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I hereby recommend that the thesis prepared under my supervision by Harold John Kersten,

entitled Examination of Electrodeposited Metals and Alloys with X-Rays,

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

Louis T More

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EXAMINATION OF ELECTRODEPOSITED METALS AND ALLOYS WITH X-RAYS

A dissertation submitted to the

Graduate School
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1938

by

Harold John Kersten
B. S. University of Wisconsin, 1923
M. S. University of Wisconsin, 1924
M. A. University of Chicago, 1926.

INTRODUCTION

This dissertation consists of eight papers which have been separately published in several journals.

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AN ADJUSTABLE LEAK FOR X-RAY TUBES

The Review of Scientific Instruments, volume 2,
number 7, page 377, July, 1931.

The adjustable leak described is suited for use with gas x-ray tubes which are to be operated at less than 50 Kv. It consists of an ordinary steel sewing needle, A, Fig. 1, which is moved back and forth in a hole B when the screw C is rotated by means of the handle D. The screw slides on two steel pins E which are fastened to the cone of the ground joint F. In order to fasten the needle to the screw, the eye end is heated and bent into a loop through which a screw is passed as is shown in Fig. 1 at G and in the details shown in Fig. 3. All parts are made of brass except the needle and the two steel rods on which the screw slides. The parts which are permanently attached to each other are heated and 'sweated' together, using ordinary solder. To prevent the ground joint from leaking, cock grease is placed in the groove at H, Fig. 1.

The high pressure side of the leak is not connected directly to air at atmospheric pressure but is connected to a 'fore-vacuum' of about two liters capacity which contains air or carbon dioxide

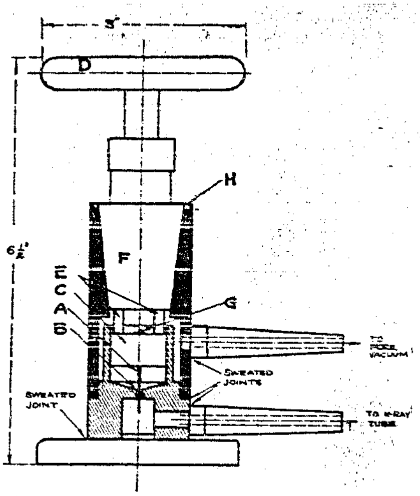
5"
D
H
$6\frac{1}{2}$"
F
E
C
A
B
G
TO FORE VACUUM
SWEATED JOINTS
SWEATED JOINT
TO X-RAY TUBE

Fig. 1.

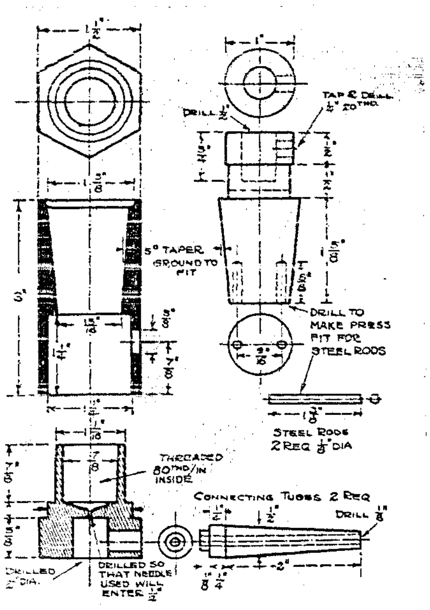
5° TAPER GROUND TO FIT
TAP & DRILL 1/4" 20 THD.
DRILL 1/2"
DRILL TO MAKE PRESS FIT FOR STEEL RODS
STEEL RODS 2 REQ 1/8" DIA
THREADED 80 THD/IN INSIDE
CONNECTING TUBES 2 REQ
DRILL 1/8"
DRILLED SO THAT NEEDLE USED WILL ENTER 1/2"

FIG. 2.

at a pressure of about one centimeter. Changing the fore-vacuum pressure changes the quantity of gas admitted to the x-ray tube for each turn of the leak handle. Carbon dioxide causes the tube to operate with greater stability and does not oxidize the mercury in the diffusion pump as rapidly as air.

All other necessary information is given on the drawings shown in Fig. 1, 2, 3, and in the photograph in Fig. 4.

The author wishes to express his thanks to Dr. S. J. M. Allen and to Dr. D. A. Wells for their help and interest in this work.

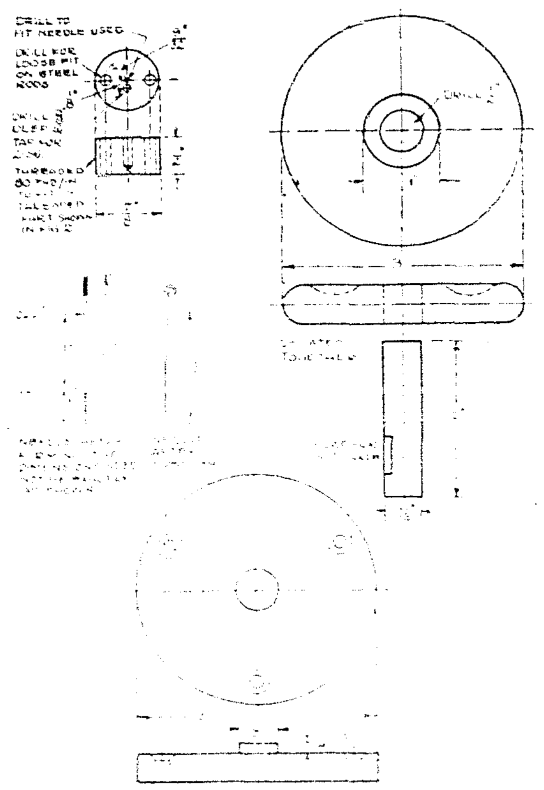
DRILL TO FIT NEEDLE USED
DRILL FOR LOOSE FIT ON STEEL RODS
THREADED 80 THD/IN
DRILL 1/2"
3

Fig. 3.

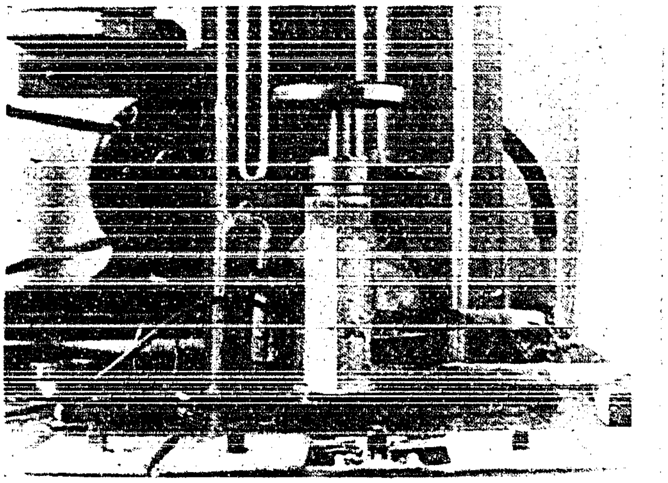

Fig. 4.

ELECTRODEPOSITED METAL FOILS

Reprinted from The Review of Scientific Instruments, volume 2, no. 10, October, 1931.

Metal foils may be produced electrolytically by making use of the fact that electrodeposits do not adhere well to polished stainless steel. This paper gives a description of the apparatus, methods, and plating baths used.

A convenient arrangement of the apparatus needed is shown in Fig. 1, in which the slide wire rheostat is capable of carrying three amperes continuously and has a resistance of about fifty ohms. It is connected directly across a twenty volt direct-current supply and is used as a potentiometer. From the terminal M a wire leads to the ammeter and then to the anode I. This is usually made from the same metal as that being plated but if it is not at hand, carbon rods may be used instead. Anodes of some metals go into solution well enough to prevent the bath from becoming depleted in metal ions, while in the case of others, additions of the salt containing the ions of the metal being plated must be made from time to time. If carbon anodes are used, all of the metal plated must come out of the solution so that

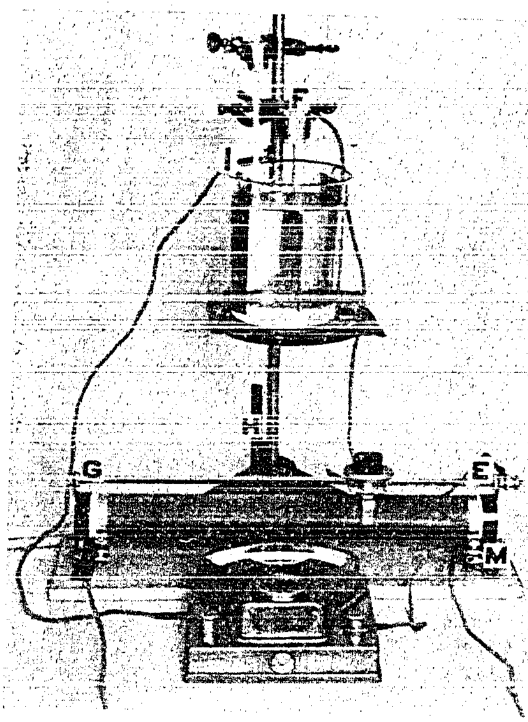

Fig. 1. *Apparatus for electrodepositing metal foils.*

if a large quantity of metal were to be plated, additions of the salt would have to be made. In the case of plating done in the laboratory on a small scale, there will be no trouble due to the depletion of the ions in solution when carbon anodes are used.

A one-liter beaker makes a convenient container for the electrolyte. It may be supported by a ringstand so that it may be heated when necessary by a Bunsen burner which is shown at H in the figure. The cathode is hung in the solution by a wire held by a rod at F. This is connected to the terminal E of the potentiometer, thus completing the circuit. A convenient size for the cathode is 5 cm x 10 cm so that its total area is 1 dm. It must be well polished and free from grease.

