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INFLUENCE OF CRYSTAL PLANE AND SURROUNDING ATMOSPHERE ON SOME TYPES OF FRICTION AND WEAR BETWEEN METALS

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

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SUMMARY

The influence of crystal plane on dry static friction has been determined between two single crystals of copper from the surface of which all oxide had been removed. The coefficient of friction between the (100) faces was greater than 100, and that between the (111) faces was approximately 25. The difference between the coefficients for the two sets of faces is attributed largely to the digging-in and greater area of contact with the (100) faces. Exposure of the surfaces to air lowered the coefficients for both sets of surfaces to about 1. The strength of adhesion between two crystals placed in contact, as determined from the area of contact and the vertical pull required to disengage the crystals, was roughly equal to the tensile strength of bulk copper.

The influence of the surrounding atmosphere on wear between two dry polycrystalline copper surfaces has been determined by measuring the time required for a copper sphere to wear through a film of copper deposited on a cylindrical steel rotor. The atmospheres used were hydrogen, and nitrogen containing 0.2 percent of oxygen. In an atmosphere of hydrogen at 300° C the sphere wore through the copper film in about 10 seconds, whereas in the nitrogen-oxygen mixture the sphere had not worn through the film after 90 minutes.

An attempt was made to determine the effect which variation in roughness with plane due to etching had on wear. The times required for several faces of a copper crystal previously etched in stearic acid at 185° C to wear through a lead film in mineral oil at room temperature were measured. The (110) face, which becomes very rough on etching in stearic acid, wore through the lead film in excess of 200 times faster than the (111) face, which remains very smooth.

The influence of atmosphere on wear through a lead film by a polished copper sphere in mineral oil at room temperature was studied. In an atmosphere of hydrogen the sphere wore through the film approximately 200 times faster than in an atmosphere of air.

The recrystallization of the surface of a copper single crystal upon quenching from a high temperature was shown to vary greatly with plane. The metal in the (100) region recrystallized into many small crystals to a great depth. A few experiments were carried out on the influence of sunlight on the atmospheric tarnishing of copper crystals.

INTRODUCTION

In reference 1 experiments were described which were concerned with the chemical action of oils and gases on isolated metal surfaces unaccompanied by mechanical friction and wear. These experiments showed in general that the chemical properties of the individual crystals of a number of metals varied with plane. They emphasized the fact that measurements made on apparently bare metal surfaces are generally made on invisible films which greatly alter the results. It was especially shown that invisible films of oxide, in the formation of which the rate varied with plane, greatly affected both chemical and physical processes.

In attempting to identify the factors which increase or decrease friction in lubricated systems where many materials are present, the behavior of a bare metal surface free of contaminating oxide films must be used as a reference standard. Once the behavior of a bare surface is correctly understood, the influence of other materials in the system may be determined. In an attempt to obtain a true measure of the behavior of a bare surface, several simple types of friction and wear have been studied in the present investigation on surfaces from which all traces of oxide were removed. The values obtained for friction and wear were much higher than those generally recorded for bare surfaces, this result indicating that oxide films are responsible for a larger share of lubrication than is commonly believed. When the oxide film was removed, a variation in dry static friction with plane was also detected. The present investigation includes studies of some mechanical processes and a few studies of combined mechanical and chemical processes. Special emphasis has been placed on the influence of crystal plane and surrounding atmosphere.

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DESCRIPTION OF EXPERIMENTS AND RESULTS

INFLUENCE OF CRYSTAL PLANE AND SURROUNDING ATMOSPHERE ON DRY STATIC FRICTION BETWEEN TWO SINGLE CRYSTALS OF COPPER

Method of Experiment

The general method consisted in determining the pull required to move a single crystal sphere resting on the flat surface of another crystal, both crystals being so oriented that the same two faces were in contact. The direction of pull was parallel to this face. A diagram of the apparatus is shown in figure 1.

The two crystals were placed in contact along a common plane by the following method: Each crystal was held by two pointed screws which pressed tightly into the metal at two opposite (110) poles. Since the great circle equidistant from these two poles contains most of the important planes (the (100), (311), (111), and (110)), two like faces were brought in contact by revolving each sphere about its axis until the desired face on the upper crystal was located on the lower side of the sphere and the flat face on the lower crystal was located on the upper side. Then by lowering the upper crystal onto the lower one the two desired faces were in contact.

The location of the various faces on the sphere was determined from the oxidation pattern obtained by heating the crystal in air for 10 minutes at 200°. Temperatures in the present paper are given in degrees centigrade. Flat surfaces parallel to the (111) and (100) planes were cut on the lower crystal by the following method: A (100) pole which appears as a small cross in the oxidation pattern was located on the great circle. With this position as a center, a circle, 10 millimeters in diameter, was marked on the surface of the sphere with a pair of dividers. A plane surface with the inscribed circle as boundary was carefully ground on the sphere by pressing it against a metallographic grinding belt of medium-grade emery paper. Another plane surface was similarly ground at a (111) pole on the same great circle, the pole being located on the oxidation pattern at the center of a small triangle. After these surfaces had been mechanically and electrolytically polished, their location was checked by lightly scratching with a pin. The slip lines on the (100) face should intersect each other at 90° and those on the (111) intersect each other at 60°.

The (100) and (111) pole positions on the upper crystal were located on a great circle equidistant between two opposite (110) poles, and two punch marks were made about 3 millimeters from and directly opposite each pole position, one mark being on one side of the great circle and the other on the other side. The upper sphere was rotated about its axis until the

punch marks opposite the desired pole were directed downward, so that when this crystal was lowered, it rested on the desired position.

The lower crystal containing the flat faces was supported by screws held in the uprights of the base plate A, and the upper crystal was supported by screws held in the yoke B. The base plate A was prevented from moving forward by a copper wire attached to the uprights of the base plate and slipped over a nickel hook welded to a tungsten lead C which was sealed into the end of the glass tube. A copper cylinder D, with a groove in the top, was placed on the end of the base plate to support the shaft of the yoke B during evacuation and before the crystals were placed in contact.

Purified hydrogen passed in through E and left through the ground-glass joint F held in a rubber stopper which fitted tightly into the open end of the glass apparatus. A small cork with a hole in it, just large enough for the shaft of the yoke B to pass through, was inserted into the end of this glass joint. A clearance of about 1/2 millimeter between the shaft and the hole in the cork was obtained. During the tests the gas passed out through this annular space, and the shaft of the yoke did not touch the walls of the cork. Prior to passing hydrogen through the apparatus it was evacuated by attaching to F the other half of the ground-glass joint, which was connected to a Hyvac pump. The glass apparatus consisted of a tube about 5 centimeters in diameter and 35 centimeters in length and enlarged at one end as shown.

The hydrogen used was tank hydrogen purified by passage over copper wire heated to 450°, Dehydrite, and Ascarite. All parts of the apparatus were handled with soft tissue paper. The base plate A and cylinder D were put into the apparatus by means of long brass tongs. The ground-glass joint F was sparsely lubricated with silicone grease. The apparatus was heated by a portable resistance furnace slipped over the end.

A uniform procedure was adopted. The base plate A containing the lower crystal was placed in the apparatus and attached to the nickel hook to prevent movement during the measurement. The copper cylinder D was put in position on the base plate. The yoke B containing the upper crystal was placed in the vessel and the shaft was allowed to rest in the groove in the top of the cylinder. The other end of the shaft was slipped through the small opening in the cork within the ground-glass joint F as the rubber stopper was forced tightly into the end of the glass apparatus. The outside half of the ground-glass joint was attached to F and the system was evacuated for 15 minutes. Hydrogen was then allowed to sweep through the system, the pump was cut off, the pressure raised to atmospheric, and the outside half of the ground joint removed. The rate of flow of hydrogen was maintained at 6 cubic feet per hour.

The important step of placing the top crystal onto the bottom one, while at the same time preventing it from rolling sideways after it was in place, was accomplished by the mechanism shown in figure 1. G consisted of a horizontal shaft, 1/4 inch in diameter, with a small circular disk, 3/4 inch in diameter, attached to one end of the shaft. The crank arm H,

a flat strip of brass 1/4 by 1/16 by 6 inches long, was attached to a small pin located 1/4 inch off center in the circular disk. A short section of circular shaft I was connected to the vertical crank arm H so that the short section could be revolved in a vertical plane about the pin connecting it to the crank arm but could not be moved sideways or turned about its own axis. On the end of the shaft I was a small sleeve with set screws near each end for clamping I rigidly to the shaft of yoke B. The top sphere was placed on the bottom one by the following procedure. With the shaft of the yoke resting in the groove of the copper cylinder and the yoke in a horizontal position, the shaft was connected rigidly to the small sleeve by means of a set screw. The circular disk G with its shaft was moved forward toward the main apparatus with the yoke B remaining in position, until the crank arm H had revolved about the pin in G in a counterclockwise direction by an angle of about 25°. The disk G with its shaft was next moved directly downward until first, the shaft of the yoke rested on the cork in the ground-glass joint F and second, the yoke holding the crystal was raised 3/4 inch above the copper cylinder on which it had been resting. The crank arm H was then revolved about the pin in G until H was in a vertical position. This should bring the top crystal directly above the center of the flat face on the bottom crystal. By turning G about its shaft the arm H was slowly raised upward until the crystal rested on the lower one and the shaft of the yoke took up its position in the center of the small hole in the cork in the glass joint F.

The furnace was placed over the end of the apparatus within about 6 inches of the rubber stopper, and the apparatus was heated for about 30 minutes until the temperature within the furnace as measured by a thermometer reached 500° to 520°. It was held at this temperature for 15 minutes and the heat was then cut off. With the furnace left in place the temperature dropped to about 300° in 25 minutes and the furnace was removed. After about 30 minutes the apparatus had cooled to room temperature. A balance pan which could be loaded with mercury at a constant rate was connected to the bottom of the crank arm H by means of a small steel wire. Mercury was run into a beaker on the balance pan at the rate of 200 grams per minute. A platform was placed about 1/2 inch below the pan to stop the motion of the upper crystal after it had moved across the flat surface of the lower one.

The crystals were mechanically polished with number 1 emery paper until all traces of scratches from the preceding run were removed. They were then polished with papers numbers 0 to 0000 and finally electrolytically polished in phosphoric acid solution. Care was taken that all strained layers were removed by lowering the current density and noting the sharpness of the etch pattern formed. In order to obtain a smooth surface on the flat faces of the lower crystal it was necessary after the first electrolytic polishing to polish again mechanically on papers numbers 000 and 0000 and to polish electrolytically for an additional 10 to 15 minutes. The crystals were always polished immediately before a run and placed directly into the apparatus. In order to prevent digging-in of the top sphere into the flat surface, the bottom crystal was set so that the flat surface had a forward

angle of 2° to 3° downward from the horizontal. A small shaft, 3/16 inch in diameter by 1/2 inch in length (not shown in fig. 1), extends from the side of each crystal to serve as a handle in the preparation of the crystal. The location of the shaft on the sphere varied with each crystal, but in marking the desired faces on the sphere the great circle was so selected that the shaft would not interfere with the yoke or vertical supports.

