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THE ELECTROLYTIC POLISHING AND
DEPOSITION OF METALS.

AN ELECTRON DIFFRACTION STUDY.

By

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THE ELECTROLYTIC POLISHING OF METALS.

I. INTRODUCTION.

During the past decade, the steady progress in importance which electrolytic polishing of metals has achieved is distinctly remarkable. This importance emerges alike in the purely theoretical and in the technical aspects of the subject. The process is no longer the laboratory curiosity that it was a few years back, to be used by metallographers for preparing specimens for microscopic examination. From the strictly utilitarian point of view, industry was not slow to appreciate the advantages, and electropolishing processes are now in use on a commercial scale in production.

Electrolytic polishing is apparently accomplished by preferable anodic solution of high points on the surface of the metal in a suitable electrolyte, under conditions which leave the surface smooth and bright.

The object of the present investigation is to elucidate by electron diffraction the nature of the electropolished metal surface and to throw some light on the mechanism of electrolytic polishing.

1. History and Development.

A brief survey of the history of electropolishing should prove of some interest in relationship to its status today. Anodic methods of cleaning metals have been known for a long time (e.g. Madsen, 1925; Laban, 1930). It was realised with a proper regulation of bath conditions, bright cleaned surfaces could be obtained (Burns and Warner, 1928; Hogaboom, 1932). The brightening of anodes during electrodeposition has also been noted by workers in the field from time to time (e.g. Schwartz, 1923; Thompson and Rice, 1935).

In 1930 Figour and Jacquet undertook a systematic investigation of certain electrochemical processes with the object of obtaining highly polished metal surfaces. They developed for that purpose two different solutions. The first was a mixture of orthophosphoric acid (60°Be) and ether and was suitable for polishing copper. The second, suitable for several other metals (Ni, Al, Zn, Fe, Pb and Sn), was a solution of perchloric acid (55°Be) and glacial acetic acid. The metal to be polished was made anode and corroded in such a way that its surface became bright. The authors noted that best results were obtained in solutions as free from water as possible. Although this method was immediately

applied in France for the preparation of nickel pieces used in the construction of radio valves, it seemed to be quite unknown in other countries.

In 1935 Jacquet observed that, in the case of copper and its alloys, it was not necessary to use an anhydrous solvent, a fact which greatly facilitated the industrial application of the method. He studied the anodic behaviour of copper in aqueous solutions of the three phosphoric acids (1936 a,b) and described the method whereby copper could be polished in orthophosphoric acid under prescribed conditions of current and E.M.F.

Faust (1946) claims that before the main articles of Jacquet appeared in 1935, industrial applications for electrolytic polishing were being investigated at the Battelle Memorial Institute, Ohio, U.S.A. However, it must be admitted that it was only due to Jacquet's original papers in 1935-36 that the subject attracted the attention of the metallurgical world and has since been the object of much interest. Jacquet has since extended his method to the electrolytic polishing of aluminium and its alloys (1937 a, 1938, 1943a), tin (1939a), iron, steel and stainless steels (1939 b,c), lead and nickel (1940), all in perchloric acid - acetic anhydride baths, and of magnesium, zinc, and lead bronzes in an orthophosphoric acid ethyl alcohol bath (1943b, 1944).

Soon after Jacquet had published his researches on the electrolytic polishing of copper, other workers in the field published different methods for polishing various metals. Thus the polishing of zinc in 25% aqueous potassium hydroxide was described by Vernon and Stroud (1938) and in perchloric-acetic acid electrolyte by Capdecorme and Orliac (1941, 1942). Elmore polished cobalt (1938a), electrolytic iron and iron silicon alloys (1939) in aqueous solutions of orthophosphoric acid. Uhlig (1940) using phosphoric acid with glycerine or other addition agents polished 18-8 stainless steel mild steel and chrome steel.

A detailed study of sulphuric - phosphoric acid baths for polishing stainless steel has been done by Faust and Pray (1941a,b) and for polishing plain carbon steels by Imboden and Sibley (1942). Suitable compositions and optimum conditions for working on an industrial scale were given in each case. The effect of various addition agents on such baths has recently been investigated by Sparks (1946).

Kuhn (1939), and Brown (1940) described the "Nital" process for the electrolytic polishing of phosphor bronze, silicon bronze, nickel, monel, nichrome and other metals in a mixture of two parts absolute methyl alcohol and one part concentrated nitric acid. The "Brytal" process for the production of aluminium reflectors was described by Pullen

(1936) and by Ensor (1942). Briefly it consists in anodic polishing in an aqueous solution of sodium carbonate and tribasic phosphate followed by anodising in aqueous sodium bisulphate to produce a protective oxide layer which does not reduce reflectivity.

Recently Evans and Whitwham (1947) developed a new bath composed of a mixture of ethyl alcohol, normal butyl alcohol and water in which zinc and aluminium chlorides are dissolved. The bath has been used successfully for the polishing of metallographic specimens of aluminium, zinc, tin, 18-8 stainless steel, nickel, cobalt and chromium. Also many aluminium alloys have been polished including simple binary alloys containing nickel, chromium, iron, magnesium and copper, as well as commercial alloys such as duralumin and hydronalium.

(Hothersall and Hammond (1940) showed that electroplated nickel articles could be polished in a bath of 73% by weight sulphuric acid.) Gilbertson and Fortner (1942) succeeded in anodically polishing silver in complex cyanide baths. Cadmium has been polished in perchloric acid medium by Capdecemme (1943) and in cyanide solution by Liger (1944). A 0.25 - 0.5 N sodium hydroxide solution has been used by Hughes and Coomes (1939) for the anodic polishing of tungsten.

The literature contains information on many other electrolytes reported to be satisfactory for the electrolytic

polishing of different metals. Surveys of such electrolytes as well as of the technique, applications and future of electrolytic polishing have been published by Jacquet (1943e, 1947), Wernick (1943, 1948), Zmeskal (1945) and Wein (1948), where numerous other references are to be found.

