (110) in 6 hours; new crystal in oxidized acids preferentially wets (111).	Completely wet
Gold	Completely wet	
Lead	Film breaks and snaps off crystal, leaving a few drops; no preferentiality visible	Completely wet
Nickel	Preferentially wets (111) after 16 to 24 hours	Completely wet
Silver	Completely wet	Completely wet
Chromium	Completely wet	
Iron	Preferentially wets (111); beautiful wetting patterns	Completely wet
Cadmium	Film breaks and leaves violently agitating drops; no preferentiality visible	Completely wet
Magnesium		
Zinc	Completely wet	Completely wet
Bismuth	Film breaks and slowly crawls; film becomes very viscous	Completely wet
Tin	Completely wet	Completely wet
Indium	Completely wet at 100°	

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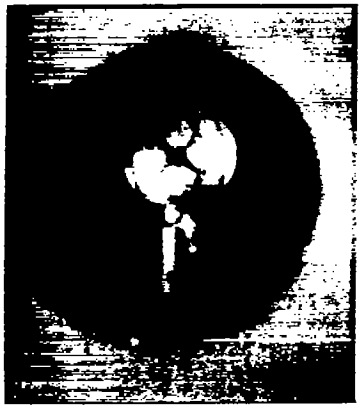

Figure 1.- Oxidation of a copper single crystal in air at 200° for 30 minutes. Normal to (100).

Figure 2.- Oxidation of a nickel single crystal in air at 400° for 3 days. Normal to (100).

Figure 3.- Oxidation of a lead single crystal in air at 200° for 10 minutes. Normal to (100).

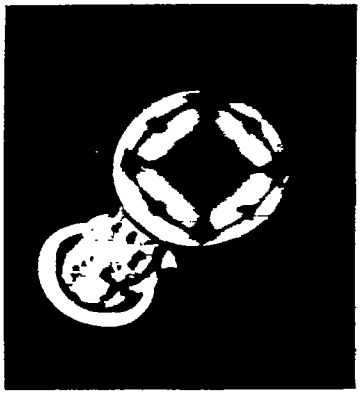

Figure 4.- Oxidation of an iron single crystal in oxygen at 240° for 3 hours. Normal to (100).

Figure 5.- Oxidation of a cadmium single crystal in air at 200° for 19 hours. Normal to (0001).

Figure 6.- Oxidation of a zinc single crystal in air at 400° for 2 days. Normal to (0001).

Figure 7.- Alternate immersion in mineral oil and air of a silver single crystal at 200° for 30 hours. Normal to (100).

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Figure 8.- Preferential etching of a copper single crystal in stearic acid and air at 200°. Normal to (100).

Figure 9.- Preferential etching of a nickel single crystal in stearic acid and tank hydrogen at 200°. Normal to (100).

Figure 10.- Preferential etching of a zinc single crystal in stearic acid and air at 100°. Normal to (0001).

Figure 11.- Hydrogen-oxygen catalytic reaction on a single crystal of nickel at 400°. Normal to (100).

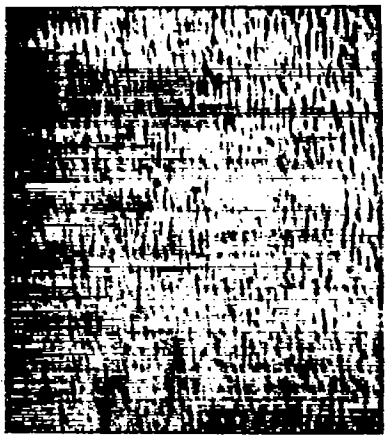

Figure 12.- Hydrogen-oxygen catalytic reaction on a single crystal of nickel at 400°. Facets developed parallel to (100). Magnified 600 times.

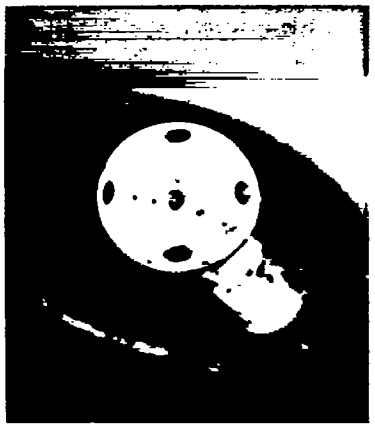

Figure 13.- Preferential wetting on (111) regions of an iron single crystal by stearic acid in air at 200°. Normal to (100).