The apparatus used for measurement of the vertical force required to separate two crystals placed in contact was similar to that used for measurement of static friction except that it was arranged vertically instead of horizontally. The base A consisted of a steel cylinder which rested on a small glass ring B. The purpose of this ring was to prevent differences in expansion of the steel and glass from cracking the wall of the glass vessel. The base A was held in place by a small piece of piano wire hooked over a bend in a nickel rod welded to the tungsten lead C in the bottom of the vessel. The lower half of the apparatus was heated to 500° in the course of 35 minutes, held at this temperature for 15 minutes, and allowed to cool to 300° in 25 minutes with the furnace in place. The furnace was then removed and the apparatus cooled to room temperature in about 35 minutes by blowing a stream of air against the walls of the vessel. The weight of the top crystal and supporting mechanism was 75 grams, and in recording the force required to separate the crystals this was subtracted from the total weight of mercury involved. The area of contact between the crystals was estimated by examination of the disrupted regions under the microscope. Regions which had adhered in general appeared rough and granular.

Results

The apparatus used in this series of experiments was constructed for the purpose of measuring coefficients of friction ranging from about 10 up to a limiting value of 100. Only the order of magnitude of coefficients less than 10 could be determined.

Static friction between crystals in an atmosphere of air at room temperature.- For purposes of comparison with oxide-free surfaces, it was desired to obtain an approximate measure of the coefficients of surfaces acted on by the oxygen in the air. After electrolytic polishing, washing, and drying, the crystals were clamped in their holders and immediately placed in contact in the apparatus. In all measurements made in air the coefficients were approximately 1. It was not possible with this apparatus to determine differences between coefficients in air for pairs of (100) faces and pairs of (111) faces.

Static friction between crystals placed in contact after heating in hydrogen.- At first it was attempted to measure the friction between crystals which were placed in contact after heating in hydrogen. The results were not accurately reproducible but definitely fell within certain

ranges for each set of faces. The crystals were polished, placed in the apparatus, heated in hydrogen, and cooled in hydrogen to room temperature before being placed in contact. The coefficients for the (111) faces ranged from 10 to 20 and for the (100) faces from 62 up to 100, the limit of the apparatus. Slip lines were visible on both the upper and lower surfaces in both instances, but they were always much more prominent on the (100) faces than on the (111) faces. Pairs of (111) faces had only a slight tendency to dig into each other, and the upper crystal slid smoothly over the lower one. Pairs of (100) faces had a decided tendency to dig in, which removed sizeable chunks from the lower crystal. Pits as deep as 0.20 millimeter were observed, and the sides of the pits showed regular facets which could not be definitely identified but which were probably parallel to (111) planes. When an attempt was made, by twisting and pulling the connecting rod, to separate the two crystals placed in contact by this method, the result was similar to that obtained when two adhesive materials are being disengaged. The top crystal could be rolled over, but it still remained attached to the lower one wherever it touched.

Static friction between crystals placed in contact before heating in hydrogen.- The most consistently reproducible results on the influence of crystal plane on static friction between oxide-free surfaces were obtained when the crystals were placed together before being heated in hydrogen. Most of the time employed in this series of experiments with static friction was devoted to improving and using this method of measurement. A large number of preliminary experiments, about 40, was conducted. These showed that the general trend of friction between pairs of (111) faces was much lower than that between pairs of (100) faces, but an occasional result was obtained which was completely out of line. However, with great care in setting the crystals so that there was no appreciable downward component in the pull on the upper crystal, satisfactorily reproducible results for this type of measurement were obtained. The values obtained in the final series of 10 consecutive experiments are given in table I.

TABLE I

CRYSTALS HEATED IN CONTACT IN HYDROGEN

[Pairs of (100) faces sliding in a (100) direction.
Pairs of (111) faces sliding in a (211) direction.
Slight angle between crystal plane and direction of pull.]

Crystals	Pull (g)	Coefficient of friction
(100)-(100)	Over 4000	Over 100
(100)-(100)	Over 4000	Over 100
(100)-(100)	Over 4000	Over 100
(100)-(100)	Over 4000	Over 100
(100)-(100)	Over 4000	Over 100
Average	Over 4000	Over 100
(111)-(111)	980	24.5
(111)-(111)	Moved to edge at 950; slipped off at 1380	23.7(at 950 g)
(111)-(111)	1010	25.2
(111)-(111)	960	24.0
(111)-(111)	750	18.8
Average	930	23.2

The final pull required to separate the two crystals when (100) faces were in contact could not be determined since the apparatus was limited to a pull of 4000 grams. During the loading operation in the case of (100) faces, the top crystal moved about 0.5 millimeter over the flat surface in a series of very short jerks and cut a deep furrow in the lower surface. The crystals in this case could only be separated with difficulty. This was accomplished by loosening the sleeve at the end of shaft I in figure 1 and simultaneously rocking and pulling the shaft until the upper crystal was disengaged. This so disturbed the lower surface that the amount of information obtained from a microscopic examination of the point of contact was limited. When the regions adjacent to the point of contact were examined, very prominent slip lines were always visible on both the upper and lower crystals. Three shallow depressions appearing as leaves of a three-leaf clover radiated from the center of the point of contact on the lower crystal. One was located to the right, one to the left, and one in front in the direction of pull.

In two cases after a load of 4000 grams failed to separate two (100) faces, the load was removed and the crystals were allowed to stand in

air overnight for 16 hours. When the load was again applied, the crystals were separated in one instance at 1170 grams (coefficient of friction, 29) and in the other instance at 2210 grams (coefficient, 55). In another case in an atmosphere of hydrogen the 4000-gram load was removed and then immediately applied again. The crystals did not separate. When the crystals were separated by pulling after standing in air overnight, it could be seen under the microscope that deep chunks had been removed from the initial part of the scratch on the lower crystal and several smaller chunks had been removed farther along the scratch. The sides of the pits formed appeared to be stepwise facets, but the exact planes could not be identified.

In the case of the (111) faces well-defined slip lines were visible under the microscope, but they were in no way as prominent as in the case of the (100) faces. In comparison with pairs of (100) faces there was very little tendency to dig in. With (111) faces the scratch on the lower crystal was generally continuous at the beginning but toward the end consisted of a number of parallel tracks, each one composed of a multitude of small, regularly spaced indentations or points of contact, typical of stick-slip motion.

A few measurements were made with polycrystalline spheres, and values intermediate between the high values for (100) faces and the low values for (111) faces were obtained.

Crystals	Pull (g)	Coefficient of friction
Polycrystalline	1430	35.7
Polycrystalline	1690	42.2
Polycrystalline	2240	56.0
Polycrystalline	1790	44.7
Polycrystalline	1960	49.0

Slip lines were visible only on grains in the immediate vicinity of the edge of the scratch. The lines ended abruptly at the grain boundary where they intersected a grain of different orientation. On the lower sphere the track was continuous, and the tendency to dig in appeared to be intermediate to that with pairs of (100) and pairs of (111) faces. Within a small grain it was often observed that tiny chunks had been removed from the surface and small stepwise facets could be seen in the groove.

The following two sets of experiments were performed in order to determine the influence of oxidation on the adhesion between crystals.

Static friction between crystals oxidized in air after being heated in contact in hydrogen.- The crystals were heated in contact to 500° to 520° in hydrogen and held at this temperature for 15 minutes. After cooling to 300° the hydrogen was replaced by air and the system was cooled to room temperature over a period of 30 minutes. The following results were obtained:

Crystals	Pull (g)	Coefficient of friction
(100)–(100)	510	12.7
(111)–(111)	450	11.2

Static friction between crystals reduced with hydrogen after being oxidized in air at 250°.- The crystals were oxidized in air at 250° until the oxide thickness on the face under consideration, as judged by the interference color, was about 1000 A. The crystals were cooled to room temperature, placed in contact, and then heated in hydrogen at 500°. The following results were obtained:

Crystals	Pull (g)	Coefficient of friction
(100)–(100)	Over 4000	Over 100
(111)–(111)	810	20

Static friction between crystals heated in hydrogen with a positive angle of 25° to 30° between crystal plane and direction of pull.- In order to remove any possibility of digging-in due to a downward component of the pull acting normally to the surface, the lower crystal was inclined in its support so that the flat face made a forward angle of 25° to 30° downward from the direction of pull. The crystals were placed in contact, heated in hydrogen, and cooled in hydrogen to room temperature. Various combinations of crystal faces were used. The following results were obtained:

Crystals	Pull (g)	Coefficient of friction
(100)–(100)	1020	25.5
(100)–(100)	1220	30.5
(111)–(111)	500	12.5
(111)–(100)	910	22.7
(100)–(111)	480	12.0

In order to aid in the interpretation of the results obtained for static friction, a few experiments were carried out to determine the general order of magnitude of the vertical force required to separate crystals placed in contact under various conditions. In using these measurements to interpret the results for static friction, allowance should be made for the fact that the total weight pressing the crystals together in these experiments was 75 grams, whereas the effective weight in the friction experiments was 40 grams.

Vertical force required to separate two crystals placed in contact in air.- The crystals were electrolytically polished, washed in water, dried in air, and immediately placed in contact in the apparatus shown in figure 2. As would be expected, there was no detectable adherence either between (100) faces or (111) faces.

Vertical force required to separate two crystals placed in contact after being heated in hydrogen.– In order to remove the invisible films of oxide, the crystals were heated apart in hydrogen at 500° to 520° for 15 minutes. The crystals were placed in contact after cooling to the desired temperature and the vertical force required to separate them was determined at room temperature. The following results were obtained when the crystals were placed in contact at room temperature:

Crystals	Pull (g)	Estimated area of contact (sq mm)
(100)–(100)	100	Approximately 0.003
(111)–(111)	120	Approximately 0.003

The following results were obtained when the crystals were placed in contact at 300° and the measurement was made at room temperature:

Crystals	Pull (g)	Calculated area of contact (sq mm)	Calculated strength (lb/sq in.)
(100)–(100)	350	0.010	48,800
(111)–(111)	360	.011	45,200

Slip lines were observed when the crystals were placed in contact at both 300° and room temperature. The lines were more intense in the former case.

Vertical force required to separate two crystals placed in contact before being heated in hydrogen at 500°.– The following measurements were made after the system had cooled to room temperature.

Crystals	Pull (g)	Estimated area of contact (sq mm)	Calculated strength (lb/sq in.)
(100)–(100)	1550	0.046	47,500
(100)–(100)	1910	.054	50,000
(100)–(100)	1240	.032	54,700
(100)–(100)	1300	– – – –	– – – –
(100)–(100)	1120	– – – –	– – – –
(100)–(100)	1780	.049	51,500
Average	1480		50,400
(111)–(111)	1490	.045	47,000
(111)–(111)	1200	.036	48,300
(111)–(111)	1500	– – – –	– – – –
(111)–(111)	1600	– – – –	– – – –
(111)–(111)	1060	.031	48,000
Average	1370		48,000

In experiments with (100) faces, slip lines which intersected each other at 90° could be seen under the microscope adjacent to the point of contact, and with (111) faces, lines intersecting each other at 60° could be seen. The lines were more striking in these experiments when the crystals were heated in contact in hydrogen at 500° than in those when they were placed in contact at 300° or room temperature. In several cases the disrupted material at the points of contact on the (100) faces showed stepwise facets similar to those observed in friction measurements on the (100) faces.