In general the solutions for electrolytic polishing may be placed in either of two categories.

Category A. Solutions of low electrical resistance requiring low voltage supply from 4-15 volts. This includes solutions based upon phosphoric acid and such acids as sulphuric, chromic, hydrofluoric, citric, etc. with or without organic addition reagents such as glycerol, alcohol, carbitol. Alkaline solutions for polishing Zn, W, Al, Cd, Ag are also in this category.

Category B. Solutions of high electrical resistance requiring high voltage from 25-220 volts. These are solutions based mainly on perchloric acid and organic reagents like acetic anhydride, acetic acid, alcohol and ether.

Solutions of the second category should be operated cold (temperature not exceeding 30°C.). External cooling is always necessary since the solution is heated by the current input. Most solutions of this category contain small proportions of water to increase the conductivity.

Solutions of the first category which are used for

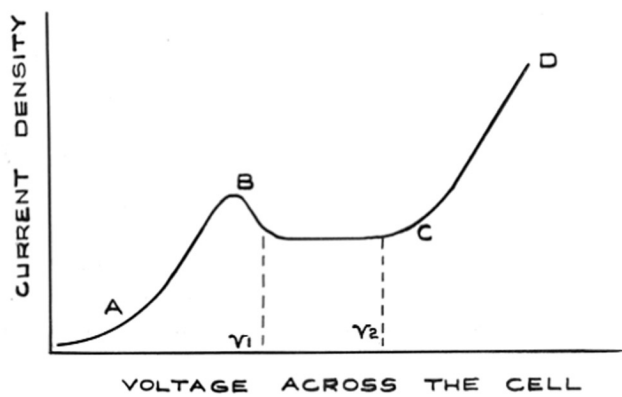


Fig. 1.

stainless and plain carbon steels must be operated at high temperatures for best performance. The range varies between 40°C. and 150°C. depending upon the electrolyte. Electrolytes used for other metals are usually operated at room temperature, In most cases solutions of this category contain a higher percentage of water than Category B.

2. Electrical Relationships (E.M.F./Current Density of the Polishing Process.

In most cases the variation of anode current density with the voltage across the cell (circuit Fig.6) could be represented by a curve of typical shape established by Jacquet in 1936 for copper in orthophosphoric acid and is shown diagrammatically in Fig.1. It is essentially similar to those reproduced by Muller and by Hedges (1937) in their study of anodic reactions. The curve is composed of three distinct zones (a) a straight line AB, along which the anode dissolves at a rate increasing linearly with the applied voltage; (b) a horizontal section BC corresponding to an abrupt increase in cell voltage, while the current remains practically constant, though there is sometimes a slight increase in current at the beginning; (c) a sloping part CD along which a slight increase in voltage corresponds to a relatively large increase in current density.

Each of these three zones is associated with a characteristic appearance of the anode surface.

a). Along AB the anode is etched and a matt surface is obtained.

b). Within the voltage range ($v_1 v_2$) corresponding to the almost horizontal zone BC, the anode surface becomes bright especially if the cell voltage is close to v_0 . On the other hand if the cell voltage has a value closer to v_1 , the anodic attack may produce a surface with a relatively lower reflectance and the structure of the metal is revealed.

c). Under the conditions represented by the zone CD, the surface is always bright. At voltages close to C, however, the anode surface, though bright, has numerous irregularities (small areas in relief). Probably these are the areas covered by very fine oxygen bubbles which adhere to the metal surface rather tenaciously (at least for a short time at the beginning of the electrolysis, before they are evolved) and protect the underlying metal from anodic attack.

Vigorous agitation of the anolyte results in a perfectly bright and even surface since oxygen bubbles adhere to the anode only momentarily. At higher current densities, no stirring of the electrolyte is necessary to produce an even surface since the gas discharge is so intense that the bubbles are evolved as soon as they appear at the anode.

It is natural that under these conditions of high current density the anode solution efficiency is far below 100% whereas at the lower current densities it is always close to 100%.

A similar type of curve has always been found in the electropolishing of zinc and tungsten in alkaline solutions, of zinc and magnesium in phosphoric acid-alcohol mixture, and of iron and cobalt in phosphoric acid, and of aluminium in perchloric-acetic anhydride mixture.

It must be stressed, however, that the above form of curve is dependent on the use of the "potentiometer type" of circuit; (see Fig.6 later) the potentiometer "tapping resistance" in parallel with the cell should be small compared with cell resistance. Under such conditions relatively large increases in cell resistance due to anodic polarisation have a negligible effect on the resistance of the joint system and hence on the voltage across the cell. In other words the potential difference across the cell terminals is controlled by that fraction of the potentiometer in the joint circuit. On the other hand with a low tension source and a series resistance, or with a potentiometer arrangement where the tapping resistance is high compared with the cell resistance, the cell voltage cannot be externally varied throughout the range investigated, since it is mainly

determined by the cell resistance itself.

3. Influence of Various Factors on the Electropolishing Process.

The general shape of the curve in Fig.1 for the anodic behaviour of copper in orthophosphoric acid is practically not modified by the various features of the electrolysis. These may have, however, an important effect on the horizontal region BC where the electrolytic polishing occurs without gas evolution. Thus:-

1. The higher the electrolyte concentration the lower will be the current density at which the horizontal region BC appears in the curve. Furthermore, the width of this region BC increases as the concentration of the electrolyte increases.

2. Agitating the electrolyte results in an increase of the current density at which the horizontal section BC appears.

3. The higher the temperature, the higher the current density at which BC occurs.

4. The position of the anode has also a distinct effect on the current density at which the horizontal region BC occurs. This current density is higher with a vertical anode than with the same anode placed horizontally.

✓ These results seem to suggest that all the factors which favour the diffusion of the products of anode dissolution necessitate the use of a higher current density for electropolishing; in other words these factors reduce the efficiency of the process. Jacquet (1936b) therefore assumed that the abrupt increase in cell voltage which takes place on reaching a certain current density (point B) is due to the accumulation of the products of anodic attack in the immediate vicinity of the anode.