The principal variables in electrodeposition from a given solution are time, temperature, and current density (amperes per sq dm). If all the other variables are held constant, the thickness of the deposit is determined by the time, so that theoretically deposits of any thickness could be obtained. The thickness is limited on the lower limit since the foil must have some mechanical strength to permit it to be removed from the cathode. The temperature in some cases has no noticeable effect but in other cases high temperatures cause the metal to deposit in large crystals in which case the holes between the crystals may be seen with the naked eye. With each formula given below a suitable temperature is given at which good foils can be produced. The current density is an important variable. If it is made large, there will be not enough metal ions in the vicinity of the cathode to carry all of the current so that some of it will be carried by the hydrogen ions in the water and an excessive amount of hydrogen will be liberated at the cathode along with the metal and cause the latter to be spongy. For this reason, the current densities given with the formulas below should be used.

All of the metals have not been produced satisfactorily electrolytically. Among those which have, there are some which are either too brittle to be removed from the cathode in the form of a foil, or adhere too well to be removed. Hence all of the common metals are not included in the list given below.

Cobalt:

Water	1 liter
Cobalt sulphate, $CoSo_4:7H_2O$	300 gm
Sodium chloride, NaCl	20 gm
Boric acid, H_3BO_3	30 gm
Temperature	50° C
Current density	0.5 amp/dm^2.

Nickel:

Water	1 liter
Sodium citrate, $2Na_3C_6H_5O_7:11H_2O$..	35 gm
Nickel sulphate, $NiSO_4:7H_2O$	40 gm
Temperature	50° C
Current density	0.25 amp/dm^2.

Copper:

Water	1 liter
Sodium carbonate, (anhydrous) Na_2CO_3	10 gm
Sodium sulphite, (anhydrous) Na_2SO_3	20 gm
Sodium bisulphite, $NaHSO_3$	20 gm
Copper potassium cyanide, $K_4Cu_2(CN)_6$	30 gm
Potassium cyanide, KCN (100%)	1 gm
Temperature	15-20° C
Current density	0.3 amp/dm^2.

Copper (continued):

Special directions for mixing: Place 1/2 liter of the water in the container to be used for the bath. Warm the remaining water to about 50° C. Dissolve the first two chemicals in part of this warm water and pour it into the bath. Dissolve the third chemical in another part of the warm water and pour it slowly into the bath. Stir the bath until the chemical action resulting has ceased. Dissolve the two cyanides in the remaining warm water and add to the bath.

Silver:

Water	1 liter
Silver nitrate, $AgNO_3$	1 gm
Potassium cyanide, KCN (100%)	70 gm
Temperature	15-20° C
Current density	1 amp/dm^2

Cadmium:

Water	1 liter
Cadmium potassium cyanide, $K_2Cd(CN)_4$	10 gm
Potassium cyanide, KCN (100%)	10 gm
Temperature	15-20° C
Current density	0.5 amp/dm^2

Tin:

Water	1 liter
Sodium pyrophosphate, $Na_4P_2O_7$	40 gm
Tin chloride (fused) $SnCl_2$	16 gm
Tin chloride (crystals) $SnCl_2:2H_2O$	4 gm
Temperature	50° C.
Current density	0.5 amp/dm^2

Special directions for mixing: Dissolve the chemicals in the order given. (The bath may have a milky appearance but this will not affect its operation.)

Gold: (A gold anode should be used with this bath.)

Water	1 liter
Potassium cyanide KCN (100%)	15 gm
Gold chloride, $AuCl_3:H_2O$	1.5 gm
Temperature	50° C
Current density	0.05 amp/dm^2

Brass (Copper-zinc):

Water	1 liter
Sodium carbonate, (anhydrous) Na_2CO_3	14 gm
Potassium copper cyanide, $K_4Cu_2(CN)_6$	20 gm
Sodium sulphite, (anhydrous) $NaSO_3$	20 gm
Potassium zinc cyanide, $K_2Zn\ (CN)_4$	20 gm
Potassium cyanide (100%)	1 gm
Ammonium chloride	2 gm
Temperature	25° C.

Brass (continued)

Current density...................... 0.3 amp/dm^2.

Special directions for mixing: Dissolve the chemicals in the same way as is given under copper, except that in this case there are three cyanides to be dissolved together, and the ammonium chloride to be dissolved and added last.

The composition of the brass may be altered by changing the temperature or the current density.

The deposits are removed from the stainless steel cathode by loosening the edges and separating the foil with the help of a safety-razor blade.

The nickel foil makes a very good filter for the radiations from a copper target x-ray tube. Fig. 2 shows a Laue photograph of copper foil in which the left half of the film was covered with nickel foil of 0.01 mm in thickness. It can be seen that the inner ring, which is due to diffraction of the K rays from the (111) planes is nearly all absorbed by the nickel foil while the other rings are of about the same intensity. Placing the foil next to the film also has the advantage of absorbing much of the scattered radiation so that the rings stand out more sharply.

FIG. 2. *The effect of a nickel filter on a Laue photograph of copper with copper radiation. Right: unfiltered. Left: filtered.*

THE CRYSTAL STRUCTURE OF COPPER ELECTRODEPOSITED IN THE PRESENCE OF GELATINE

Reprinted from The Journal of Physical Chemistry,
Vol. XXXV, pp. 3644-3646, December, 1931.

Introduction

Electrodeposited metals are usually more microcrystalline when the baths from which they are deposited contain colloids. In the case of copper plated from an acid bath containing gelatine it has been shown[1] that some of the gelatine is deposited with the copper. Fig. 1 shows that such copper is more brittle than that obtained from the same bath without the addition of gelatine. The two kinds of copper shown were plated on stainless steel (to which most electrodeposits adhere poorly) and partly stripped to show the difference in brittleness.

In view of these differences in physical properties one might expect a difference in the crystal structure of the deposits. Trillat[2] examined such samples by means of x-rays and found apparent, but not conclusive, evidence for a difference in the length D, Fig. 2, of the edge of the unit crystal lattice for

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[1] Müller and Bahntje:Z. Elektrochemie, 12, 317 (1906).
[2] Trillat:Rev. Métallurgie, 25, 286 (1928).

Fig. 1
Left, copper without gelatine.
Right, copper with gelatine.

the two kinds of copper.

This paper describes a new determination which shows that any difference in the length of the unit lattice for the two kinds of copper must be less than 0.01 Ångstrom.

Experimental

The x-rays were supplied by a Siegbahn-Hadding type of x-ray tube having a copper target. A special camera shown in Fig. 3 was constructed, in which the x-rays passed through the slits in the ends of the tube A and struck the samples B and C nearly at a tangent. These samples were electroplated on gold-plated brass tubes so that if any x-rays were diffracted by the under metal this fact could be noticed in the picture because the distance D of Fig. 2 for gold is much different from that of copper. The samples B and C were of the same outside diameter and fitted snugly over the pin D. This made the distance from the slit to the film the same for both samples. The film was enclosed in a paper envelope and held on the circumference of the hoops E by a rubber band. Next to the film was placed a piece of 0.02 mm nickel foil which acted as a filter giving approximately monochromatic beams. The place where the two samples joined was aligned with the partition F which prevented

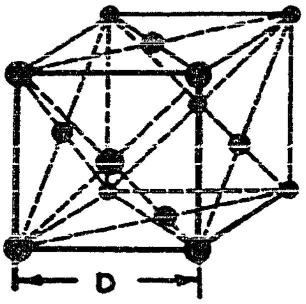

FIG. 2
Unit crystal lattice of copper.

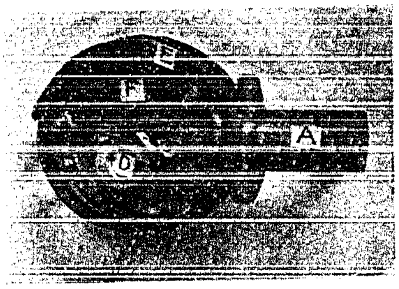

Fig. 3
Special x-ray camera

the diffracted beams from one of the samples crossing over to the part of the film which was intended to receive the beams from the other sample. An enlarged photograph, taken with this camera, is shown in Fig. 4.

The plating baths used had the following composition:

Water	1 liter
Copper sulphate crystals	200 gm.
Concentrated sulphuric acid	30 gm.

The other bath had the same composition except that it contained 100 gm of gelatine. The baths were connected in series and since the cathodes had the same area, the current density was 2 amp per dm^2 for each sample. The temperature was kept constant at 25° C by placing the beakers containing the electrolyte in a water-bath. A sufficiently thick deposit was obtained in one hour.

Theoretical

To show that the difference in the length of the edge of the unit lattice must be less than 0.01 Å. for the two kinds of copper, Bragg's law is used:

$$n\lambda = 2\ k\ D \sin \theta,$$

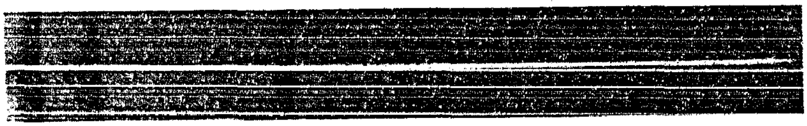

FIG. 4
Enlarged photograph taken with the camera shown in Fig. 3. Upper part, copper containing gelatine. Lower part, copper not containing gelatine.

where:

n = order of the reflection (1, 2, 3, etc.),

λ = wave length of the x-ray beam,

k = a factor which when multiplied by D gives the distance between corresponding planes (for the 111 planes $k = 0.577$),

D = length of the unit crystal edge (Fig. 2),

θ = angle between the incident x-ray beam and the diffracting plane.