Vertical force required to separate two crystals which were first oxidized in air and then placed in contact and heated in nitrogen at 500°.– The crystals were electrolytically polished, washed in water, dried in air, and immediately placed in contact in the apparatus. It can be assumed that an invisible film of oxide formed on the crystal during this time. The crystals were heated at 500° to 520° for 15 minutes in an atmosphere of nitrogen from which oxygen had been removed by passing over hot copper. The apparatus was then cooled to room temperature and the following measurements made:

Crystals	Pull (g)	Estimated area of contact (sq mm)	Calculated strength (lb/sq in.)
(100)–(100)	520	0.017	41,800
(111)–(111)	580	.018	42,000

The crystals were heated in air at 200° until oxide films of a thickness of approximately 500 A had formed on the faces concerned. They were placed in contact in the apparatus and no adhesion between the crystals was obtained. They were then heated in contact in nitrogen at 500° to 520° for 15 minutes, cooled to room temperature, and the following measurements made. During the heating in nitrogen much of the color due to the oxide film disappeared and the surface became roughened.

Crystals	Pull (g)	Estimated area of contact
(100)–(100)	190	Not continuous
(111)–(111)	220	Not continuous

In order to determine the influence of heat alone on thin oxide films, a crystal which had been treated in air to form a striking color pattern was heated in a vacuum at about 10^{-4} millimeter of mercury for 30 minutes. The interference color pattern was converted to a pattern of rough and smooth regions. A faint reddish deposit could be seen on the walls of the vessel; this indicated that evaporation of the oxide had taken place. However, it is not believed that evaporation took place in nitrogen at atmospheric pressure, but that the loss of oxide in this case was due to slight solution in the copper.

INFLUENCE OF SURROUNDING ATMOSPHERE ON WEAR BETWEEN TWO DRY POLYCRYSTALLINE SURFACES

Method of Experiment

The essential parts of the apparatus used in these studies are shown in figure 3. The cylindrical steel rotor A, 1 inch in diameter and 1 inch in length, was fitted tightly by means of an arbor press onto steel shaft B, 1/2 inch in diameter and 15 inches in length. The upper end of the shaft B was held in the chuck of a drill press C and the speed of the press was controlled by varying a resistance in series with the armature windings of a direct-current motor. The copper sphere D was held in the steel yoke E by two set screws. The sphere was pressed against the rotor with a known force by means of a special T-balance. The yoke E was permanently screwed into a $\frac{3}{8}$-inch steel rod F which passed out of the glass vessel through the brass sleeve G. The cross arm H was silver-soldered to the brass sleeve G, and weights were applied to a balance pan at J. Counterweights were applied to the other end of the cross arm to compensate for the weight of the balance. The side arm K, at a right angle to the plane of the paper and shown as a circle on the diagram, fitted through an accurately machined brass bearing so that the whole system DEFGH rotated about an axis at a right angle to the plane of the paper. The rotor and

crystal were enclosed in a glass vessel having two large necks L, a gas inlet tube M, and a glass outlet tube N. The two rubber stoppers at the top of the necks L were made of neoprene. A gas-tight seal was maintained around the revolving shaft B by means of a rubber tube which fitted over the shaft and the brass sleeve as shown in the diagram. The bearing surface between the shaft and rubber tube was lightly lubricated with Dow Corning silicone stopcock grease. The rod F passed through a brass sleeve in the rubber stopper, and the joint was made vacuum tight by slipping a piece of rubber tubing over the brass sleeve and a large steel ring silver-soldered to the rod F. There was sufficient clearance within the brass sleeve for the rod F to move back and forth so that the sphere could be brought into contact with the rotor or moved about 1 centimeter away from it without contact between the rod F and the brass sleeve.

During the course of a series of experiments it was necessary to change the bearing surface of the copper sphere without exposing the system to the air. This procedure was accomplished by means of the $\frac{1}{16}$-inch-diameter steel wire P, which was attached to the shaft of the copper sphere D and passed through the rubber stopper at the top of the glass neck L. By raising or lowering the wire a new position on the sphere could be obtained. The wire was lubricated with silicone grease at the point where it passed through the stopper. The ability of all the joints to maintain a vacuum was shown by the fact that when the system was completely evacuated with a Hyvac pump and the pump was shut off from the system, a pressure of less than 1 millimeter of mercury was maintained for over 15 minutes. All rubber tubing was heated in boiling 15-percent potassium hydroxide solution.

The glass apparatus up to about 6 inches below the rubber stoppers was heated by a resistance furnace, the front of which contained two ports, one for observation and another for a spotlight. The interior walls of the furnace were coated with asbestos sheet, and a 100-watt projection lamp was mounted over a Pyrex glass window in the roof of the furnace. The lamp was arranged so that the light was reflected off the white walls to give diffuse illumination. The temperature was measured with a nitrogen-filled mercury thermometer. The chuck of the drill press and the upper ends of the glass necks L were cooled with rapid streams of air.

Commercial tank hydrogen was purifed by passage over copper wire heated to 450°, calcium chloride, Dehydrite, and Ascarite. The nitrogen-oxygen mixtures were prepared from water-pumped tank nitrogen and tank oxygen and were stored over water in glass vessels. The mixture was purified by passage over calcium chloride, Dehydrite, and Ascarite.

The copper spheres used in the experiments were polycrystalline and were mechanically and electrolytically polished in a manner similar to that used for the single crystals. The steel rotor was copper plated and surfaced down to the desired thickness in the following manner. The rotor

was mechanically polished with number 000 metallographic emery paper and the diameter was measured at nine separate points with a micrometer. After thoroughly degreasing in alcohol, ether, and water, a preliminary copper strike was made from a bath having the composition, 22 grams of cuprous cyanide, 38 grams of sodium cyanide, and 15 grams of sodium carbonate per liter of solution. The copper was plated at a temperature of 45° to 48° at a current density of 0.3 to 1.5 amperes per square decimeter for 10 to 20 minutes. The rotor was washed free of solvent and given a heavier plate from an acid sulphate bath containing 202.5 grams of hydrated copper sulphate and 48.8 grams of sulphuric acid per liter of solution. The bath was operated at 45° to 48° at a current density of 2 to 4 amperes per square decimeter for 1 to 3 hours, the conditions depending on the desired thickness. The rotor was then mechanically polished with metallographic emery papers numbers 1 to 0000 and electrolytically polished until the final desired thickness and surface finish were obtained.

The general procedure in making an experiment was as follows. The crystal and rotor were annealed in hydrogen at 400° for about an hour and the system was then cooled to the temperature at which the run was to be made. Between runs the drill-press chuck was moved up or down to change the position of contact at which the sphere pressed against the rotor, and the point of contact on the sphere was changed by pulling or pushing on the wire P. Thus new surfaces could be rapidly obtained without interrupting the experiment or in any way opening up the system to the air. Wear was measured by noting the time necessary for the first appearance of the steel on the rotor and the rate at which the steel surface increased. A crude estimation of friction could be obtained by noting the deflection of the steel rod F holding the sphere.

Results

The apparatus was heated for an hour at 420° in an atmosphere of hydrogen to insure complete reduction of any oxide. The temperature was then lowered to the desired point and the experiments were carried out in hydrogen or a mixture of nitrogen and oxygen. Although this section has been placed in the present order in this report for purposes of proper sequence in presentation, these experiments were the last to be conducted, and it has been possible to complete only experiments at 300°. The values of reported thrust are the forces pressing the two surfaces together.

In an atmosphere of hydrogen.- When a thrust of 200 grams was applied, the sphere firmly adhered to the rotor. When the rotor was slowly turned by hand, the sphere was carried along with the rotor and the shaft was bent to an extent which was later found to require a force in excess of 3000 grams. In order to break the weld it was necessary to pull perpendicularly to the surface. A chunk of copper, the size of the area of contact, was found adhering to the sphere. The chunk was firmly welded and it could not be scraped off along the original line of contact.

Similar welding occurred with thrusts as low as 30 grams, but below 30 grams the weld was usually broken by the restoring force of the steel shaft. With thrusts as low as 1/2 gram welding and subsequent tearing of the rotor surface occurred.

A thrust of 1/2 gram was applied, the rotor turned several times, and badly torn surfaces were produced on both the sphere and the rotor. The load was removed and the balance so adjusted that the sphere cleared the surface of the rotor by a small amount. As the rotor was turned, some of the projections from the torn surfaces touched and adhered so that the sphere was carried around with the rotor for a short distance before disengaging. Initial roughness in this experiment was not a factor in either friction or wear as the electrolytically polished surfaces were very smooth. Because of welding and tearing, however, the surfaces rapidly became roughened. The particles of copper removed from the one surface and welded to the other were sometimes $\frac{1}{2}$ millimeter high, and as the rotor continued to turn the roughness of the surface was increased.

By utilizing a copper thickness on the rotor of 0.0015 inch, a rotor speed of 80 rpm, and a thrust of 2 grams, it required 1 minute and 50 seconds for the first bit of steel to appear and 35 minutes to expose 0.031 square inch of steel. With a thrust of 15 grams in one instance it required 5 seconds to expose the first signs of steel and $6\frac{1}{2}$ minutes to expose 0.052 square inch. In another instance it required 10 seconds to expose steel and 4 minutes to expose 0.009 square inch of steel. It was impossible to make quantitative runs at higher thrusts because of the severe seizing already discussed. At the completion of a run the steel was exposed in large areas rather than in a continuous wear streak. Throughout any run the sphere continually adhered to the rotor and bent the shaft considerably before the weld was broken. Severe jolting and vibration of the entire apparatus was the outstanding characteristic of all runs made in hydrogen.

In an atmosphere of 500 parts of nitrogen and 1 part of oxygen.- After several runs had been performed in an atmosphere of hydrogen, the hydrogen was evacuated and a mixture of 500 parts of nitrogen and 1 part of oxygen was admitted and continuously passed through the system during the run. The sphere and rotor slowly oxidized throughout the experiment with the development of oxidation colors.