This diffusion layer which limits the current density ✓ that can pass through the cell seems to play an important role in the mechanism of electrolytic polishing.

4. The Mechanism of Electrolytic Polishing.

Hitherto, it has been found difficult to account for the exact mechanism of the anodic polishing. From his experiments on the anodic polishing of copper in phosphoric acid, Jacquet has been led to attribute a particular importance to the liquid layer covering the anode. This "diffusion layer" is produced by the slow diffusion of the products of anodic dissolution into the bulk of the electrolyte and is assumed to have a higher electrical resistance and has been observed by Jacquet (1936b) to cover the anode surface evenly. In other words it does not closely follow the irregularities of the

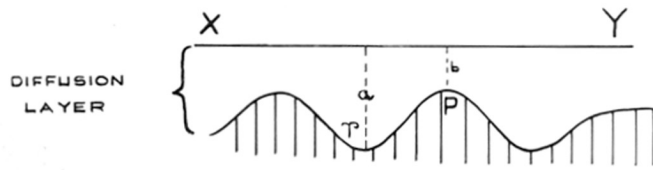


Fig. (2)

surface but represents a rectilinear margin XY (Fig.2). Thus the thickness of the diffusion layer at a projection "p" is less than at a recess "r" ($b < a$), with the result that the electrical resistance across the film is smaller at the projections than at the recesses. Consequently, Jacquet concludes, a greater current density results on the projections "p" than on recesses "r" and the former thus tend to dissolve preferentially. The surface, accordingly, will be made more nearly level.

Later Elmore (1939, 1940) has modified this simple explanation to the extent that the rate of diffusion of the dissolved anode material into the electrolyte, and not an Ohm's law resistance, is the main factor. Elmore assumes that the concentration gradient of the dissolved metal at the anode is proportional to the current density. An upper limit to this concentration is set by the limit of solubility of the metal in the electrolyte next to the anode. When this limit is reached, the gradient will be greatest near projecting portions of the surface and these portions will, therefore, dissolve more rapidly than the rest of the surface resulting in a polishing effect.

A critical discussion of both the Jacquet and Elmore mechanisms will be set forth later.

5. The Nature of the Electropolished Metal Surface.

(i) The Study of Surface Structure by Electron Diffraction.

The experimental proof of the wave properties of moving electrons has put into our hands a most efficient research tool for the study of surface structure. Electron waves, unlike X-rays, are associated with no electric charge and are therefore very efficiently scattered by atoms, mainly by the nucleus, whereas, in the case of X-rays, the orbital electrons play the chief role in this scattering. At a grazing incidence on a smooth surface the depth to which electrons are penetrate coherently below the surface is limited to only a few atomic layers and the information which can be given under these conditions by electron diffraction is confined to these surface layers. On the other hand, X rays, owing to their high penetrating power, effectively reveal only the average structure of the underlying mass.

An efficient electron diffraction technique has been developed by Professor G.I.Finch in this laboratory and has been applied by Finch and his collaborators (1933-1948) to a variety of problems of surface structure, such as the structure of polish, the structure of electrodeposits as influenced by substrate effects and bath conditions, the structure of anodic

films and the problem of crystal growth from the vapour state and from solution. Excellent surveys of the application of electron diffraction to such problems have been given by Finch and Wilman (1937a), Finch and Fordham (1937) and by Finch (1938).

(ii) Electron Diffraction Study of Mechanically and Electrolytically Polished Surfaces.

Beilby's original ideas (1921) that a mechanical polishing causes the surface material to flow and the resulting surface is glass-like and amorphous were not universally accepted. The evolution of the electron diffraction method of examination has offered a new and powerful tool for confirming or disproving his hypothesis. It was applied by Thomson (1930), French (1930), Kirchner (1932, 1935) and Raether (1933), but their results left in doubt the issue as to whether the polished layer is crystalline or amorphous. It was only settled in favour of the amorphous layer by experiments carried out in this laboratory by Finch, Quarrell and Roebuck (1934).

When the electrolytic polishing method of polishing metals was introduced by Jacquet, the question immediately arose as to whether the surface layer was crystalline or amorphous and whether it was the metal or one of its oxides formed by the anodic treatment. Needless to say, the

electron diffraction technique was soon employed for this purpose.

Moore (1938) examined electrolytically polished copper by electron diffraction. (When the original specimen was polycrystalline, the surface consisted of cuprous oxide with strong (110) orientation. With an electrolytically polished 110 face of a copper single crystal, the oxide crystals arranged themselves with a cube edge parallel to a cube of the copper crystal. With a (100) copper face, several orientations of the Cu_2O were observed, but the one which occurred most frequently was (111), the cube face diagonal of the Cu_2O being approximately parallel to the cube edge of the underlying copper crystal.)

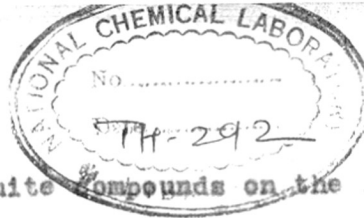
Two years later Nelson (1940) claimed that electrolytically polished copper always gave a pattern due to Cu_2O . He also found that iron, aluminium and stainless steel polished electrolytically gave electron diffraction patterns identical with those from the same surfaces mechanically polished, i.e. diffuse haloes. (Since the electrolytic method cannot produce a layer of amorphous metal, he concluded that a thin film, probably an oxide, covered the surface of electrolytically polished surfaces and gave rise to the diffuse halo pattern.) Nelson, however, did not publish any of his electron diffraction patterns, neither did he give the conditions under

which he polished the metal surface.

In 1944, Kranert, Leise and Raether investigated electropolished metal surfaces by electron diffraction. Although they investigated Al, Fe, Pb and Cu, only patterns of the latter metal are shown. Their results can be summarised as follows. (A single crystal surface is polished better than a polycrystalline one. A polycrystalline surface gave a pattern which showed elongated spots in place of the usual rings. However, a pattern of the surface before electrolytic polishing was not given for comparison. The authors also found that under certain conditions not clearly defined nor reproducible an orientated or polycrystalline film of copper oxide was detected on the patterns from electropolished surfaces as previously recorded by Moore.