From this, θ is computed for the various planes which may cause diffraction, assuming the distance D for copper to be its usual value of 3.61 Å., as well as 3.60 and 3.50 Å. The theoretical positions of the lines thus determined are plotted in Fig. 5 from the computed values given in Table I.

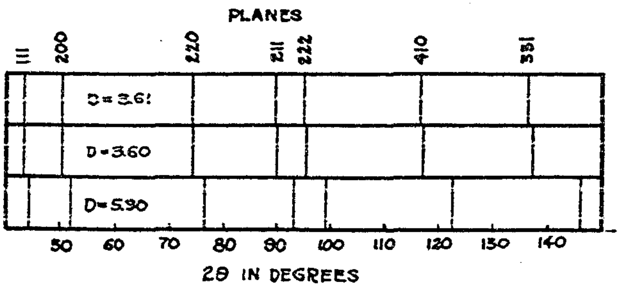

Fig. 5
Theoretical positions of the lines for various values of D.

TABLE I

Values of 2 θ for various values of D

	2 θ for D =		
Planes	3.61	3.60	3.50
111	43° 16'	43° 24'	44° 42'
200	50° 24'	50° 32'	52° 6'
220	74° 2'	74° 16'	76° 46'
311	89° 50'	90° 6'	93° 28'
222	95° 2'	95° 21'	99° 2'
400	116° 46'	117° 16'	122° 52'
331	136° 14'	137° 2'	146° 20'

In the computations, λ was taken as 1.537 Å.

From the table and from Fig. 5 it is evident that the greatest difference in the positions of the lines occurs on the right-hand end. Turning to Fig. 4, the difference between the positions of the 331 lines is not as great as that between the same lines in Fig. 5 for D = 3.61 and D = 3.60 Å. Hence we conclude that any difference in the unit crystal lattice edge is less than 0.01 Å.

A GAS X-RAY TUBE FOR CRYSTAL STRUCTURE ANALYSIS

Reprinted from The Review of Scientific Instruments, vol. 3, no. 3, March, 1932.

The gas x-ray tube described below was designed to produce intense x-ray beams for crystal structure analysis. The intensity was attained by providing sufficient cooling to allow for large current carrying capacity, by making use of cellophane windows and by placing the slit or pinhole systems in the evacuated space so as to approach near the target.

Fig. 1 shows the upper part of the x-ray tube, mounted, ready for use, with two Laue cameras and one Hull-Debye-Scherrer camera. The fourth opening is shown closed by a plug.

Fig. 2 shows the interior of the tube. The cooling water for the grounded parts enters at A, flows past the target I, through the four tubes B on the target part into four similar tubes to the jacket FGJ and out through the tube BB. The cooling water for the ungrounded end of the tube flows through twenty feet of 3 mm glass tube from the water main to Y, where it enters the inner copper tube N, strikes

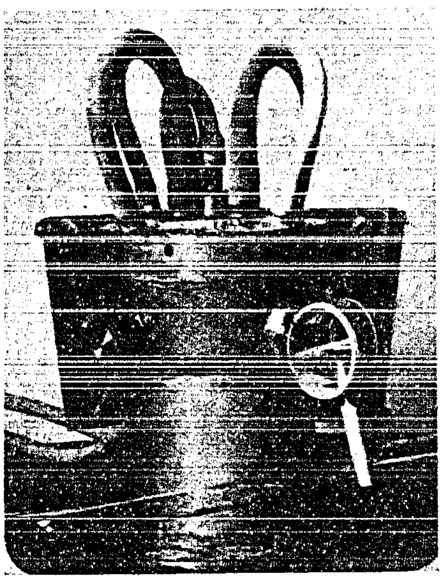

FIG. 1. *The upper part of the x-ray tube.*

the cathode, flows through tubes V and W and finally through another twenty feet of 3 mm glass tube to the drain. It was found that less than two milliamperes passed through this part of the electrical circuit. The copper plug L and the brass ring X were soldered in place. The cooling tubes for the cathode were held in place by the cathode K, which is screwed to the outer tube at L, and by the ring T, fastened to the outer tube by the set screw S.

In addition to being grounded through the water circuit, the upper part of the tube was also grounded by a wire attached at AA. The high voltage terminal is shown at Z. The radius of curvature of the cathode K was 8 cm. The insulator[1] was cemented to the upper part of the tube at P and to the cooling tubes U with picein[2]. It was found that no other support than that provided by the picein was needed to hold the insulator in place.

---

[1] Suitable insulators may be obtained from J. B. Hayes, Urbana, Illinois, or from the Staatliche Porzellanmanufaktur, Berlin-Charlottenburg, Germany. The one shown in Fig. 2, at R, was obtained from J. B. Hayes.

[2] Picein is made by the New York Hamburg Gummi-Warren Compagnie, Hamburg, Germany.

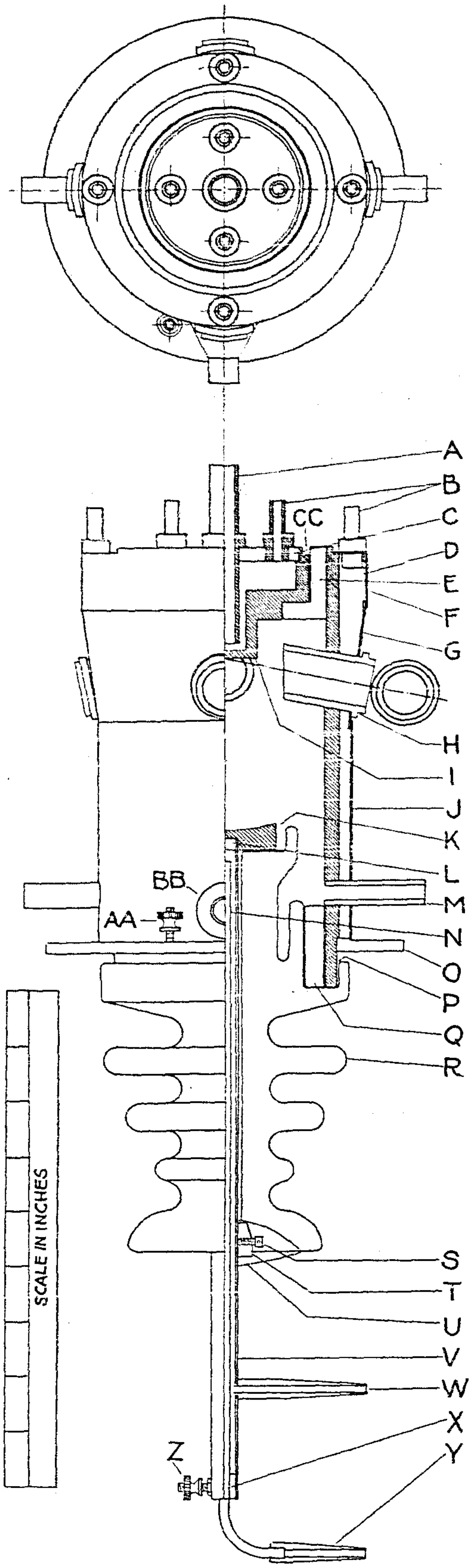

Fig. 2.

The target, consisting of the inlet tube A, four outlet tubes B, the plate C, and the body I was soldered together and cemented in place with picein at CC. To remove the target a stream of hot water was passed through the cooling tubes of it to soften the picein. This same kind of heating will soften the picein at P if the hot water also enters the jacket FGJ. The support E, for the target was soldered to the wall of the tube. The opening in this support was made large enough so that the cathode K could be unscrewed from the cooling water tube by a special pincers and replaced by a new one without completely dismantling the tube. The body I of the target may be made of copper or iron when these two elements are desired for targets, or the target material may be soldered at I to the remaining part when the latter is made of brass. It is well to have the water strike directly against the target material rather than against the material to which it is fastened because the heat may be conducted away too slowly to prevent the target from melting at the focal spot. A molybdenum target may be made by pressing a molybdenum plug[1] into a hole at I. Chromium, electroplated to a

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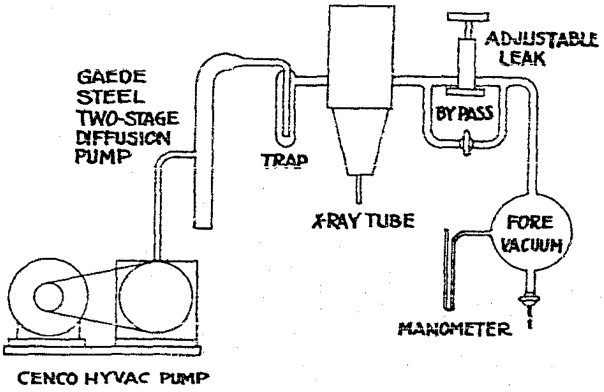
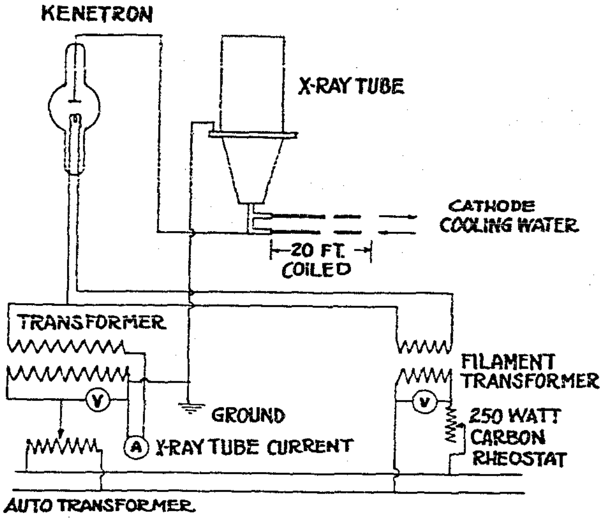
[1] The molybdenum plug may be obtained from the Fansteel Products Co., Inc., North Chicago, Ill.

brass target will serve when that metal is desired for a target.