With thrusts below 150 grams no galling or adhesion was observed and the sphere rode along smoothly without any vibration of the shaft. The surfaces mated with the development of only a very slight roughness. With a thrust of 150 grams there was intermittent light sticking between the sphere and rotor but no noticeable increase in roughness. The presence of the oxide color films and a difference in the extent of oxidation of the wear streak and the remainder of the rotor made it difficult to distinguish the first appearance of steel. The following procedure was adopted to determine accurately when wear-through had occurred. A series of separate runs on different portions of the sphere and rotor was made for successively increasing times. At the completion of the experiments, 1:1 nitric acid was placed in the wear streaks and at once washed off. The acid removed

the oxide and a negligible amount of copper, and the difference in color between the steel and copper was very apparent. By utilizing this technique it was found that for a copper thickness of 0.0015 inch, a rotor speed of 80 rpm, and a thrust of 15 grams, the wear-through occurred between 90 and 190 minutes, and after 190 minutes only 0.006 square inch of steel was exposed. The sharp contrast between the rates of wear in hydrogen and the dilute oxygen mixture is strikingly brought out when the values of 5 seconds and over 90 minutes are compared.

INFLUENCE OF CRYSTAL PLANE ON WEAR THROUGH A FILM OF LEAD BY A COPPER CRYSTAL ROUGHENED BY ETCHING IN STEARIC ACID

Method of Experiment

An apparatus was constructed which was capable of measuring the rates of wear between a single crystal sphere of a hard metal and the plated surface of a soft metal under controlled conditions of thrust, speed, temperature, and liquid. A diagram of the apparatus is shown in figure 4. The cylindrical lead-plated copper rotor A, $1\frac{1}{2}$ inches in diameter and 1 inch in length, was fitted tightly by means of an arbor press onto an accurately alined steel shaft B, 1/2 inch in diameter by 7 inches in length. During an experiment the shaft B was held in the chuck of drill press C and the speed was controlled by driving the press with a direct-current motor containing a variable resistance in series with the armature windings. The single crystal sphere D was held in the steel yoke E and pressed against the revolving rotor A with a known force. The application of the known force was achieved by having the yoke serve as the stem of a T-shaped balance, the fulcrum of which was at the cross of the T. Weights were added to a balance pan F, which was connected to one end of the cross arm H by means of a spring G, and the thrust at the points of contact was calculated. The other end of the cross arm H was loaded with a counterweight J in order to balance the weights of the balance pan F and the spring G. In practice it was found that at low loads the balance was sensitive to weight changes of about 0.1 gram. The system of yoke E and rotor A was immersed in oil contained in a 600-milliliter beaker.

Relative rates of wear were determined as follows: The copper rotor was plated with lead, the copper crystal was pressed against the revolving rotor with a known thrust, and the wear streak was investigated with a magnifying lens or a microscope with a magnification of 60 situated outside the containing vessel. The first signs of the copper basis metal on the rotor were observed and the increase in area of exposed copper with time was estimated with the aid of a copper ruler placed in the solution alongside the rotor.

The lead plating solution was prepared from commercial Harshaw lead fluoborate plating solution, concentration-66 Baume and specification-106.

The actual bath used contained 239 milliliters of the commercial lead plating solution, 761 milliliters of water and 0.38 gram of LePage's liquid glue. The rotor was prepared for plating by polishing with metallographic emery paper number 0000 and degreasing the surface with alcohol, ether, and water. The plating cell was a cylindrical glass dish and a cylindrical lead anode, 2 inches removed from the sides of the rotor. The bath was operated at 2 amperes per square decimeter and a potential of approximately 0.5 volt for 10 minutes. The estimated thickness of the coat was approximately 0.0005 inch. In any one series of runs the thickness was constant since the same plate was used for many measurements by simply raising or lowering the height of the chuck of the drill press. The plating conditions were always the same so that direct comparisons between runs could be made. A uniform rate of revolution of 77 rpm was used in all experiments. This rate corresponds to a linear velocity of 362 inches per minute.

Because of its simplicity the apparatus shown in figure 4 was very satisfactory for initial exploratory experiments to determine the most satisfactory conditions of plating thickness, speed of revolution, and thrust. However, it was found that the apparatus shown in figure 5 and described under INFLUENCE OF SURROUNDING ATMOSPHERE ON WEAR THROUGH A FILM OF LEAD BY A COPPER SPHERE was much more satisfactory for all experiments, especially those conducted with thrusts of about 2000 grams. Both types of apparatus gave similar results.

Results

It has been shown in NACA TN No. 982 that different planes of a copper single crystal are roughened to different extents upon etching in stearic acid and air at 200°. As a preliminary step to studying the effect of crystal plane under conditions of simultaneous etching and wearing action, it was decided to determine first the effect of crystal plane under wear conditions in an inert medium after previous etching in stearic acid. A copper single crystal was mechanically and electrolytically polished and etched in stearic acid and air at 185° for 10 hours by alternately raising the crystal above the level of the liquid and lowering it below the surface at a rate of 15 times per minute. At the end of this time the crystal exhibited excellent preferential roughening of the surface. The (110) regions were very rough and consisted of a series of ridges which resembled the surface of a file, whereas the (111) regions were almost as bright and smooth as the original electropolished surface. Several crystals prepared in an identical manner were used in the experiments and all gave similar results.

During the course of determining the most suitable thickness of electrodeposited lead and the proper speed of the rotor, many qualitative experiments were conducted. In all experiments the rough (110) face wore through to the copper basis metal at a much greater rate than the smooth (111) face. Only a few conditions were used for quantitative measurements. These results were checked several times and are given in table II.

TABLE II

EFFECT OF CRYSTAL PLANE OF A COPPER CRYSTAL PREVIOUSLY ETCHED IN STEARIC ACID AND AIR AT 185° ON RATE OF WEAR THROUGH A LAYER OF ELECTRODEPOSITED LEAD IN MINERAL OIL IN AIR

Thrust (g)	Time necessary for first signs of copper to appear (min)	
	(111) face (smooth)	(110) face (rough)
200	3600	15 to 20
400	180 to 240	----
2000	20 to 35	1 to 3

The rate at which the copper basis metal was exposed is shown in figure 6 for a thrust of 2000 grams.

The lead wearing surface under a thrust of 200 to 2000 grams rapidly became discolored and passed through the colors red, blue, purple, and gray when the smooth (111) face was bearing against it. A continual cloud of tiny black particles poured from the wear streak and the mineral oil soon became quite murky. In the case of the (110) face at high loads the copper wore through the lead so rapidly that no signs of discoloration were visible on the lead. However with thrusts of about 100 to 200 grams a similar tarnishing of the lead wearing surface was noted.

INFLUENCE OF SURROUNDING ATMOSPHERE ON WEAR THROUGH A FILM OF LEAD BY A COPPER SPHERE

Method of Experiment

A diagram of the apparatus used for measuring wear in a controlled atmosphere is shown in figure 5. The containing vessel A was a 600-milliliter beaker, the lip of which had been removed by means of a glass cutting wheel. The copper rotor B, $1\frac{1}{2}$ inches in diameter and 1 inch in length, was fitted tightly by means of an arbor press onto a steel shaft C, 1/2 inch in diameter and 7 inches in length. The steel shaft C passed through a sleeve in the large rubber stopper D and was attached to the chuck of a drill press E. A gas-tight fit was obtained at the bearing surface by slipping a small piece of rubber tubing F over the sleeve and shaft and lubricating the turning surface with silicone grease. The copper sphere G was clamped in the yoke H by means of two set screws which fitted into small holes in the

crystal. The long, $\frac{1}{4}$-inch-diameter sidearm J to the yoke H fitted through the long, tight-fitting sleeve K, and the height of the crystal was regulated by means of the set screw ring L. The force with which the sphere pressed against the rotor was adjusted by varying the load M. The force was applied to a sidearm, shown in the diagram as a dashed circle at the top of the shaft J. Gas entered the vessel through N, passed through the liquid and out through P. Air was prevented from diffusing back into the system by operating under a slight positive pressure. In order to protect the rubber stopper from the action of the oil, it was painted with Dow Corning DC 933 high temperature insulating varnish and cured for several days slightly below 100°.

Dissolved oxygen was removed from the white mineral oil by heating the oil to 180° and bubbling hydrogen through the liquid. A slow stream of hydrogen was passed through the system until the oil was transferred to the apparatus. Prior to an experiment it was necessary to expose the oil to the air during the process of pouring the oil from an Erlenmeyer flask into the apparatus. The oil was slowly poured down the sides of the vessel to prevent undue admixture with the air by splashing, and the system was immediately flushed out with hydrogen.

The rotor was plated with lead in the same manner as described under INFLUENCE OF CRYSTAL PLANE ON WEAR THROUGH A FILM OF LEAD BY A COPPER CRYSTAL ROUGHENED BY ETCHING IN STEARIC ACID. The thickness of lead was approximately 0.0005 inch and the rotor was operated at 77 rpm.

Results

Electrolytically polished polycrystalline sphere.- In air the rate of wear under all thrusts was quite slow, varying in the range of 20 to 35 minutes for the first appearance of copper under a thrust of 2000 grams to 3 to 4 hours under a thrust of 400 grams whereas no signs of copper were visible after 6 hours at 200 grams. At the commencement of a run the sphere pushed aside some lead to form a smooth, clean lead wear streak, but within 1 minute the streak had become discolored and the lead wearing surface passed through the colors red, blue, and purple and finally assumed a dark gray to black color. During the course of the run the copper rode on the colored surface and a continual cloud of tiny black particles poured from the wear streak. After some time a tiny spot of copper appeared near the center and the spot grew into a fairly even fine line of exposed copper which ran all around the rotor. The streak would generally widen with continued wear. In some instances the process was not quite so simple and the first few spots of exposed copper on the rotor were smeared over with lead on subsequent revolutions.

In hydrogen no colored films formed on the wear streak during the experiments. The first signs of copper were visible in about 30 seconds under a thrust of 2000 grams and in about 1 to 2 minutes under a thrust of

400 grams. In less than 1 minute after the first signs of copper were visible, the entire wear streak contained a small line of exposed copper.

The results showing the effect of atmosphere on the rate of wear are listed in table III. The rate of wear of the lead-plated rotor by an electrolytically polished copper sphere under different conditions of load and atmosphere is shown in figure 7. The results also apply to the rates of wear of a (111) face of copper previously etched in stearic acid, since the etched (111) face and an electrolytically polished surface gave identical results.

TABLE III

EFFECT OF ATMOSPHERE ON RATE OF WEAR OF A LEAD

PLATE BY COPPER IN WHITE MINERAL OIL

Wearing surface	Thrust (g)	Minutes necessary to give first sign of exposed copper	
		In air	In hydrogen
Polished polycrystalline	200	Greater than 3600	------
Polished polycrystalline	400	180 to 240	1 to 2
Polished polycrystalline	2000	20 to 35	0.5

MISCELLANEOUS EXPERIMENTS

Influence of Crystal Plane on Recrystallization during Heating and Rapid Cooling

An electrolytically polished crystal of copper was heated to an orange-red color in the oxidizing flame of a bunsen burner and immediately dropped through a height of 2 feet into an 8-inch column of water. The crystal was covered with a thin black coating which scaled off in irregular spots. After standing at room temperature for 40 hours, it was mechanically polished and then electrolytically polished for 20 minutes. It was electrolytically etched for 5 minutes and the customary etch pattern was obtained except that many small crystals had formed in square regions at each of the (100) poles. At this depth of etching no small crystals were visible in the other regions. The crystal was sawed in half by means of a jeweler's saw and the flat was mechanically polished, electrolytically polished, and electrolytically etched. After inspection under the microscope, it was estimated that the polycrystals extended to a depth of about 1 millimeter.