6. Object of this Investigation.

Previous work in this laboratory, directed by Professor Finch, has provided by electron diffraction experiments a much clearer understanding of the structure of electrodeposits and the growth of the metal crystals at the cathode, (Sun, 1935). The electron diffraction technique in this laboratory has also elucidated the nature of mechanically polished surfaces (Finch, Quarrell and Roebuck, 1934) and has indicated, in the case of certain anodic



reactions, the formation of definite compounds on the anodes under different polarising conditions (Lanthen, 1937). The present experiments extend these investigations to the study of the anodic polishing of metals.

The previous section outlines the contradicting conclusions arrived at by Moore, Nelson and Kranert and his co-workers. In the same manner as the problem of a mechanically polished surface was finally settled by electron diffraction in favour of an amorphous "Beilby layer" in this laboratory, it was felt necessary to elucidate decisively the problem of the nature of an electrolytically polished surface. A clear and definite picture of the nature and structure of the polished metal surface is essential before the formulation of any theory of electrolytic polishing could be attempted.

Moreover, the foregoing review shows that the mechanism of electrolytic polishing is not yet sufficiently clarified. Until now metals were electropolished in electrolytes developed by the method of trial and error. The experimenter is only guided by certain vague conditions which are largely empirical and the absence of a coherent and preferably quantitative theory retards the progress of this new branch of electrochemistry. Such a theory would assist in finding new conditions for polishing and perfecting the techniques already in use. The importance of such progress

to other branches of scientific research as well as for the metallurgical and industrial world can hardly be overestimated.

It was therefore felt necessary to carry out research expressly directed to investigating the theoretical aspects and as far as possible establishing the details of the mechanism. For this purpose the measurement of anode potential of the metal undergoing electrolytic polishing and under different conditions would be of more direct theoretical interest than the usually measured voltage across the cell. The system copper-phosphoric acid was chosen for a detailed investigation on account of the low voltage required and the ease of polishing at room temperature. The study was also extended to other metals, aluminium and silver.

It was also of interest to compare, in general, the properties of electrolytically and mechanically polished surfaces, and in particular the substrate effect of such surfaces on the growth of electrodeposits.

ELECTRON DIFFRACTION CAMERA.

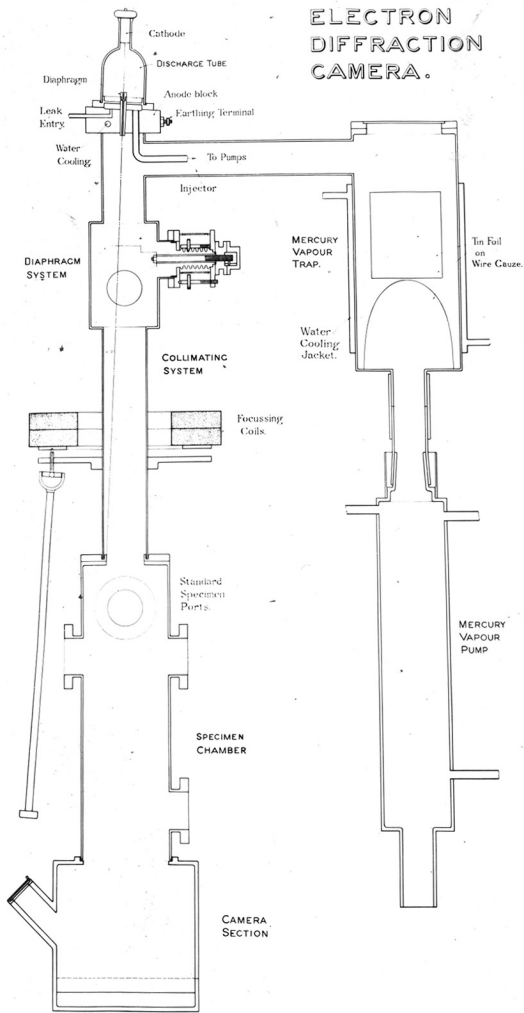
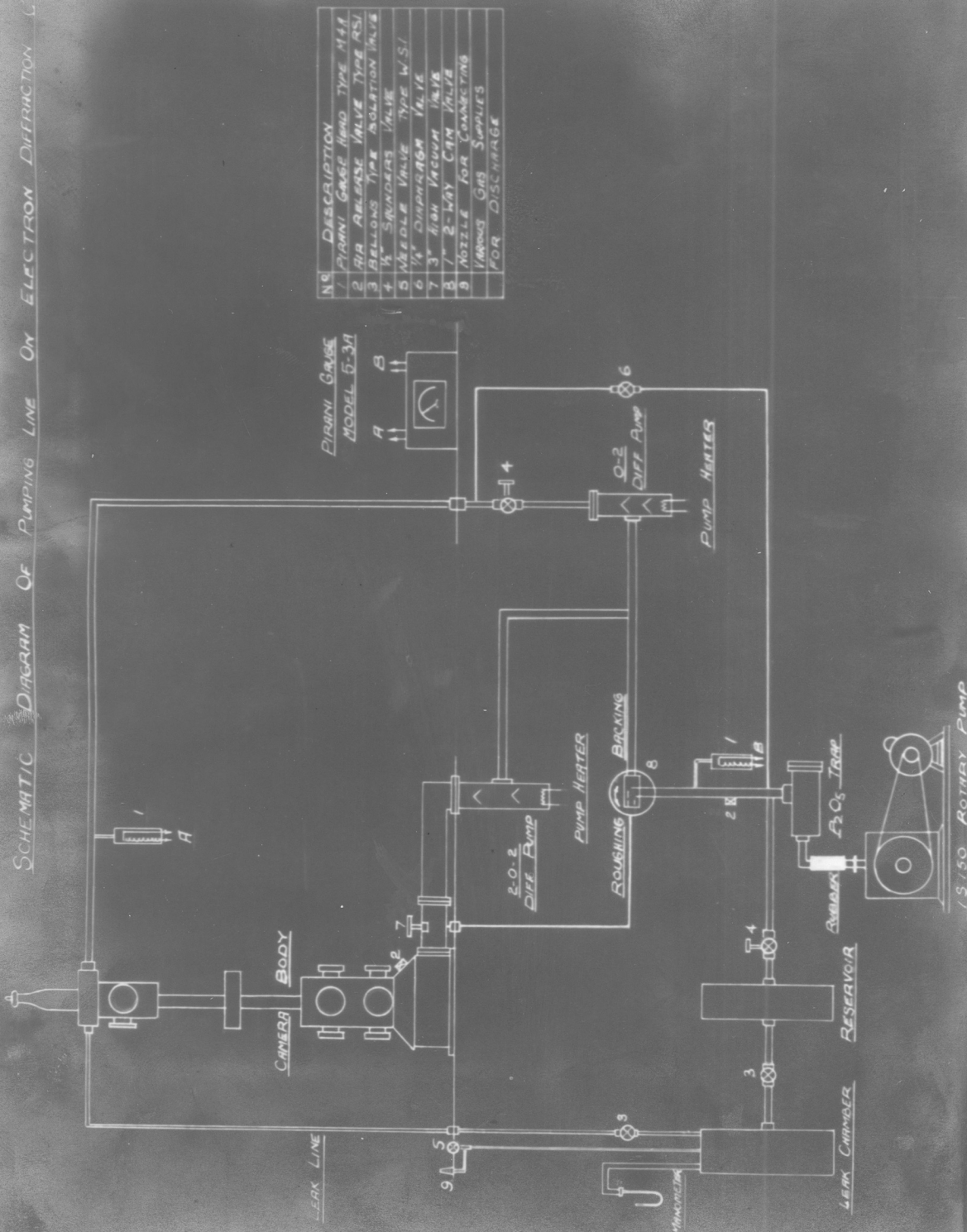