Figure 14.- Preferential deposition of silver on a copper single crystal dipped in 0.01 N silver nitrate. Normal to (111).

Figure 15.- Preferential scaling of gold deposited on a copper single crystal suspended in 0.01 N gold chloride. Normal to (111).

Figure 16.- Pattern formed by electrodeposition of indium on a lead single crystal. Normal to (100).

Figure 17.- Hexagonal-shaped facets formed parallel to (0001) on evaporation in a vacuum at 400° from a zinc single crystal. Magnified 90 times.

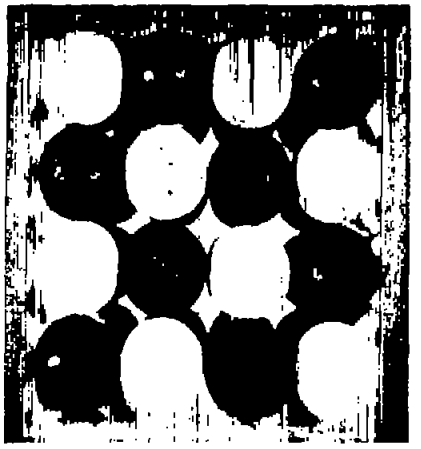

Figure 18.- Sodium chloride type lattice (ferrous oxide, nickel oxide). Normal to (100).

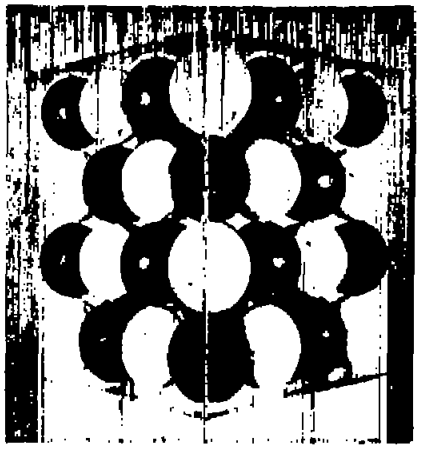

Figure 19.- Sodium chloride type lattice (ferrous oxide, nickel oxide). Normal to (110).

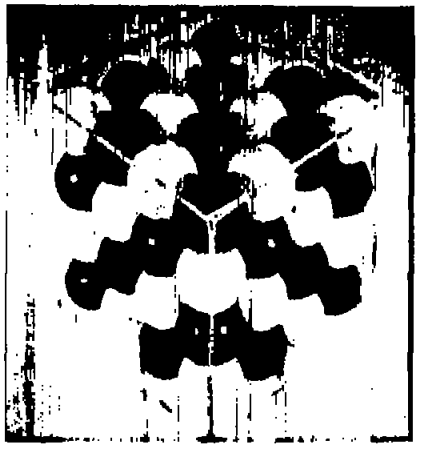

Figure 20.- Sodium chloride type lattice (ferrous oxide, nickel oxide). Normal to (111).

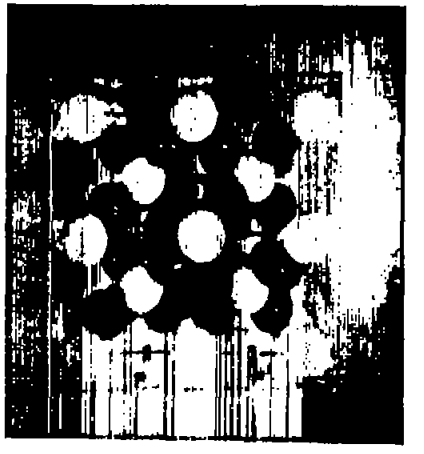

Figure 21.- Cuprous oxide type lattice of interpenetrating face-centered cubic copper atoms and body-centered oxygen atoms. Normal to (100).