Effect of Sunlight on Atmospheric Tarnishing of Copper Crystals

Several experiments were conducted on the atmospheric tarnishing of copper single crystals in the presence and absence of direct sunlight. The results may be briefly summarized as follows.

Advanced preferential tarnish films formed in 3 to 4 days when crystals were suspended in direct sunlight outside the laboratory window. Previous annealing in hydrogen at 550° had no appreciable effect on the rate. Tarnishing always occurred most rapidly on the side of the sphere which was exposed to the direct sunlight. A crystal suspended in the laboratory with no access to direct sunlight tarnished in 40 days to the same extent as crystals exposed to direct sunlight in 3 to 4 days. The tarnish films formed preferentially with crystal plane but by no means as striking as crystals exposed to direct sunlight. Crystals exposed to sunlight behind a pane of glass either inside the laboratory or outside the laboratory window tarnished in a very preferential manner and at a rate which was intermediate between tarnishing in direct sunlight and tarnishing with no access to direct sunlight.

DISCUSSION OF RESULTS

This discussion should be considered from the viewpoint of first obtaining information on the most elementary system and then working toward systems of increasing complexity.

STATIC FRICTION

The coefficient of static friction between metals in air is generally below 1. Shaw and Leavey (reference 2) obtained coefficients of static friction as high as 2.3 for copper and 3.1 for aluminum when the metals were annealed in a vacuum and the measurements carried out in a vacuum. Holm and Stormer (reference 3) found that powerful adhesion occurred between metals heated to a high temperature in a good vacuum. The adhesion was maintained in the presence of a rare gas, hydrogen, and nitrogen, but disappeared on the introduction of oxygen. Bowden and Hughes (reference 4) obtained coefficients of dynamic friction near 5 for metals heated to a high temperature in a good vacuum. The highest value was 30, which was obtained for gold sliding on gold at 600°.

When one crystal sphere standing in air was placed in contact with another, the coefficient of static friction was below 1 and only a very faint scratch could be seen on the lower surface. Apparently the top

crystal rode along on a film of oxide and no appreciable metal-to-metal contact was obtained.

In attempting to measure friction between bare metals, it should be emphasized that the ordinary methods of cleaning a surface and heating in a vacuum do not remove the protective layer of oxide unless the heating is carried out at a sufficiently high temperature to cause evaporation of the metal. Heating in a vacuum may cause some of the oxide to dissolve in the metal or to evaporate but the amount of oxide remaining on the surface is still unknown. In fact there is no completely satisfactory method of obtaining a clean metal surface free of both oxide and adsorbed gas. The best that can be done at present is to approach as closely as possible to a clean surface, specifying the method of preparation and taking into consideration in the interpretation the possible influence of contaminants.

Since the glass apparatus used in the friction measurements must be opened frequently for setting and repolishing the crystals and since the simplest method of applying a load to the top crystal was by means of a shaft extending through the walls of the vessel, it was not attempted to carry out the measurements in a high vacuum, but the simple apparatus as described was used. It is hoped to supplement later the present measurements with those made between surfaces which have been heated by electrical induction until evaporation of metal is obtained. As previously described, two methods were used in obtaining an approach to metal-to-metal contact. The first method consisted in heating the crystals, not in contact, in hydrogen at about 500° and then cooling to room temperature in hydrogen and placing in contact. It is assumed that heating in hydrogen gives an oxide-free surface and that hydrogen does not form a compound with copper but only an adsorbed film. However it should be emphasized that the exact chemical effect of hydrogen on copper, or on any metal, is not definitely established, especially as far as the influence which the adsorbed film has on metal-to-metal contact. Any gas which can give the high heat of adsorption on tungsten as found by Roberts (reference 5) and the striking gas-structure effects on nickel as found by Davisson and Germer (reference 6) in electron diffraction experiments should not in the final analysis be considered an inert gas or as one giving a bare metal surface. In this first method the oxide film formed by standing in air was reduced, and the water vapor produced was carried off in the excess hydrogen which was passed continuously through the apparatus. The final surfaces were always covered with a film of hydrogen. Furthermore, as the crystals cooled down to room temperature, before being placed in contact, their surfaces may have been slightly oxidized by oxygen from two sources: (1) as an impurity in the hydrogen purified by passing over a long tube of hot copper, and (2) from diffusion of a small amount of air into the apparatus through the small space between the shaft and the neck of the ground-glass joint. Diffusion was reduced to a small amount by having a rapid stream of hydrogen pass outward through this space. Another difficulty in this method was the variation in the force

with which the two crystals were placed in contact. However, with this method, the horizontal pull required to disengage two crystals placed in contact along the (100) face was on the average definitely higher than that required along the (111) face. The failure to obtain satisfactory reproducibility was attributed to the possibility of slight oxidation and to the variation in the force with which the crystals were placed in contact.

In order to remove the possibility of the formation of a thin oxide film, the two crystals were first placed in contact, then heated in hydrogen and cooled to room temperature before the measurements were made. This method had the further advantage that the two crystals were pressed together always with the same force, equal to the weight of the upper crystal, as the thin oxide film was reduced and metal-to-metal contact established. It had the disadvantage of placing the metals in contact at 500° at the same time that reduction took place, thereby giving the atoms additional mobility and possibly increasing the welding action. However, both the (100) and (111) faces received the same treatment so that the results should be comparable. Furthermore, results of the same order of magnitude were obtained when the crystals were placed together after heating in hydrogen and cooling as when placed together before heating and cooling, except that in the latter case the results were more reproducible.

A source of difficulty in both methods was the setting of the two crystals so that the plane of the flat face on the lower crystal and the direction of pull were accurately in the horizontal plane. The digging-in is greatly influenced by the force normal to the surface, and if the direction of pull is slightly downward relative to the flat face, the component of the force normal to the face will be appreciable when the total pull is above 500 grams. In these measurements the apparatus was so arranged that the direction of pull was slightly upward, by an angle of 2° to 3°, to the flat surface.

As shown in table I the coefficient of static friction as determined by this second method was over 100 for pairs of (100) planes and approximately 25 for pairs of (111) planes. The term coefficient of friction as used herein should be qualified somewhat, since the process in the case of (100) faces seems to consist of several consecutive steps as described in the following explanation of the reason for the greater friction on the (100) face.

It has been known that when a copper single crystal was placed under sufficient stress, slip occurred along the (111) planes, which are the planes having the greatest density of atoms and are consequently the farthest apart. When flat (111), (100), and (110) faces of copper and silver crystals were punched or scratched with a steel pin, it was found in these experiments that very striking slip lines were observed on the surface adjacent to the scratch. The electrolytic method of polishing the surface makes these lines especially striking. On the (111) planes

three sets of slip lines make angles of 60° with each other, and on the (100) planes two sets make angles of 90° with each other. Elam (reference 7) states that in tensile tests on copper single crystals the greatest movement occurs by slip along the (111) planes. In the friction experiments described in this report striking slip lines making angles of 60° on the (111) faces and 90° on the (100) faces were visible.

As indicated by slip lines, all four sets of (111) planes are involved during friction measurements along either (111) or (100) faces. On a (111) face there are three (111) planes which make angles of 71° with the surface and one (111) plane which is parallel to the surface. Since the minimum stress is required to cause shear along the (111) plane, it would be expected that friction would be least along the (111) face. Little or no tendency to dig in would be expected, and this was borne out by these experiments.

On a (100) face four sets of (111) planes make angles of 55° with the surface, and one set of (111) slip lines is at right angles to the direction of pull and another set is parallel to the direction of pull. When the force was applied to the upper crystal, stress was applied to the metal in and adjacent to the welded joint. The weight of the crystal acted down and the pull acted horizontally. A slight movement took place as the metal sheared downward and upward along (111) planes. Because of this shearing motion along a plane not parallel to the surface the top crystal dug into the bottom one. The area of contact was increased, and an interlocking of the steps thrown up on the surface was apparently obtained. This effect is analogous to rubbing together the ends of two stacks of cards, the plane of one stack of cards being slightly inclined to the other. The increased area of contact and interlocking of the sections increased the resultant friction. On the other hand the action which takes place when two (111) faces are in contact is analogous to the sliding of one stack of cards over another when the faces of the cards are in contact and force is exerted parallel to the plane of the cards. In the case of friction along the (100) faces the shearing and interlocking may explain the initial slight movement and final failure to be dislodged at 4000 grams. The larger groove seen under the microscope in the case of the (100) faces confirms the interlocking and greater area of contact in this case.

In the case of polycrystalline surfaces, when the crystals were heated to 520° in contact in hydrogen, the coefficients ranged from 36 to 56, which range is intermediate between the low values for (111) faces and the high values for (100) faces. This variation seems reasonable since the orientations of the grains in contact would vary with each run. The coefficients never reached the high values attained for (100) faces, but this is probably due to the fact that continued slip downward along (111) planes was blocked by neighboring grains of different orientations and the area of contact increased only a limited amount.

The effect of oxygen in the experiments with single crystals was striking. As previously emphasized, the coefficient of friction of crystals exposed to the air was about 1. In this case the oxide film was not thick enough to produce interference colors; this means that it was less than 400 A. The fact that crystals placed in contact, after being heated in hydrogen in order to remove the oxide film, gave coefficients of the same order of magnitude as those heated in contact indicates that either no oxide film formed after heating in hydrogen or that it was so thin that the top crystal cut through it and formed metal-to-metal contact. When two crystals were first heated in contact in hydrogen at 520° and then oxidized in air at 300° for 3 minutes, the coefficients were greatly reduced compared with that for oxide surfaces. The deep oxidation produced at this temperature probably weakened the weld, and also the first slight movement due to slip transferred the upper crystal to an oxygen-covered surface where strong adherence was not obtained. In experiments in which the crystals were placed in contact before being heated in hydrogen, the thickness of the original oxide film up to a certain point did not seem to affect the coefficients. The same results were obtained when the initial oxide film, before being heated in hydrogen, was of a thickness of 1000 A or when it was an invisible one formed by letting the crystal stand in air at room temperature.

It was impossible by examination with the microscope to determine accurately the area of contact in the friction measurements since the complete outlines of the region were destroyed by the sliding of the upper crystal. However, a fair estimate of the actual area in friction measurements can be obtained from other experiments. In experiments concerned with the vertical force required to disengage two crystals, the crystals were placed together and heated in the same manner as in the friction experiments but the initial regions of contact were not destroyed by the sliding crystal. Therefore the regions of contact at the start should be roughly the same for the two types of experiment if the same load and type of surface were used. In examining the regions of contact for the vertical-force experiments, it appeared that continuous contact was established throughout, and this was confirmed by the fact that the tensile strength, as calculated from the vertical force and area of contact, was of the same order of magnitude as the strength of polycrystalline copper (reference 8). The area of contact could hardly have been greater than that defined by the outside dimensions of the disrupted regions, and the strength of annealed single-crystal copper would not exceed that of polycrystalline material. Therefore it seems that continuous welding over the region defined by a disrupted surface was obtained when the crystals were placed in contact and heated by the method prescribed in both the friction and vertical-pull measurements.