Fig.3.

Fig 4

SCHEMATIC DIAGRAM OF PUMPING LINE ON ELECTRON DIFFRACTION CAMERA



No	DESCRIPTION
1	PIRANI GAUGE HEAD TYPE M44
2	AIR RELEASE VALVE TYPE RS1
3	BELLOWS TYPE ISOLATION VALVE
4	1/2" SINDERS VALVE
5	NEEDLE VALVE TYPE W/SI
6	1/4" DIAPHRAGM VALVE
7	3" HIGH VACUUM VALVE
8	1" 2-WAY CAM VALVE
9	NOZZLE FOR CONTACTING VACUUM OIL SUPPLIES FOR DISCHARGE

PIRANI GAUGE MODEL 5-31



Fig.(5) Finch Electronic Diffraction
Camera - Commercial Pattern
(W.Edwards & Co. - London).

II. APPARATUS AND TECHNIQUE.

1. The Electron Diffraction Camera.

The examination of the specimens was made by a Finch type of diffraction camera (Finch and Wilman (1937a), evacuated by means of a three-stage mercury vapour diffusion pump backed by a rotary oil pump (Fig.3). In the later part of the present investigation the new version of the Finch camera as manufactured by W.Edwards and Co. (London) was used. A diagram of this camera is shown in Fig.4 and a photograph in Fig.5. In this camera two oil pumps, one for the discharge chamber and another for the specimen chamber, were used instead of the mercury pump. The diffusion pump could be isolated during the preliminary pumping of the camera and breaking of the vacuum. This was of great advantage in the examination of metal specimens which demanded a speedy examination to avoid oxidation or contamination with sulphide films.

Camera lengths of 50 cms. and 25 cms. were used with accelerating potentials between 50-60 KV., corresponding to a wavelength of $.053 \text{ \AA} - .049 \text{ \AA}$. The electron beam was focussed by adjusting the focussing current and by tilting the coil, the beam is biased, to fall on the specimen. With a

reflection specimen the angle of incidence is made of the order of $\frac{1}{2}^{\circ}$ to 1° . By varying the tilt of the focussing coil, different parts of the specimen can be explored. When the clearest possible diffraction pattern characteristic of the whole specimen has been found, the diaphragm above the specimen is brought into position, the photographic plate exposed for about 5 seconds and the voltage measured by a 10 cm. diameter sphere gap. Ilford Special Rapid plates were used.

2. The Electrolytic Polishing Cell and Circuit.

The electrolytic polishing as well as the potential measurements were conducted in a glass beaker of 250 cc. capacity placed in a 2-litre glass vessel which was kept at constant temperature. The amount of electrolyte used in each experiment was about 180 cc. A thermometer clamped against the side of the beaker served to indicate the temperature of the electrolyte. Fresh quantities of electrolyte were used in each experiment of anode potential current measurements since the contamination and enrichment of the electrolyte by metal ions largely affected the electrical relationships. The electrodes were of the same pure metal sheet, 2 x 2 cms. for the anode and 4 x 4 cms. for the cathode. The metal was 0.5 mm. thick.