The four tubes H were reamed out to the same inside diameter and soldered to the inner wall and water jacket in such a way as to point to the center of the target and make an angle of 80° with the vertical axis of the tube. The cameras were fastened to tubes which fitted into the four tubes H, and which contained the pinhole or slit systems. These inner tubes also contained the cellophane windows which were fastened to a flange D (shown in the lower part of Fig. 3) with warm picein and then clamped in place with the flange G which had been previously warmed to soften the picein under the cellophane. The slits or pinholes are shown at A. Since the cellophane itself shows a hazy diffraction ring, it is necessary to put a pinhole or slit in the flange G to cut out this diffracted part of the beam. After the camera is fastened to the tube containing the pinholes or slits it is properly aligned with respect to the latter, ''tinned'' with picein, slipped into one of the tubes H, (Fig. 2) against the flange C (lower part of Fig. 3) making a vacuum-tight joint. The cellophane is kept cool by the cooling water and is too far away


ADJUSTABLE LEAK
GAEDE STEEL TWO-STAGE DIFFUSION PUMP
BY PASS
TRAP
X-RAY TUBE
FORE VACUUM
MANOMETER
CENCO HYVAC PUMP


KENETRON
X-RAY TUBE
CATHODE COOLING WATER
20 FT. COILED
TRANSFORMER
FILAMENT TRANSFORMER
V
GROUND
V
250 WATT CARBON RHEOSTAT
A
X-RAY TUBE CURRENT
AUTO TRANSFORMER

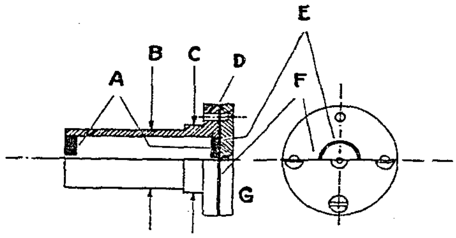

E
B
C
D
A
F
G

FIG. 3.

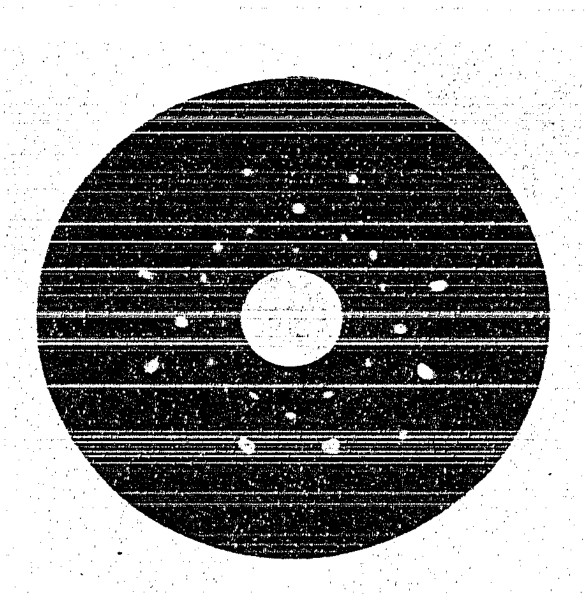


Fig. 4. *Laue pattern of rock salt, 0.7 mm thick. Iron target. 30 kilovolts, 50 milliamperes, 6 hours.*

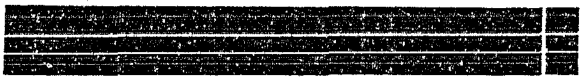


FIG. 5. *Debye-Scherrer-Hull photograph reflected from the surface of tin foil. Chromium target, 30 kilovolts, 50 milliamperes, ½ hour.*

from the target to be sputtered so that it remains transparent and seldom needs to be replaced. The ring E is cut into the flange G (lower part of Fig. 3) to prevent the picein from getting into the slit or pinhole. The ordinary kind of cellophane used for wrapping material was found to be completely satisfactory.

The vacuum circuit[1] is shown in the upper part of Fig. 3 and the electrical circuit in the middle part of the same figure. Photographs taken with this tube are shown in Fig. 4 and in Fig. 5.

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[1] The adjustable leak shown in the vacuum circuit is described in the R. S. I. 2, (7) 377, July, 1931.

INFLUENCE OF HYDROGEN ION CONCENTRATION ON THE CRYSTAL STRUCTURE OF ELECTRODEPOSITED COBALT

Reprinted from Physics, vol. 2, no. 4, pp. 274-275, April, 1932.

Abstract

Cobalt crystallizes in the cubic and hexagonal systems. This paper shows by means of x-ray diffraction analysis, that cobalt electrodeposited from high pH (alkaline) sulphate solutions has a hexagonal structure which changes into a mixture of hexagonal and cubic, as the pH is decreased.

Hull[1] has shown that cobalt has hexagonal close-packed as well as face centered cubic lattices, and that both types of lattice are obtained by rapid electrolysis of the sulphate. The purpose of this investigation was to determine whether the hydrogen ion concentration of the electrolyte influences the structure of the electrodeposited cobalt.

Experimental

Cobalt was deposited from an electrolyte having the following composition:[2] Cobalt sulphate ($CoSO_4:7H_2O$), 504 gm/liter; sodium chloride (NaCl),

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[1] Hull, Phys. Rev. 17, 571 (1921).

[2] Blum and Hogaboom, Principles of Electroplating and Electroforming, 2nd ed., p. 280, 1930.

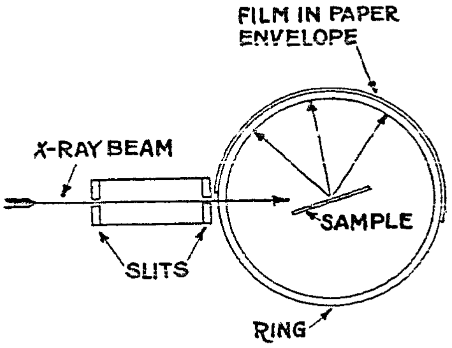

Fig. 1. Schematic diagram of the camera

17 gm/liter; boric acid (H_3BO_3), 45 gm/liter, at 30°C and 1 amp/dm^2 with cast cobalt anodes (98-99 percent pure) and stainless steel cathodes. The hydrogen ion concentration was adjusted with H_2SO_4 and NH_4OH and measured with a quinhydrone electrode.

The x-rays were supplied by a chromium target gas-type tube[1] operated at 20 kv and 40 m.a. The camera is illustrated schematically in Fig. 1. The diameter of the ring around which the film was wrapped was such that 0.025 inch on the film corresponded to 1°. The black line at the right end of each photograph in Fig. 2 was made by the main beam before the sample was put in place.

Theoretical

The positions of the diffracted images of the main x-ray beam, plotted from the data given by Hull[2], are shown for both lattice types in the lower part of Fig. 2. All the theoretically possible lines do not appear in the photographs but it is evident that the 200 Kα line, indicated by an arrow, is the best one to use as a test for the presence of cubic cobalt since it is one of the strongest lines appearing in the

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[1] Kersten, Rev. Sci. Inst. 3, 145 (1932).
[2] Hull, Phys. Rev. 17, 571 (1921).

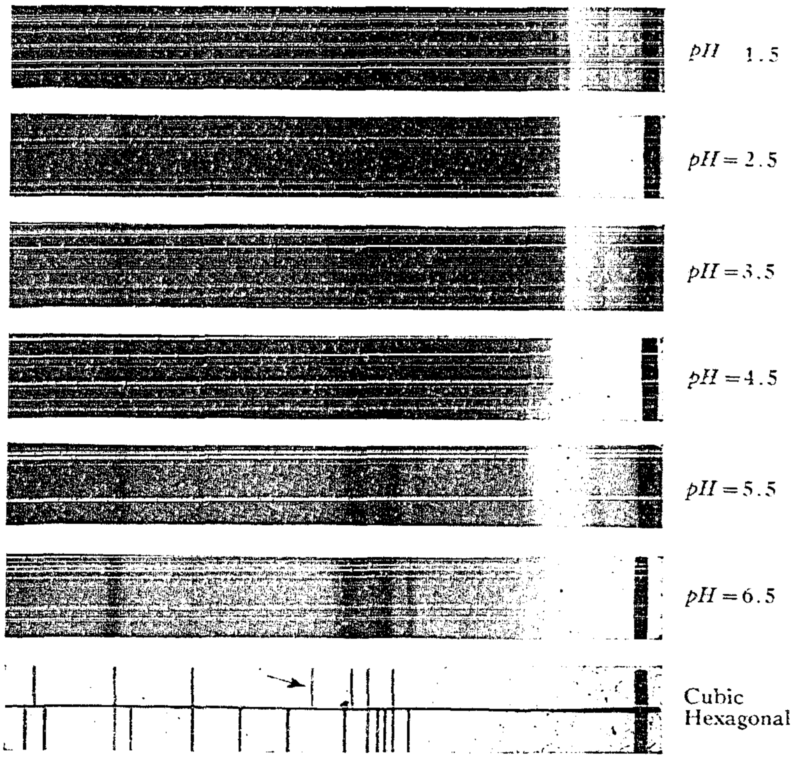

Fig. 2. Influence of *pH* on the crystal structure of electrodeposited cobalt.

photographs when a large percentage of cubic crystals are present in the cobalt.

Results

Fig. 2 indicates that hexagonal cobalt is deposited at high values of pH from the electrolyte used and that the structure gradually changes into a mixture of hexagonal and cubic as the pH is decreased.