It was only possible to devote a relatively brief amount of time to the vertical-pull experiments. They were carried out primarily to obtain information on the general order of magnitude of adhesion between the two different sets of faces in the friction experiments. A complete comparison

cannot be made of the adhesion between crystals in the friction and vertical-pull experiments since the loads pressing the crystals together were 40 grams in the friction experiments and 75 grams in the vertical-pull experiments. There was only a slight difference between the average values of the vertical pull required to separate (100) and (111) faces. No great difference would be expected in terms of slip mechanism. As previously pointed out, four sets of (111) planes intersect the (100) face at angles of 55° and three sets of (111) planes intersect the (111) face at angles of 71°. It would be difficult to calculate the difference in the vertical forces required to disengage the two sets of crystals if all the possibilities for shear and for blocking of shear were taken into consideration.

Some information on the influence of temperature on the area of contact in the vertical-pull experiments was obtained. The tensile strength, or the ratio of pull to area of contact, remained approximately the same for all methods of placing the crystals in contact. The areas of contact seemed to vary somewhat with the temperature at which the crystals were placed together, being greatest when the crystals were heated in contact in hydrogen at 520°, less when placed in contact at 300°, and still less when placed in contact at room temperature after heating in hydrogen. Too much emphasis should not be placed on this conclusion, since traces of oxide entering the apparatus and oxidizing the surface slightly before the crystals were placed in contact both at 300° and room temperature may have played some part in the reduction of the area of contact. Undoubtedly the increased mobility at the higher temperatures was in part responsible for greater areas of contact. Since the coefficients of friction as determined by placing the crystals in contact before and after heating in hydrogen were of the same order of magnitude, it would appear that the final area of contact in the friction measurement was independent of the temperature at which the crystals were placed together. This fact is in contradiction to the influence of temperature on area of contact in the vertical-pull experiments, but the difference may be explained by the possibility that in the friction measurements when the crystals were placed together after heating in hydrogen, the initial area of contact was greatly increased by the first horizontal movement and by digging-in.

The effect of heating in nitrogen crystals which had been slightly oxidized by standing in air was to increase adherence appreciably. As would be expected, the thicker the initial oxide film, the lower was the adherence. When the film was thick enough to give interference colors, heating in nitrogen caused the loss of color. The increased adherence was probably caused by loss of oxide due to partial solution in the metal and to migration of copper atoms through the remaining oxide film due to the increased mobility with high temperature. The change in adherence with the variation in thickness of the oxide film suggests that up to a certain point adherence is dependent on the thickness of the contaminating film through which the metal atoms must migrate. Although copper oxide will evaporate from a copper surface heated in a vacuum at 500°, the loss of oxide when the crystals were heated in nitrogen at atmospheric pressure

was probably due to slight solution of the oxide in the metal. Elam (reference 9) has proposed that copper oxide at high temperatures migrates through massive copper by solution of oxygen in the metal and subsequent appearance of oxygen on the surface as oxide in another place.

It should be emphasized that the primary purpose of the experiments described in this section on static friction was to determine whether static friction varied with crystal plane, and the greater part of the time available was devoted to this specific purpose. The other experiments on the measurement of such quantities as the area of contact and influence of temperature were carried out to obtain only the order of magnitude of quantities which would aid in understanding the mechanism of static friction, and time was not available for a complete study.

WEAR

With the static-friction measurements serving as basic experiments to show the influence of oxide film and crystal plane on the simplest type of friction, experiments were carried out to obtain a preliminary picture of the influence of these factors on wear between rubbing parts.

The experiments on wear between two dry polycrystalline surfaces of copper have shown that very strong adherence was obtained between moving parts when the oxide was removed. If the smallest amount of oxygen, too small to be detected by ordinary methods, was present in the gas, the wear was greatly reduced, this result indicating that the welding action was prevented by a thin oxide film. It is exceedingly difficult to remove all oxide from metal surfaces and to maintain them in a completely bare condition while measurements are being made. In order to obtain a true picture of the processes of welding, friction, and wear, it is essential that measurements be made on completely bare metal surfaces. Additional measurements of wear between like surfaces and unlike surfaces should be made in the range of room temperature to 200°.

The strong adherence between oxide-free surfaces must result from the same forces which cause solidification and give rise to a definite crystal structure in the solid state. The lack of adherence between oxide-covered surfaces may be due to the following causes. Adsorbed gas may prevent good adhesion, but this effect is expected to be small. The tensile strength of the oxide is probably considerably less than that of the metal but is not sufficiently small to explain the poor adherence. The oxide consists of two different kinds of atoms, and the chances of matching positions for a continuous lattice when the surfaces are placed together are less than the chances with metal surfaces. The failure to match positions would prevent strong adhesion. Since the oxide formed from a given amount of metal has a greater volume than the metal, the oxide is strained and, after an appreciable thickness is attained, probably becomes disengaged from the metal.

Roughness of the harder metal increases the rate of wear of the softer metal in moving parts. It was shown in reference 1 that etching by some oils roughened some crystal faces and others remained relatively smooth. One part of the present investigation was concerned with the influence of plane on the rate of wear through a film of lead by a copper crystal roughened by etching in stearic acid. A crystal given uniform treatment in stearic acid caused wear in mineral oil at a rate which was dependent on crystallographic direction. Under a thrust of 200 grams the rough (110) face wore through the lead film approximately 200 times faster than the smooth (111) face which had a rate of wear about equal to that of an electrolytically polished surface.

The results concerned with the influence of surrounding atmosphere on the rate of wear through a film of lead by a copper sphere showed that the rate of wear in a lubricant free of dissolved oxygen was much greater than the rate of wear in a lubricant containing oxygen. When the lubricant was squeezed out and the surfaces came in contact, the oxide film acted as an additional lubricant and wear preventive. Lead oxide was worn away since a continual cloud of tiny black particles streamed from the wear streak. However, in the absence of oxygen the particles which were removed from the streak were of shiny lead and were much larger.

If the presence of an oxide film plays a substantial role in preventing metal-to-metal contact even in the presence of a lubricant, as these experiments suggest, it would be expected that bearings made of silver, gold, or platinum would be likely to produce seizure at elevated temperatures because of the low decomposition temperature of their oxides.

MISCELLANEOUS EXPERIMENTS

A few miscellaneous preliminary results have been described. It is significant that a process such as recrystallization was influenced to a depth of 1 millimeter by the orientation of the metal at the surface. Additional experiments must be conducted to obtain a satisfactory explanation of this effect. Since the crystal was heated in an oxidizing flame and the (100) face on which recrystallization took place is the face which oxidizes the most rapidly, it seems that oxidation may be a controlling factor. It is interesting in the electrodeposition of copper onto a copper crystal from a copper sulphate-sulphuric acid bath that polycrystals formed on the (100) face at medium current densities whereas the deposit in other regions was monocrystalline. This process of recrystallization may be important in machinery in which metal under a strain and exposed to corrosive gases is heated and cooled rapidly.

The influence of sunlight on the oxidation of copper crystals suggests that ultraviolet light accelerates oxidation. Evidence for this is given by the fact that the rate is reduced on the shady side of the crystal and also on a crystal placed behind a piece of ordinary glass. The influence

of sunlight on a crystal placed in a quartz vessel will be determined. The exact role of water vapor should also be investigated. These experiments are of interest in connection with an understanding of the mechanism of oxidation.

CONCLUSIONS

The relation of the strictly chemical results reported in NACA TN No. 1460 to the processes of friction and wear should be considered. It was reported that the rate of a number of chemical and electrochemical reactions with a large number of metals varied with crystal plane. The influence of the surrounding atmosphere on the oil-metal interface was also shown to be great.

The experiments described in NACA TN No. 1460 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. When all oxide was removed, values were obtained for static friction between single crystals of copper which were considerably higher than any previously reported, and the static friction was found to vary greatly with plane. The rate of wear between two dry polycrystalline surfaces reduced in hydrogen was very great, being decreased nine hundredfold at 300° when the metal was exposed to an atmosphere containing only 0.2 percent oxygen in nitrogen. Similarly when a copper sphere wore through a lead film in mineral oil at room temperature, the rate was 200 times faster in hydrogen than in air. The rate of wear due to roughness caused by etching varied with plane. These few results so far obtained indicate the great effect which crystal plane and thin films of oxide can have on friction and wear. A very low concentration of oxygen in the surrounding atmosphere, in the neighborhood of 1 percent, was effective in these experiments in preventing high values of friction and wear. Since most friction and wear experiments are carried out on surfaces from which the oxide films have not been completely removed, these results indicate that oxide films are responsible for a greater part of total lubrication than is generally realized. No information is now available in the literature on the influence of crystal plane on friction and wear, and a very small amount of information is available on the influence of oxygen and oxide films.

A few statements of opinion regarding the general significance of these studies with single crystals seem to be justified in this section. The first statement has to do with the necessity of obtaining basic information on a number of processes before any one particular surface process can be fully understood. The second is concerned with the practical uses to which the information already obtained may possibly be put.

The experience obtained in this investigation has definitely shown that before any one particular surface process can be fully understood, a number of processes must be understood. For example, friction and wear are dependent on oxide films formed on metal surfaces. The rate of formation of an oxide film appears to be dependent on the processes of diffusion and electron transfer. Electron transfer in turn is dependent on electrical conductivity of the oxide and on emission of electrons. Thus a true understanding of friction and wear may be dependent on an understanding of the behavior of electrons at metal surfaces. A study of the manifold properties of the unit crystals offers an excellent opportunity for the correlation of many apparently unrelated processes. Full advantage has in no way yet been taken of the possibilities of this method of study.

As regards the practical use of the information already obtained, it should be emphasized that the primary purpose of these studies was to obtain information on the mechanism of surface processes. At the same time it was intended to determine, insofar as studies of this type would allow, the possibilities for reducing corrosion, friction, and wear on a practical scale by a control of plane and atmosphere. Since only a few simple types of friction and wear have been studied, it still cannot be claimed that they could be reduced on a practical scale by a control of plane and gas, but it has now been shown that oxidation, corrosion, wetting, electrochemical processes, and a few types of friction and wear, all processes which are important to lubrication, vary in rate with both plane and nature of the surrounding gas. Therefore, the possibilities appear to be promising, and further experiments involving various combinations of the aforementioned processes with control of plane and atmosphere seem justified from a practical standpoint. At the present time, as previously pointed out in NACA TN No. 1460, the only deliberate case of industrial control of crystal face at surfaces is the addition of thiourea to obtain a very smooth copper electrodeposit. It was found by X-rays that the surface crystals were oriented, with the (100) planes parallel to the surface. As regards the influence which control of atmosphere may have on friction and wear, it appears from these experiments that the beneficial effect of oxide in reducing friction and wear is obtained from the first few percent of oxygen in the surrounding gas and that all oxygen in excess of this small amount largely increases corrosion without helping in other ways.