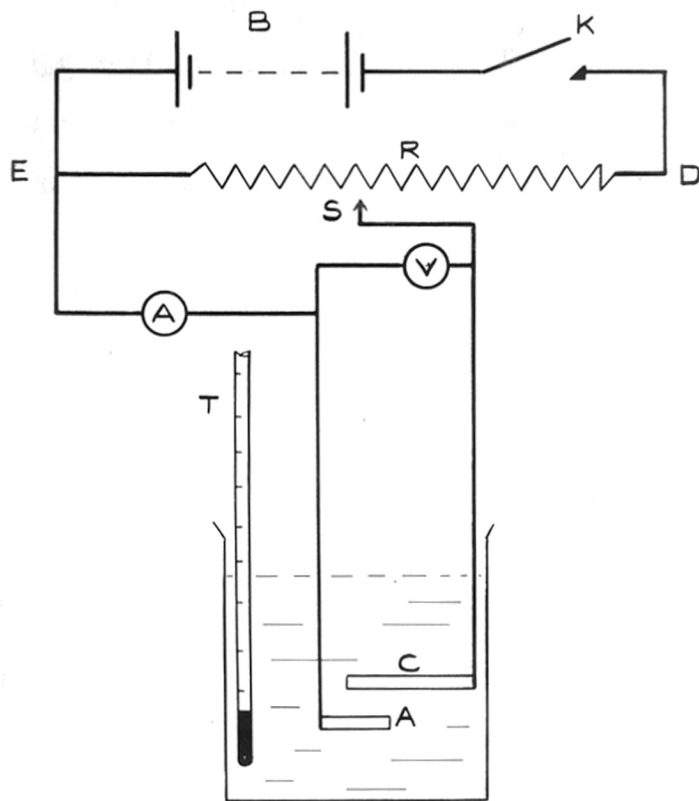


Fig.6,
The Electrolytic Polishing Circuit.

The connection to the source of current was made by means of two long stout wires of the same metal screwed in specially threaded holes at the corners of the electrodes. In this way it was possible to avoid the contamination of the electrolyte by other foreign metal ions when the two electrodes were horizontal and completely immersed in the electrolyte. Unless otherwise stated all experiments were conducted with the electrodes horizontal, two cms. apart and with the anode lying beneath the cathode.

The anode always received a preliminary abrasion with emery paper followed by degreasing in benzene vapour. It was thought safer, in the results to follow, to give the current reading as observed on the ammeter rather than dividing it by the apparent surface area of the anode (8 sq.cms.) and assigning a definite current density.

A diagram of the electrical circuit is shown in Fig.6 and is of the potentiometer type. The source of current supply was a battery "B" of four 6-volt accumulators. These are connected through a key, K, to the ends E, D of a sliding resistance R of 50 ohms. The anode "a" is connected through a milliammeter "A" with one end "E" of the resistance, and the cathode "c" with the sliding contact "S". The electrodes are connected with a sensitive voltmeter V.

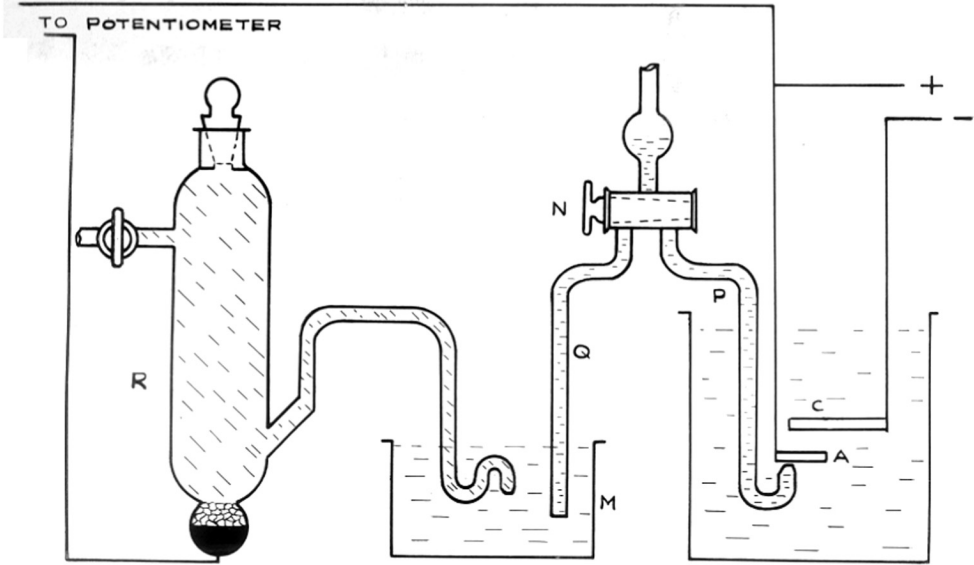


Fig.7.

As milliammeter, a "Cambridge versatile galvanometer" connected to its D.C. range box was used. This box contains shunts ranging from 20 ma. to 10 amperes for full scale reading. As voltmeter, a Model 7 Avometer was used and with its different shunts the potential difference across the cell could be easily read to the nearest .01 volt.

3. The Measurement of Anode Potential.

As shown in Fig.7, the potential of the experimental anode "a" was determined by connecting it through a suitable salt bridge N to the reference electrode R, through an intermediate vessel containing saturated KCl. The reference electrode was a saturated calomel electrode. The E.M.F. of the cell consisting of the electrodes "a" and "R" was then measured by means of a potentiometer. By adjustment of the slide contact S (Fig.6), the voltage between the electrodes could be raised in small steps (in the direction ED) and the potential of the electrode measured for each value of the current, after allowing sufficient time for stable conditions to be attained.

As a potentiometer, a Cambridge portable pH meter was used. This gave a direct reading of E.M.F.'s up to 1.4 volts, accurate to within one millivolt. For higher

values of E.M.F., a standard cadmium cell was introduced into the circuit opposing the cell "Ra".

The salt bridge consisted of two limbs P and Q. By means of a two-way stopcock "N", the limb Q was filled from the intermediate vessel R with saturated potassium chloride, while the limb P was filled with the electropolishing electrolyte. Connection between the two limbs is made by a film of saturated potassium chloride around the closed stopcock. In this way diffusion of any potassium chloride into the electrolyte was avoided when experiments at elevated temperatures were made. It was also necessary to observe that the end of the limb P must be placed outside the lines of current flow (to avoid any error in potential due to IR drop between anode and cathode) and must press close to the anode surface.