INFLUENCE OF TEMPERATURE ON THE CRYSTAL STRUCTURE OF ELECTRODEPOSITED ANTIMONY

Reprinted from Physics, vol. 2, no. 4, pp. 276-279, April, 1932.

Abstract

It is shown by x-ray diffraction methods that "explosive" antimony is amorphous before exploding and crystalline afterward. It is also shown that the crystal structure of electrodeposited antimony is influenced by the temperature of the plating bath.

Introduction

Gore[1] found that antimony, electrodeposited from a cold solution of antimony trichloride in dilute hydrochloric acid, has the property of "exploding" when scratched and that deposits from a hot bath do not have this property. The investigation described below was intended to determine whether the explosive property is associated with a particular crystal structure and to find the influence of bath temperature in general, on the structure of electrodeposited antimony.

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[1] Gore, Phil. Mag. (4) 9, 73 (1855).

Experimental

The plating bath used had the following composition: Antimony trichloride ($SbCl_3$), 200 gm; hydrochloric acid (HCl), 300 cc; water, to make, 1 liter. Cast antimony anodes and nickel-plated brass cathodes were used. The cathodes were nickel-plated to prevent the antimony from depositing by "immersion" on the brass and possibly alloying with it. The current density in all the experiments was 3 amp./cm^2.

The x-rays were supplied by a special gas tube[1] having a copper target and operated at 40 m.a. and 20 kv. The camera for holding the film and sample is illustrated in Fig. 1. The antimony was plated thick enough to prevent the diffraction lines from the nickel and brass from appearing on the film. This made it unnecessary to strip the antimony from the cathode when taking a picture.

Results

Samples plated at 5° intervals from 0° C to 100° C are shown in Fig. 2, 3, and 4. It is evident that the electrodeposited antimony has an amorphous structure when electroplated at temperatures below

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[1] Kersten, Rev. Sci. Inst. 3, 145 (1932).

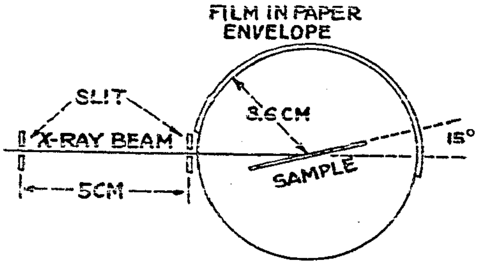

Fig. 1. Camera.

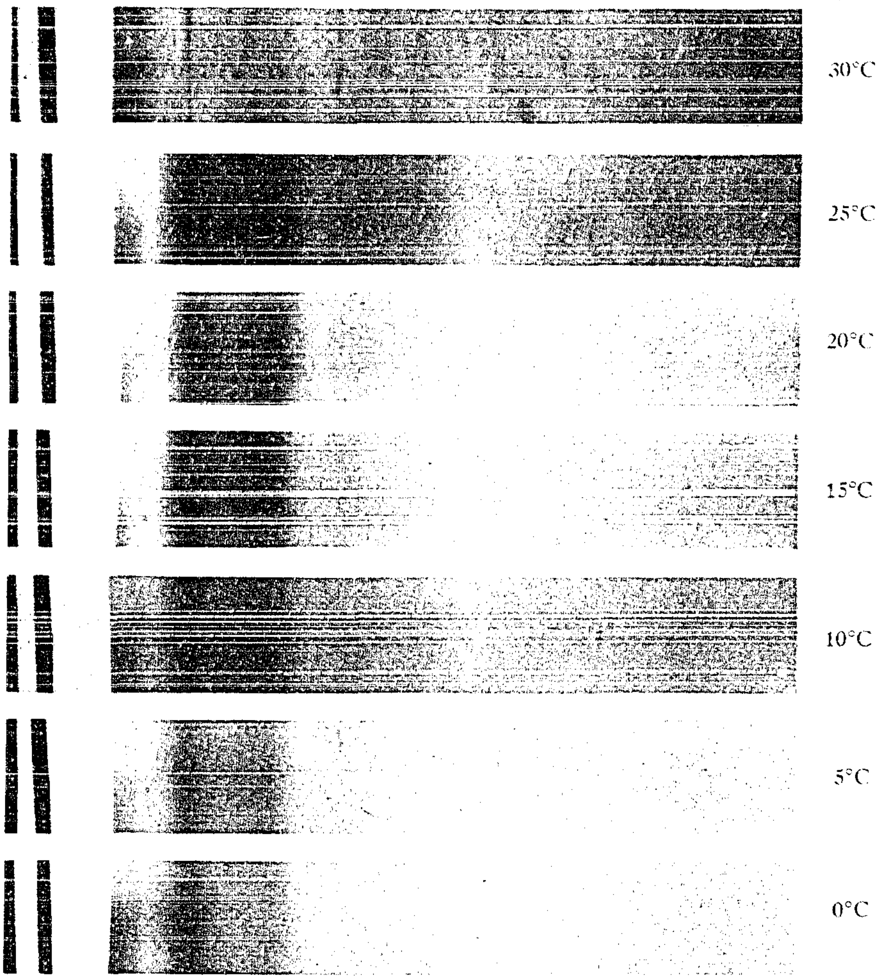

Fig. 2. Diffraction photographs of antimony.

25° C and that it changes from amorphous to crystalline between 25° and 30°. Photographs taken for samples plated in this range, but not shown in the figures, showed that the change was a gradual one. The structure from 30° to 70° is nearly constant. Above 70° there are changes in the position and intensity of lines which indicate changes in structure.

When a cathode plated with a thick layer of the amorphous modification is scratched with the point of a knife it gives off a white vapor accompanied by a hissing sound and a rise in temperature. In order to determine whether this change is accompanied by a change in structure, a sample of the amorphous variety was clamped in the camera and the photograph shown in the middle part of Fig. 5 taken. Without removing the sample from the camera, its surface was scratched to cause the explosion and another photograph, shown in the upper part of Fig. 5 was taken. These show that the antimony had changed from an amorphous to a crystalline form during the explosion. The lower part of Fig. 5 shows a photograph of chemically pure antimony. A comparison of the upper and lower photographs shows that the structure of the electrolytic amorphous antimony after being exploded, is the same as that of pure antimony.

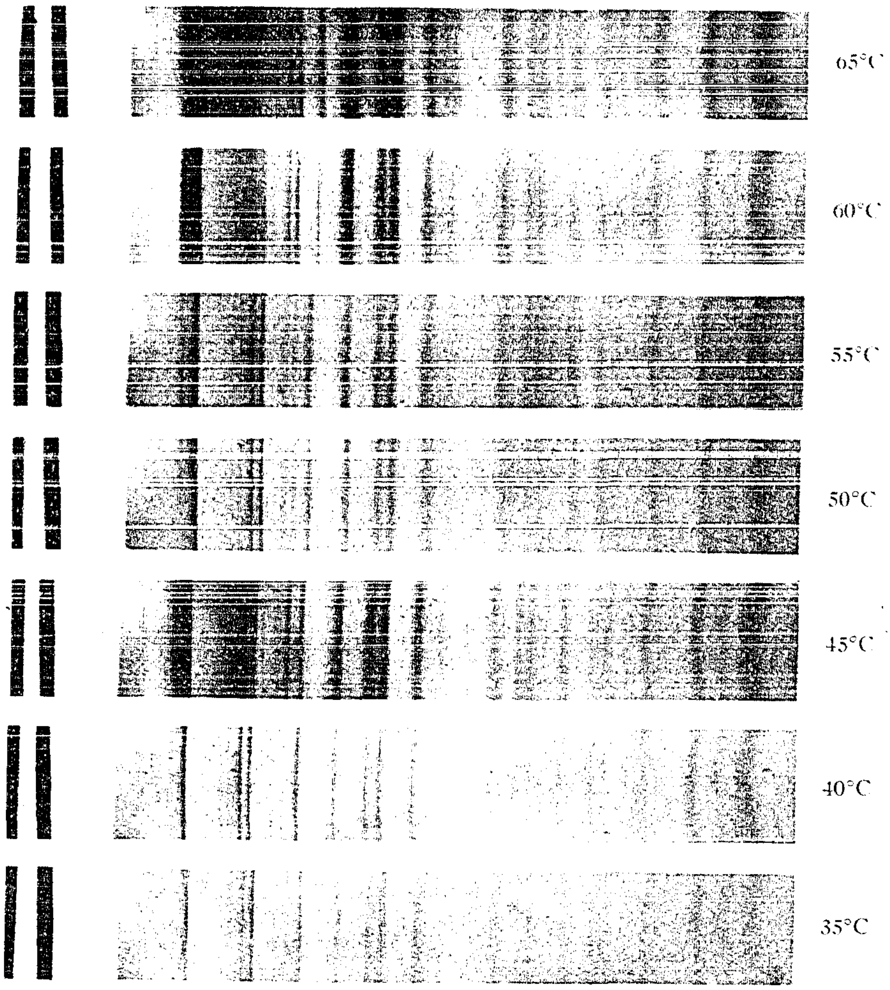

Fig. 3. Diffraction photographs of antimony.