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Charlottesville, Va., November 23, 1945

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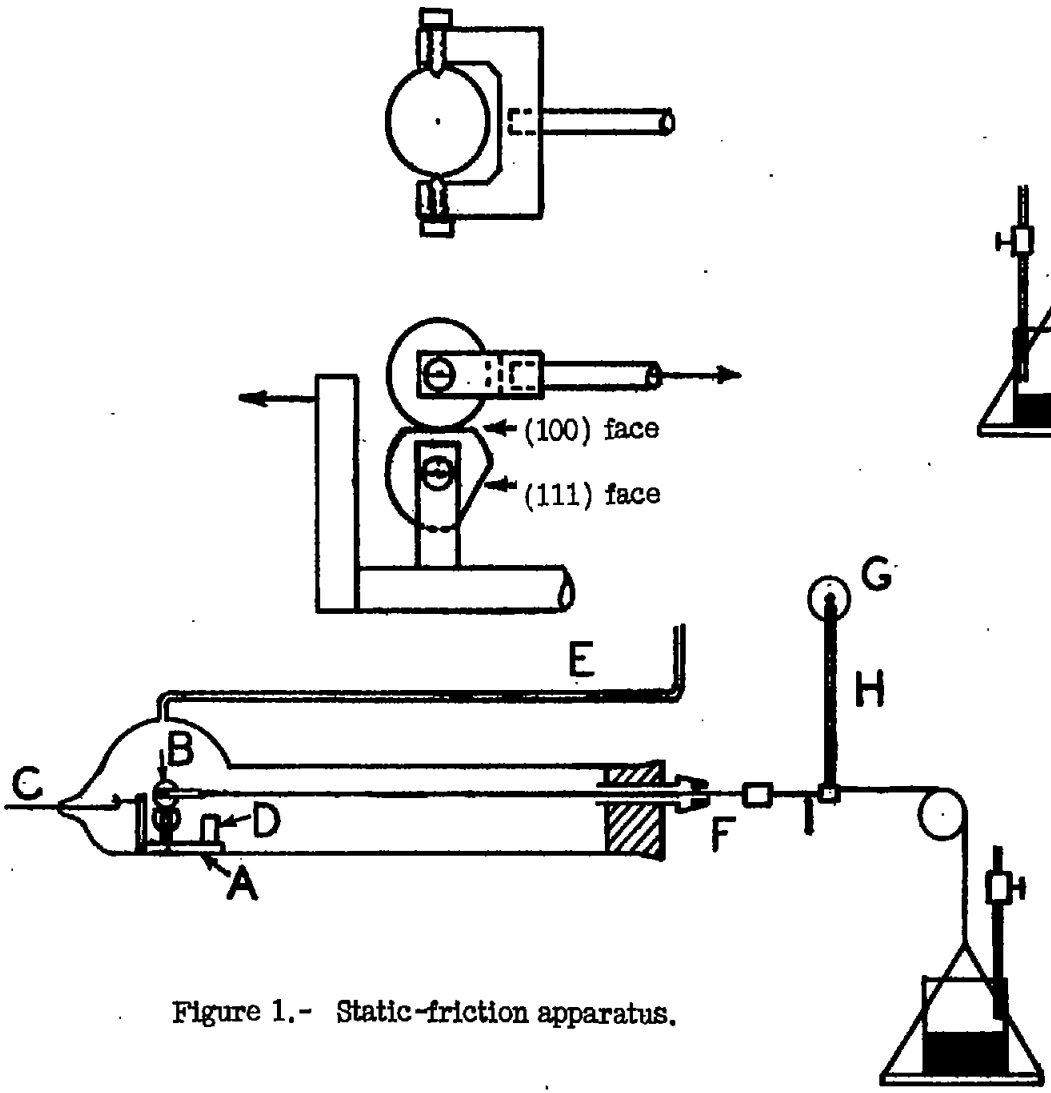

Figure 1.- Static-friction apparatus.

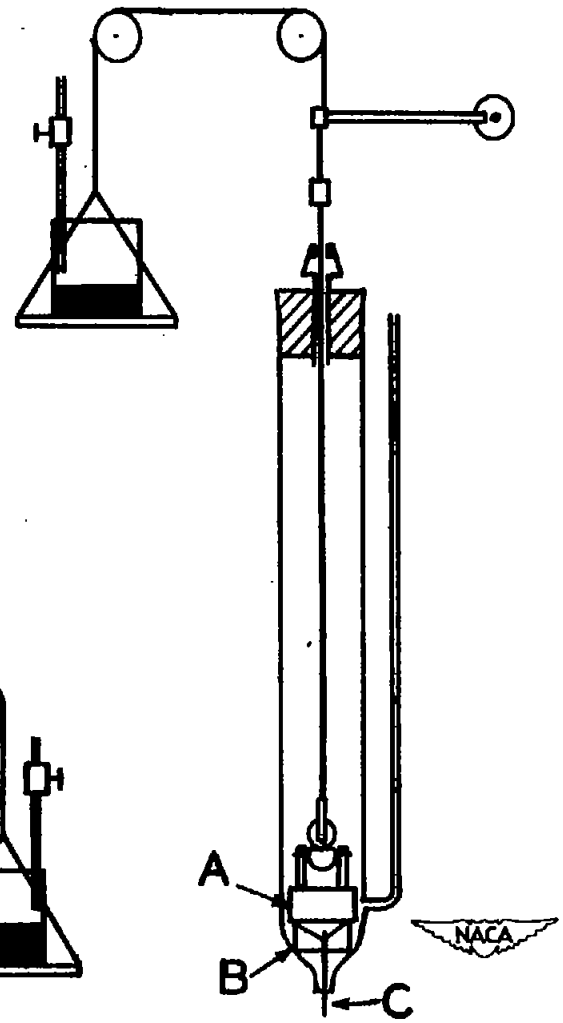

Figure 2.- Vertical-pull apparatus

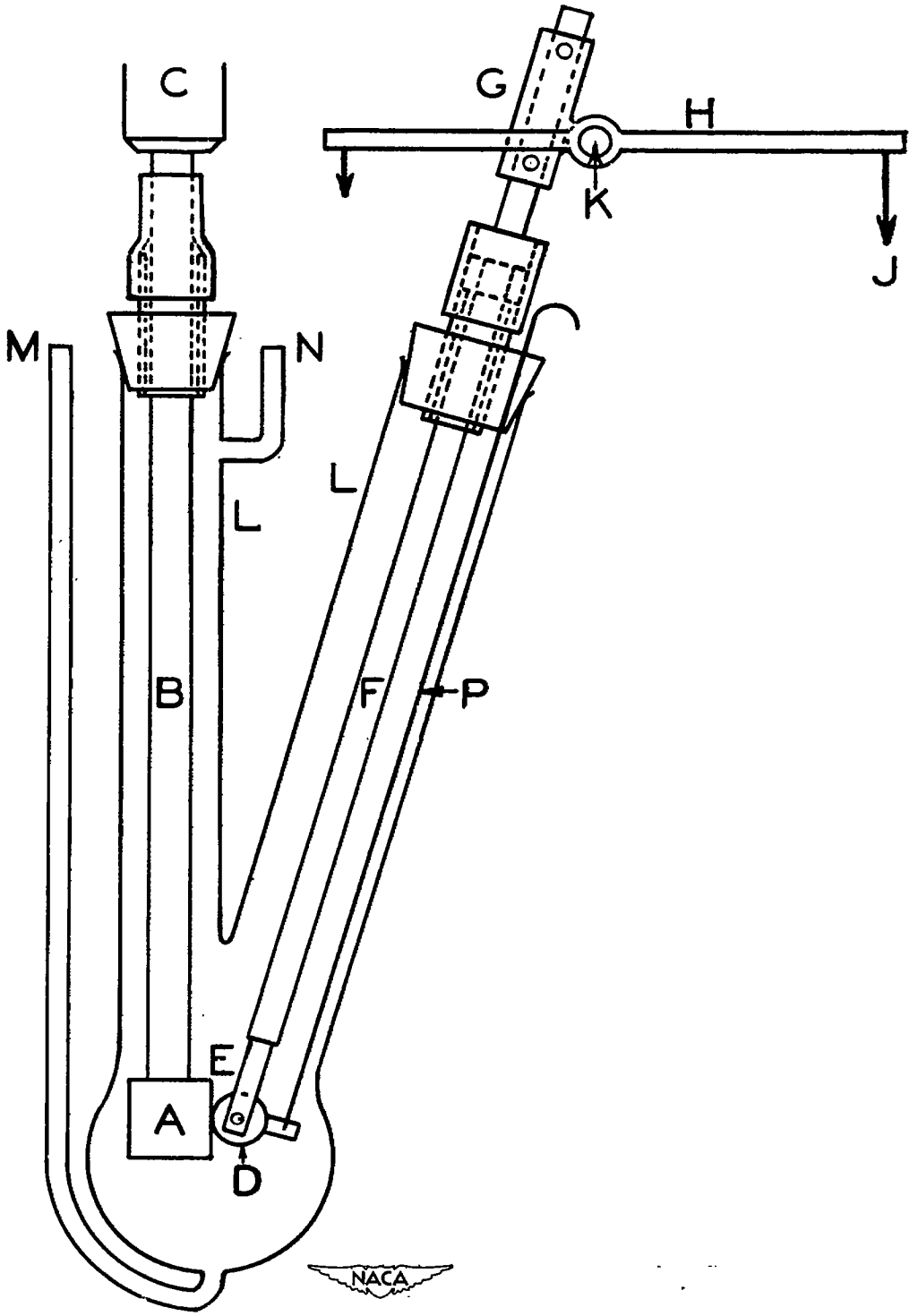

Figure 3.- Wear apparatus. Controlled atmosphere, high temperature.

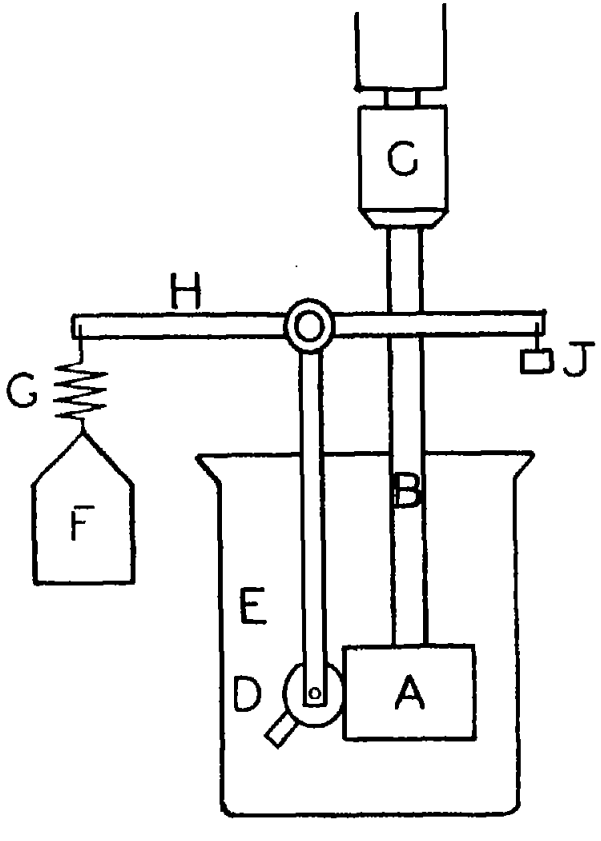

Figure 4.- Wear apparatus open to air.