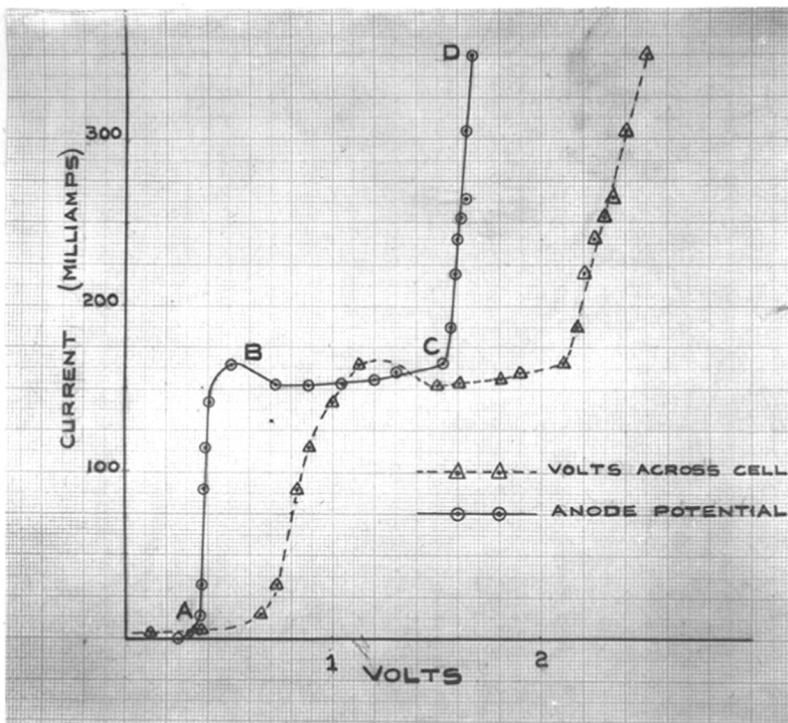


Fig. 8.

III. EXPERIMENTAL RESULTS AND THEIR THEORETICAL DISCUSSION.

1. The Electrolytic Polishing of Copper.

(i) Form of the Current-Potential Curve.

Fig.8 shows the anodic potential curve of copper in orthophosphoric acid (666 cc. per litre). The shape of the curve is similar to the voltage (across the cell) - current curves obtained by Jacquet. Experiment has shown that the deviation of the voltage-current curve from the anode potential-current curve becomes more pronounced as the anode surface area increases relative to the cathode.

From Fig.8 it can be seen that with increasing voltage, the current density rises steadily up to a maximum at B, and after a range of instability represented by the hump, there follows a horizontal section BC. When evolution of oxygen begins, the curve again takes upward bend.

The anode was polished under conditions represented by the flat portion BC. At conditions corresponding to the ascending portion CD, the anode is polished but pitted due to the tenacious adherence of very small oxygen bubbles to the metal. At very high current densities near or above D, polishing, without pitting, occurs.

(ii). The Suggested Mechanism of the Anode Dissolution of Copper in Phosphoric Acid.

The above experimental results show that an anode potential - current density curve of the type shown in Fig. 8 defines a range BC over which electrolytic polishing of copper occurs. The polarisation of the anode arises from the fact that metal dissolution results in an increase in the number of ions in contact with the metal in solution, and if the rate of cation diffusion is relatively slow, their concentration in the immediate vicinity of the anode will be greater than in the bulk of the solution. This results in an increase of anode potential which will be greater the higher the rate at which the metal dissolves, i.e. the higher the current density.

We shall now proceed to discuss in detail the consequences of diffusion as the slow rate determining process in the electrode reaction.

Relation between Concentration and Current Density.

Adopting the ideas of Earnst and Brunner (1904), later developed by Agar and Bowden (1938), we may suppose that the anode surface is covered by a "diffusion layer" of thickness δ . Outside this layer the concentration of cations is that of the bulk of the solution. We assume that convection is

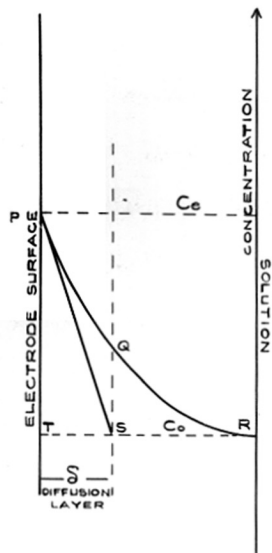


Fig. 9.

negligible inside the layer and that the metallic ions are removed from the vicinity of the anode by diffusion alone. (The current is carried to the cathode by migration of highly mobile hydrogen ions). There will be a concentration gradient in passing from the anode to the electrolyte, and this will theoretically extend to a considerable distance into the solution as represented by the curve PQR in Fig.9, where P represents the concentration of copper ions C_e at the anode and R is the concentration C_0 in the bulk of the solution. It is convenient, however, to consider this replaced by a linear gradient PS as mathematically simpler. The distance TS now represents the thickness of the diffusion layer.

According to Fick's law, the rate of diffusion of copper ions across the layer PS is equal to

$$\frac{AD}{\delta} (C_e - C_0) \dots\dots\dots (1)$$

where A is the exposed anode area, and D is the diffusion coefficient of the copper ions.

In the steady state, the rate at which copper ions are produced by the current will be equal to the rate of diffusion into the bulk of the electrolyte. If I is the current density, so that A in equation (1) is unity, the number of gram-atoms of metal dissolved per second per square centimetre of the surface is equal to I/nF where F represents the Faraday and n the valence of the cation.

It follows, therefore, that

$$\frac{I}{nF} = \frac{D}{\delta} (C_e - C_0) \dots\dots\dots (2)$$

In this deduction it has been assumed that the copper ions are removed from the vicinity of the electrode by diffusion only. In general, however, some of these will be transported by the normal process of migration. If the transport number of the copper ion within the diffusion layer is t_+ , then the rate at which ions are removed by migration from a unit area of electrode surface is t_+I/nF . At equilibrium migration and diffusion must together transport the ions through the diffusion layer to the bulk of the solution as fast as they are formed by metal dissolution, so that:

$$\frac{I}{nF} = \frac{D}{\delta} (C_e - C_0) + \frac{t_+I}{nF} \dots\dots\dots (3)$$

If t is the transference numbers in the diffusion layer of all ions other than copper, we have $t = 1 - t_+$, so that from equation (3):

$$I = \frac{D n F}{t \delta} (C_e - C_0) \dots\dots (4)$$

Comparison with equation (2) shows that migration effectively increases I by a factor $1/t$. Replacing the factor $\frac{DnF}{\delta}$ in

equation (4) by "k" for brevity, we have:

$$I = k (C_e - C_o) \dots\dots\dots (5)$$

In this deduction we assume that the thickness of the diffusion layer δ is practically constant at different current densities. Agar has developed a theoretical treatment which shows that δ in stirred solutions is independent of the difference in concentration of the bulk solution and that at the surface. In unstirred solutions δ is not entirely independent of the concentration but only varies slightly with it.