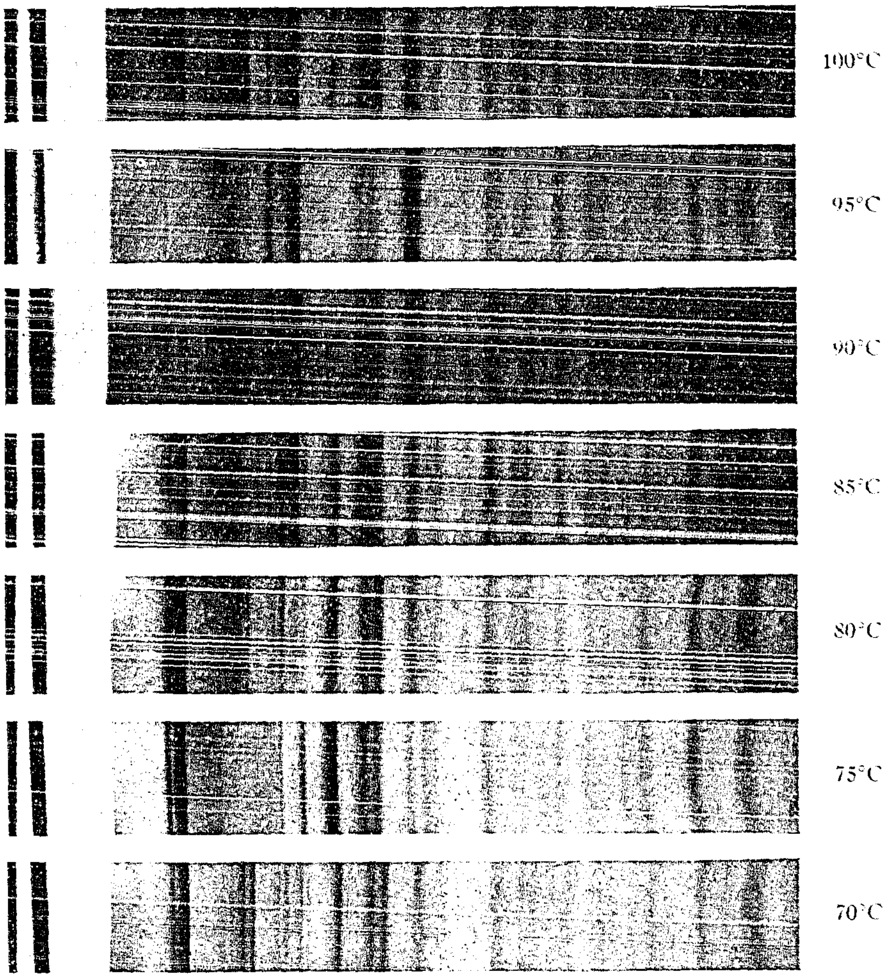

Fig. 4. Diffraction photographs of antimony.

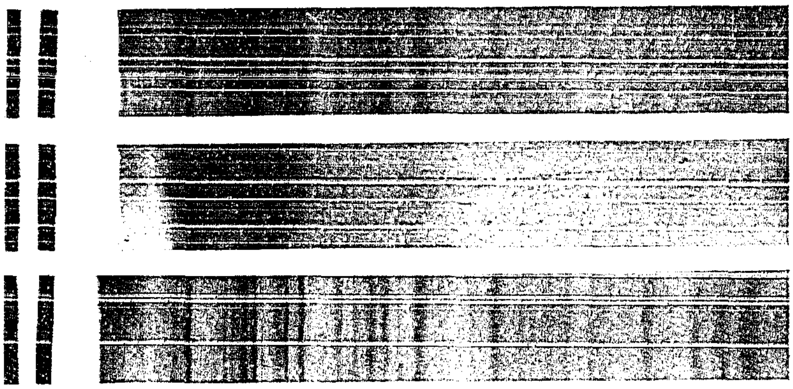

Fig. 5. Upper: Antimony after exploding; middle: Antimony before exploding; lower: Pure antimony.

EXAMINATION OF ELECTRODEPOSITED METALS AND ALLOYS WITH X-RAYS

Reprinted from Analytical Edition, vol. 4,
page 178, April 15, 1932.

The methods of x-ray crystal structure analysis may be used for examining electrodeposited metals and alloys to determine their structure, approximate chemical composition, approximate thickness, and relative grain size.

The theory of the methods has been described in several books on the subject (2, 3, 6, 9, 10) and need not be repeated here. The special apparatus required is illustrated in Figure 1 where the x-rays from a slit at B strike the sample clamped in such a way at D that its surface is on a diameter of the hoop A. The x-rays strike the sample at the center of the hoop and are diffracted so that images of the slit appear on a film held in the opaque paper envelope on the circumference of the hoop. This camera may be modified so that objects of various shapes, instead of flat samples, may be clamped in place. The x-rays may be supplied by a Coolidge tube or by a gas tube. The pictures shown were taken with the radiation from a special gas-type x-ray tube (5) having an iron target, operated at 50 milliamperes and 20,000 volts. At this voltage and current each picture required an exposure of one-half hour. All the photographs shown are full size, but much of the detail observable in the original negatives cannot be seen in the printed pictures. The strong white line which can be seen at the left of each picture was made by the main beam coming from the slit before the sample was clamped in place.

If an object is electroplated with an alloy solely to give it a desired color, as is usually the case, a comparison of colors is the only examination needed to determine whether the deposit is satisfactory. In the cases of alloys which have a constant color for a wide range of compositions, it is sometimes possible to determine their composition with a sufficient degree of accuracy by means of the methods of crystal structure analysis without stripping the deposit or damaging the electroplated object in any way. With this method it is the crystal structure of the surface layer and not its color of chemical composition which is examined. The relation between structure and chemical composition for many alloys has been investigated. A collection of these results has been published in two volumes by Neuburger (7, 8).

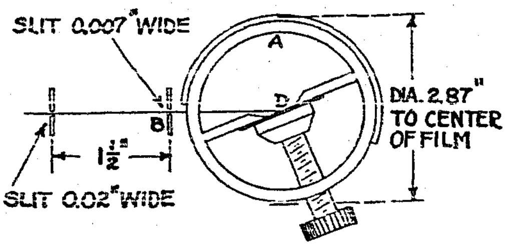

Figure 1. X-Ray Camera for Examining Electrodeposited Metals

Fig. 2 shows photographs of zinc, two kinds of brass, and copper taken with the camera described above. A comparison of these with those given by Westgren and Pragmen (11) indicates that one of the brasses belongs to the alpha phase and the other to the alpha-plus-beta phase. These samples were plated from baths having the following compositions:

ALPHA (1):

Copper cyanide (CuCN), grams..................	27
Zinc cyanide ($Zn(CN)_2$), grams..................	9
Sodium cyanide (NaCN), grams..................	54
Sodium carbonate (Na_2CO_3), grams..............	30
Water, liter..................................	1

Current density, 0.5 amp/dm^2.

Temperature, 23° C.

ALPHA PLUS BETA:

Copper cyanide (CuCN), grams..................	15
Zinc cyanide ($Zn(CN)_2$), grams..................	30
Sodium cyanide (NaCN), grams..................	75
Sodium carbonate (Na_2CO_3), grams..............	30
Water, liter..................................	1

Current density, 3 amp/dm^2.

Temperature, 53° C.

Since the alpha phase of brass may contain from 0 to 36 per cent of zinc, and since the x-ray photographs

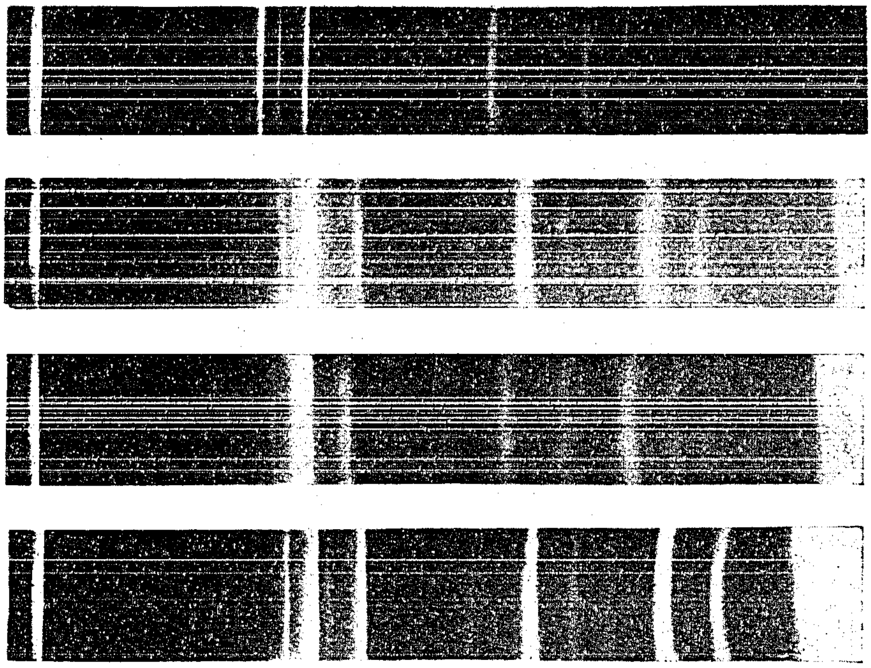

Figure 2. Electroplated Brass. Top, zinc; upper center, alpha brass; lower center, alpha-plus-beta brass; bottom, copper

for this phase do not change appreciably with composition, the x-ray examination does not give very precise information as to composition. The phase containing alpha and beta crystals, however, contains from 36 to 45 per cent zinc, so that the determination of the composition is more exact but much less so than a determination by chemical analysis.

Another illustration of the method is given in the case of copper deposited by "immersion." A piece of tin foil dipped in a solution of copper sulfate is apparently coated with copper in a few seconds. The x-ray photographs show at once that the copper has alloyed with the tin, for (Fig. 3) the lines appearing are neither those of tin nor those of copper alone, and are not entirely a super-position of both sets of lines on one photograph.