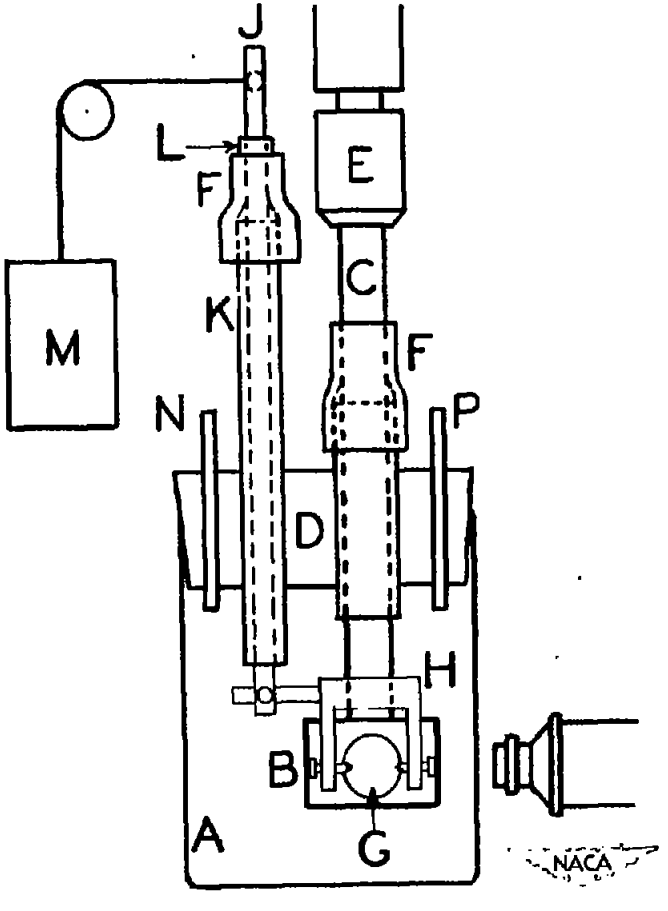

Figure 5.- Wear apparatus. Controlled atmosphere.

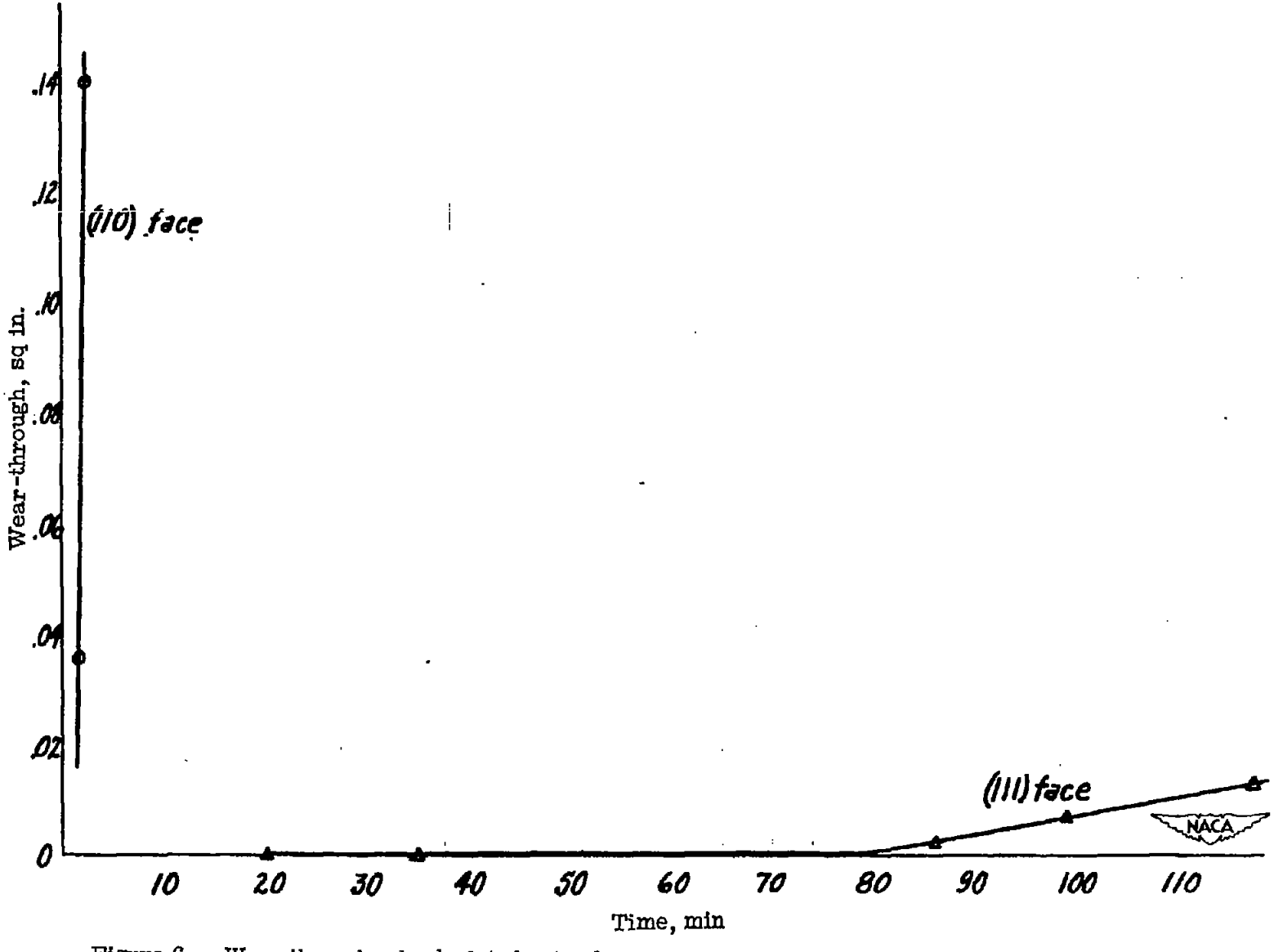

Figure 6.- Wear through a lead-plated rotor by a single crystal sphere of copper previously etched in stearic acid and air at 185° C. Lead thickness, 0.0005 inch; load on sphere, 2000 grams; rotor speed, 77 rpm; rotor diameter, 1.5 inches.

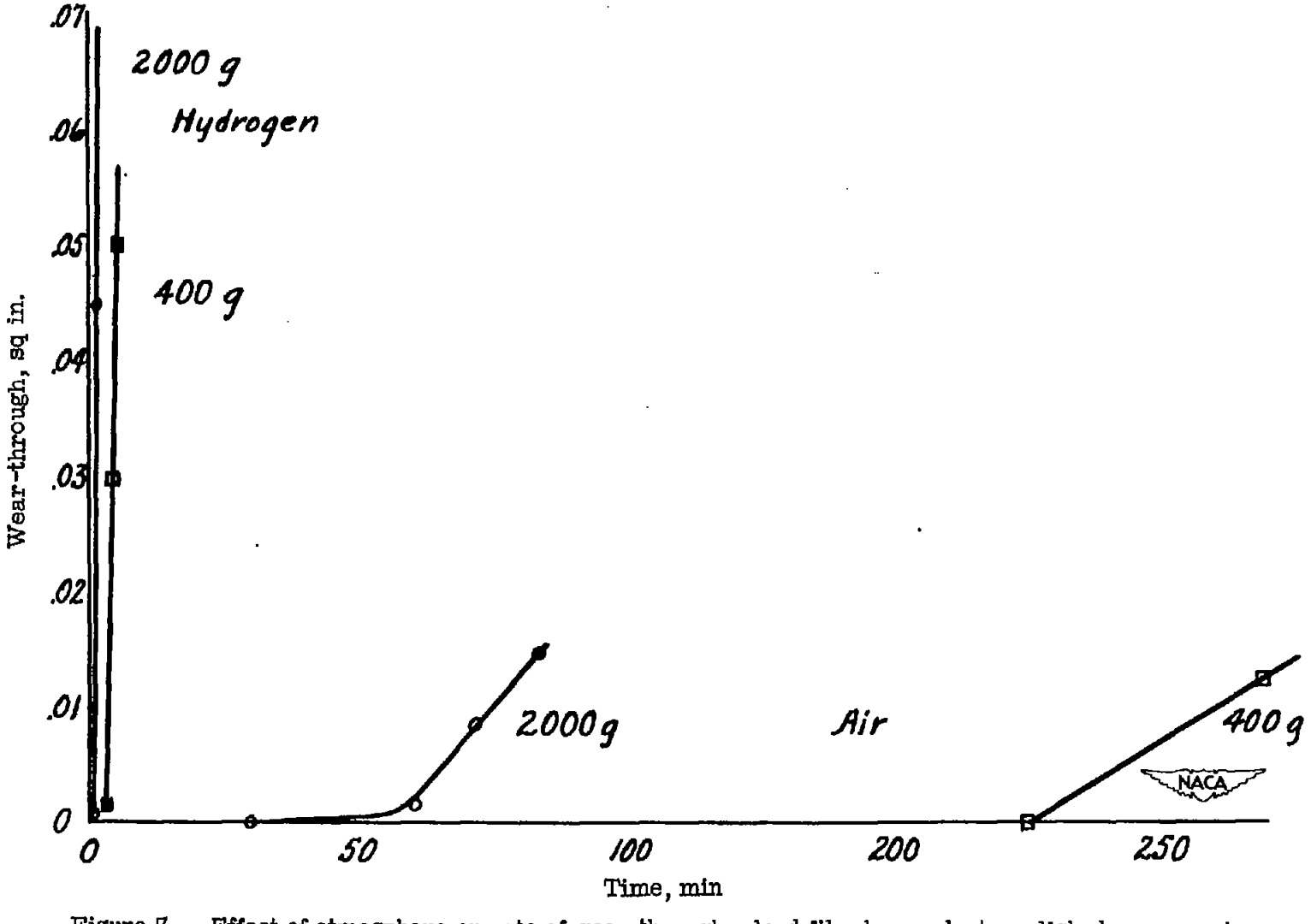

Figure 7.- Effect of atmosphere on rate of wear through a lead film by an electropolished copper sphere.