Cobalt is known to crystallize in both the hexagonal close-packed and the cubic face-centered systems (4). Electrodeposited cobalt usually consists of a mixture of both systems, the relative proportions possibly depending on the conditions under which it is deposited. Figure 4 shows the pictures for two samples of electrodeposited cobalt, one of which is plated from a saturated solution of cobalt formate and the other from a solution of the same composition except

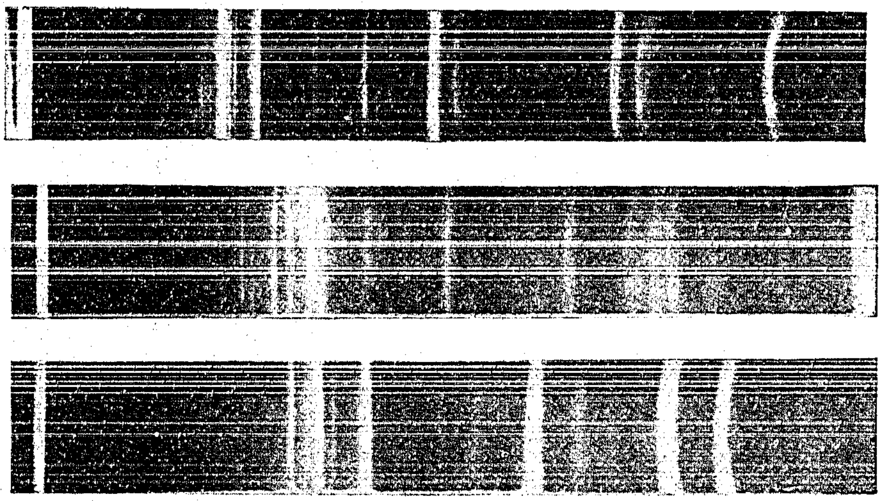

Figure 3. Tin and Copper. Top, tin; middle, tin-copper alloy formed by immersion; bottom, copper

that the acidity was changed by adding a small amount of ammonium hydroxide. The temperature and current density in each case were 23° C. and 0.5 amp/dm^2, respectively. Possibly because of the two crystal systems present, or for reasons unknown, cobalt does not give good diffraction lines, so that the photographs are not so sharp as others.

The radiation from x-ray tubes having targets of high atomic number penetrates the material which it strikes more deeply than that from tubes having targets of low atomic number. With a given target, the depth to which the radiation penetrates depends on the voltage at which the tube is operated and on the atomic numbers of the elements through which it passes. This fact makes it possible to use the methods of crystal structure analysis for the relative determination of the thickness of electrodeposited metals, when the base metal has a structure sufficiently different from that electrodeposited to permit two sets of lines being distinguished on the films.

Figure 5 shows how this method may be applied. The upper picture is of silicon steel. The middle picture was taken of the same sample after it had been given a "flash" of cadmium too thin to be measured with the ordinary micrometer. The strong speckled line of

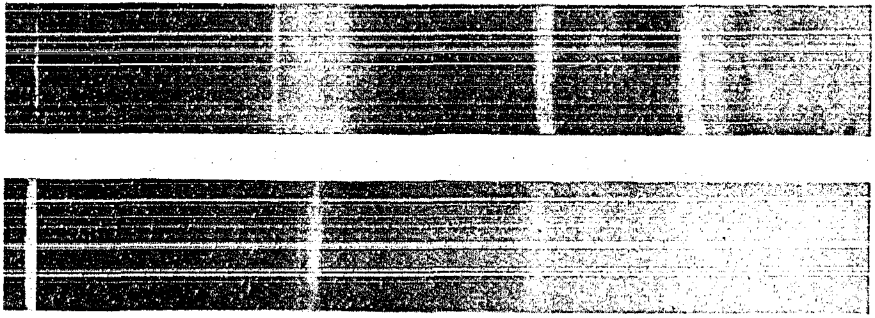

Figure 4. Cobalt. Top, from saturated cobalt formate; bottom, less acid solution

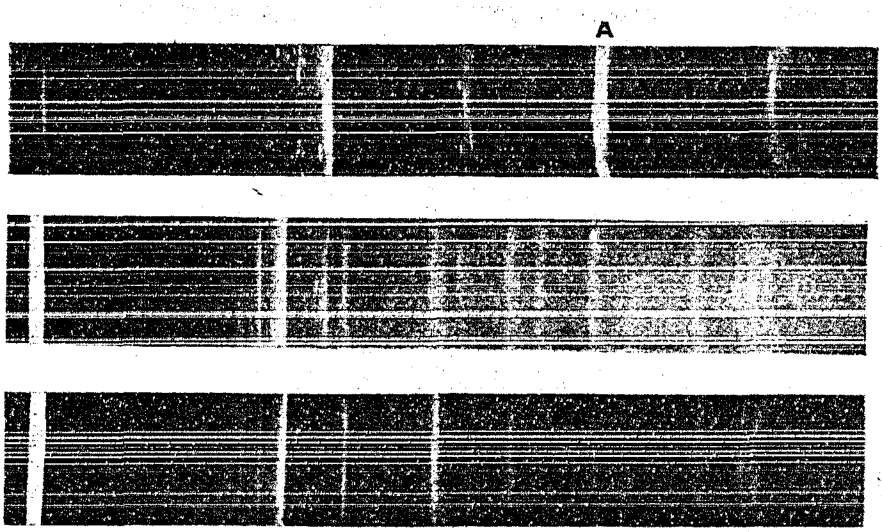

Figure 5. Silicon Steel. Top, silicon steel; middle, with flash of cadmium; bottom, with 0.015 mm. of cadmium

iron at A still shows through the cadmium. The lower picture is the same sample after having been plated with a coating of cadmium 0.015 mm thick. The speckled line of iron is nearly absent. When determining thicknesses by this method it is necessary to operate the x-ray tube at the same voltage and the same length of time, using the same kind of x-ray films in order to get comparable results. If these conditions are fixed, then a photograph of a sample plated with a coating of unknown thickness may be compared with a set of those carefully prepared from samples of known thickness to determine whether the deposit is thicker than required or not so thick. The photographs in Figure 5 also indicate that the x-ray examination concerns itself only with the surface layer when the soft radiation from a target of low atomic number is used.

The relative grain size of electrodeposited metals may also be determined with the same camera. Figure 6 illustrates this for the case of copper electrodeposited from an ordinary acid copper sulfate bath. The top picture shows the speckled lines given by the coarse-grained copper plated at 90° C., and the bottom picture shows the smooth lines of the fine-grained copper plated at 10° C.

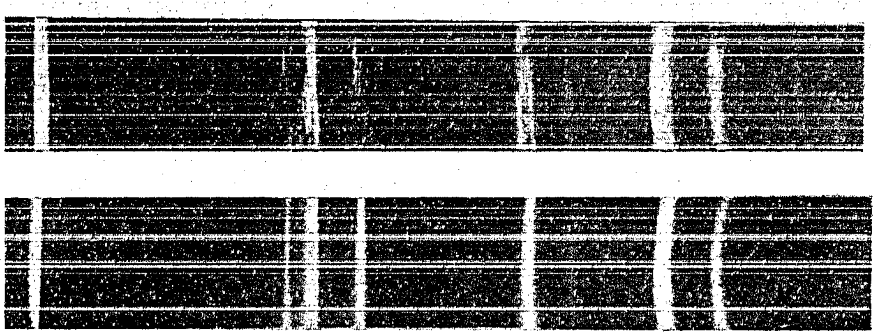

Figure 6. Copper. Top, coarse-grained; bottom, fine-grained

Owing probably to the change in composition of an alloy plating bath during deposition, a thick deposit does not necessarily have the same structure throughout. This is illustrated in Figure 7. The sample for this photograph was plated from the alpha bath at 53° C. and 3 amp/dm^2 on stainless steel to which it did not adhere well, and could be stripped. It was 0.35 mm thick. The top part of Figure 7 is a picture of the side of the deposit which was next to the cathode, and the bottom part shows the structure of the part last deposited. The lines in the lower picture show a shift toward the left, a characteristic of the alpha phase as the percentage of copper decreases.

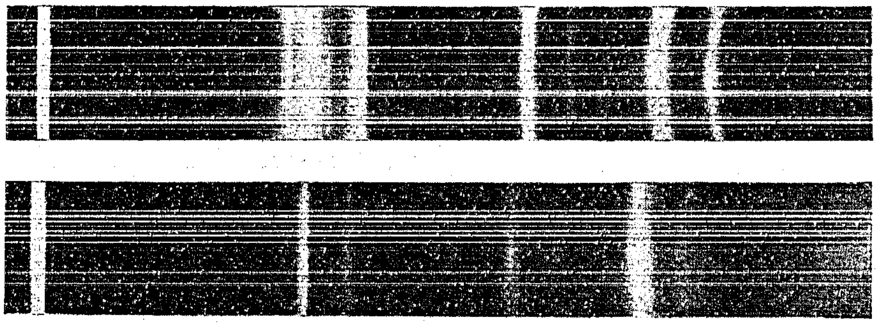

Figure 7. Brass. Top, next to cathode; bottom, away from cathode

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AN X-RAY REFLECTION SPECTROGRAPH

Reprinted from The Review of Scientific Instruments, vol. 3, no. 7, July, 1932.

The spectrograph shown in Fig. 1 and described below is intended for use with an x-ray tube recently mentioned in this journal[1] but it may be modified for use with other tubes. Fig. 2, 3, and 4 give dimensions of the parts.

The construction of the camera is best understood by referring to Fig. 2, where the tube A, which contains slits at each end is to be sealed into the x-ray tube with picein sealing wax so that the left end nearly touches the target. The plate B, which also contains a slit, clamps an ordinary sheet of cellophane to the tube A by means of two screws O (only one is visible in Fig. 2). The face of the tube is prepared for the cellophane by "tinning" it with picein and warming both the tube and plate B before the screws O are tightened. The slit is adjusted so as to be in alignment with a diameter of the ring D by adjusting the band I which slides on the screw J, until the edge of a piece of paper pasted to the periphery of the right-hand side of ring D, on a diameter, is visible through

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1. R. S. I. 3 (3). 145, March, 1932.

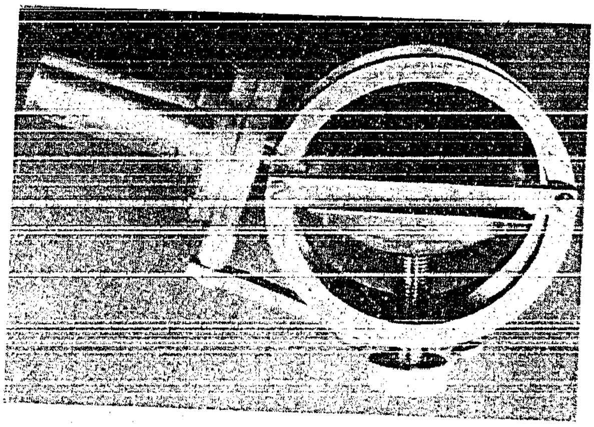

Fig. 1. *X-ray spectrograph.*

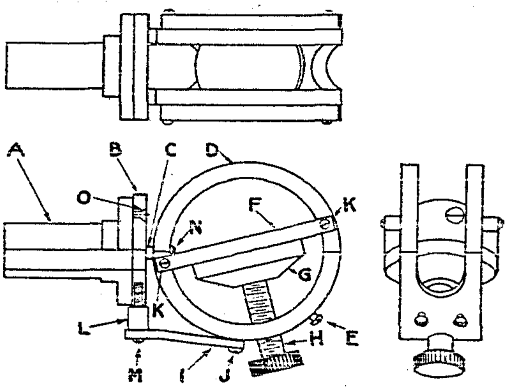

Fig. 2.

the slits. For this adjustment, G is lowered out of the line of sight.

The slits in tube A are made by cutting a strip of 1/16th inch thick aluminum to fit in the half-inch hole in the tube and filling each end with solder around the aluminum sheet with the aid of a soldering iron. The solder will not adhere to the aluminum and the latter may be pulled out leaving two slits properly aligned. Sufficient solder is used so that it may later be turned off flat with the ends of the tube. The slit in the plate B is made in a similar way using a stainless steel safety razor blade cut to fit into the half inch hole in the plate. The holes for the screws O and N are drilled after the slits have been finished.

The sample to be examined is clamped between F and G by means of the screw H. The square rods F are fastened to the ring D so that the upper surface of a sample clamped against their lower edges will be on a diameter. In this way the sample is easily placed so that the x-ray beam strikes it at the center of the ring. The film contained in a black paper envelope is wrapped around the ring D and held in place by means of a rubber band fastened around C and the screws E. The image of the main beam, from which angles are measured, is impressed on the film by unscrewing H until G is

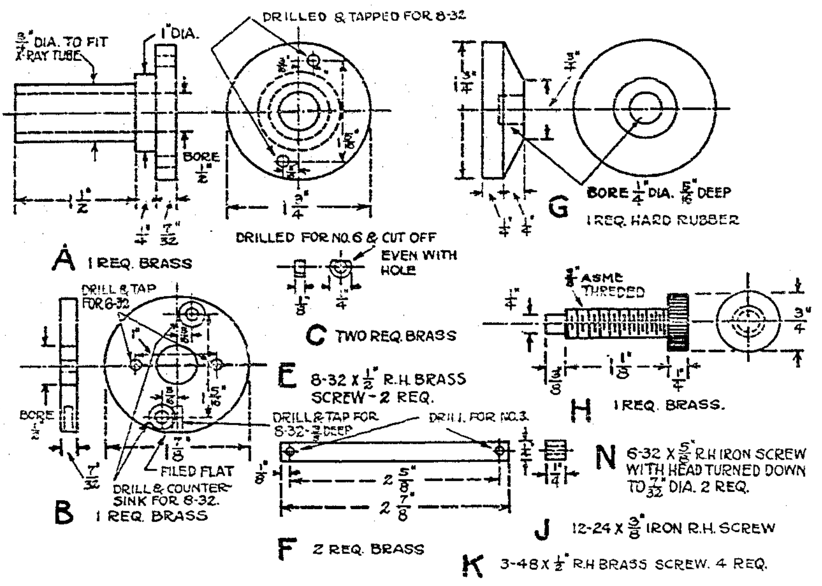
3/4" DIA. TO FIT X-RAY TUBE
1" DIA.
BORE 1/2"
1 1/2"
1/4"
7/32"
A 1 REQ. BRASS
DRILLED & TAPPED FOR 8-32
3/8"
1 5/16"
5/16"
1 3/4"
DRILLED FOR NO. 6 & CUT OFF EVEN WITH HOLE
1/8"
1/4"
C TWO REQ. BRASS
1 3/4"
3/4"
1/4"
1/4"
1/4"
G
BORE 1/4" DIA. 5/16" DEEP
1 REQ. HARD RUBBER
DRILL & TAP FOR 6-32
1"
5/16"
5/16"
1 5/16"
BORE 1/2"
7/32"
1 7/8"
FILED FLAT
DRILL & COUNTER-SINK FOR 8-32.
B 1 REQ. BRASS
E 8-32 X 1/2" R.H. BRASS SCREW - 2 REQ.
DRILL & TAP FOR 8-32 - 3/8" DEEP
DRILL FOR NO. 3.
1/8"
2 5/8"
2 7/8"
F 2 REQ. BRASS
3/8" ASME THREDED
1/4"
3/4"
3/8
1 1/8"
1/4"
H 1 REQ. BRASS.
1/4"
1/4"
N 6-32 X 5/8" R.H IRON SCREW WITH HEAD TURNED DOWN TO 7/32" DIA. 2 REQ.
J 12-24 X 3/8" IRON R.H. SCREW
K 3-48 X 1/2" R.H BRASS SCREW. 4 REQ.

Fig. 3.

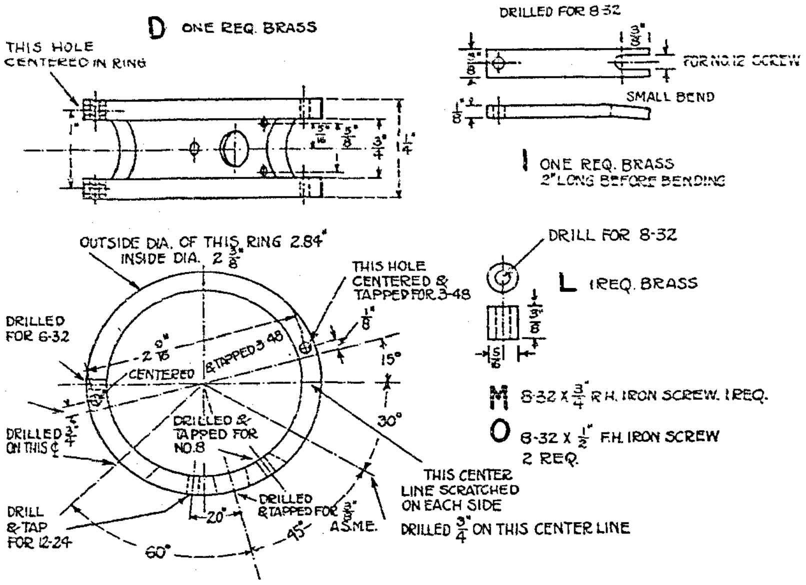
D ONE REQ. BRASS
THIS HOLE CENTERED IN RING
DRILLED FOR 8-32
FOR NO. 12 SCREW
SMALL BEND
I ONE REQ. BRASS
2" LONG BEFORE BENDING
OUTSIDE DIA. OF THIS RING 2.84"
INSIDE DIA. 2 3/8"
THIS HOLE CENTERED & TAPPED FOR 3-48
DRILLED FOR 6-32
CENTERED
& TAPPED 3-48
DRILLED & TAPPED FOR NO. 8
DRILLED 3/4" ON THIS ℄
DRILL & TAP FOR 12-24
DRILLED & TAPPED FOR 3/8" A.S.M.E.
15°
30°
45°
60°
THIS CENTER LINE SCRATCHED ON EACH SIDE
DRILLED 3/4" ON THIS CENTER LINE
DRILL FOR 8-32
L 1 REQ. BRASS
M 8-32 X 3/4" R.H. IRON SCREW. 1 REQ.
O 8-32 X 1/2" F.H. IRON SCREW 2 REQ.

FIG. 4.

out of the path of the main beam and operating the x-ray tube for a few seconds. The envelope for containing the film may be made from the black paper which comes with the x-ray films. A convenient size for the films is two by five inches. The diameter, 2.84 inches, given in Fig. 4 allows for one thickness of paper between the ring D and the film. With these dimensions, one inch on the film is equal to 40° of angle so that engineering graph paper may be used for plotting theoretical positions of lines for comparison with those on the film. Fig. 5 shows a photograph taken with this spectrograph.

The writer wishes to express his thanks to Mr. P. B. Evens who constructed the spectrograph.

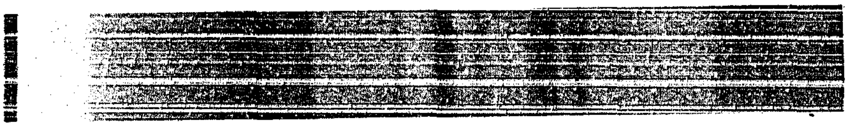

FIG. 5. *Diffraction pattern of gold. Iron radiation.*