The Variation of Anode Potential with Current Density.

When no current is flowing in the cell, the reversible potential of the electrode is given by the equation

$$E_o = E^\circ - \frac{RT}{nF} \log_e C_o$$

assuming the use of concentrations instead of activities will give sufficiently accurate results. E° is the standard electrode potential.

During the electrolysis, however, the anode potential will be almost identical with the reversible value for an ionic concentration of copper equal to C_e which is the actual

concentration at the electrode surface, so that:

$$E_0 = E^{\circ} - \frac{RT}{nF} \log_e C_e$$

The value of the "concentration overpotential" E is therefore given by the equation:

$$\Delta E = E_0 - E_e = \frac{RT}{nF} \log_e \frac{C_e}{C_0} \dots\dots\dots (6)$$

Combination of equations (5) and (6) gives the following results for the variation of polarisation with current density.

$$\Delta E = \frac{RT}{nF} \log_e \left(1 + \frac{I}{k C_0} \right) \dots\dots\dots (7)$$

and

$$\Delta E = \frac{RT}{nF} \log_e \left(\frac{1}{1 - I/kC_e} \right) \dots\dots\dots (8)$$

We have now to examine the effect of gradually increasing the current density on the values of C_0 and C_e . When a copper electrode is just immersed in phosphoric acid, the value of $C_e = C_0$ is very small. When the external source of potential is applied to make the copper an anode, C_e will start to increase gradually becoming increasingly higher than C_0 . (The rate of such increase is a function of the rate of increase of the current passing through the solution). Meanwhile the value of C_0 will remain practically constant

since the gradient $C_e - C_0$ is not yet high enough to induce an appreciable rate of diffusion. After a certain time t_1 when the current has attained a certain value, say I_1 , the concentration C_e at the anode surface reaches a maximum constant value C_m representing the limit of the solubility of the metal in the electrolyte under the given conditions. Meanwhile the now appreciable rate of diffusion will increase the value of C_0 which can no more be considered as constant. This treatment is quite justified by two simple experimental observations.

1. When colourless orthophosphoric acid is electrolysed between copper electrodes, at low current densities the bulk of the solution becomes pale blue after the current has passed for a certain time, the blue colour becoming darker as the current density is increased or as electrolysis is further continued.

2. A copper cylinder was used as anode, with the flat top in contact with the solution, whilst the other sides were protected by glass so that the products of the anodic reaction remained where they were. Owing to the restriction of diffusion in this way, a current density which normally produces a polished copper surface, resulted in the precipitation of solid salt on the anode surface. This shows that the concentration in the diffusion layer tends to saturation and unless a certain amount of metal ions are

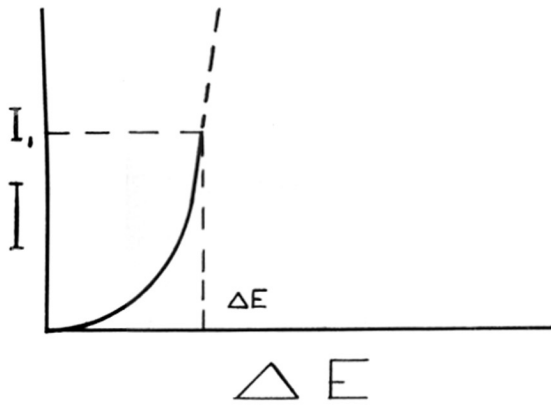


Fig.10

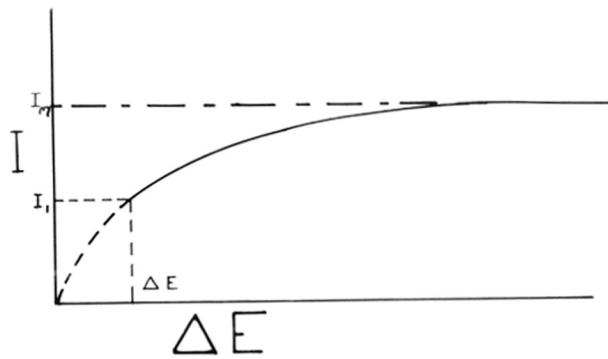


Fig.11

transported to the bulk by a reasonable rate of diffusion, further dissolution of anode material results in the crystallisation of the salt.

Fig.10 represents the relation between ΔE and I as given by equation (7) as long as C_0 remains practically constant. After a time t , when I has attained the value I_1 and C_0 is no more constant, whilst C_e has already attained its maximum constant value C_m , then the relation between

E and I can be plotted as shown in Fig.11, according to equation (8). From this equation it is seen that as the value of I approaches kC_m , the value of ΔE will increase rapidly. In practice a finite increase of potential occurs until another anodic process, namely oxygen evolution, takes place. The current density at which this rapid increase of potential takes place is the "limiting current density" since the current is limited according to equation (5) by the concentration gradient which exists at the anode. The magnitude of this limiting current density is given by:

$$I_m = k(C_m - C_0) = \frac{DnF}{t\delta} (C_m - C_0) \dots\dots\dots (9)$$

Naturally the value of ΔE_1 at I_1 will be the same whether calculated from equation (7) or (8) and will be given by

$$E_1 = \frac{RT}{nF} \log \frac{C_m}{C_0}$$

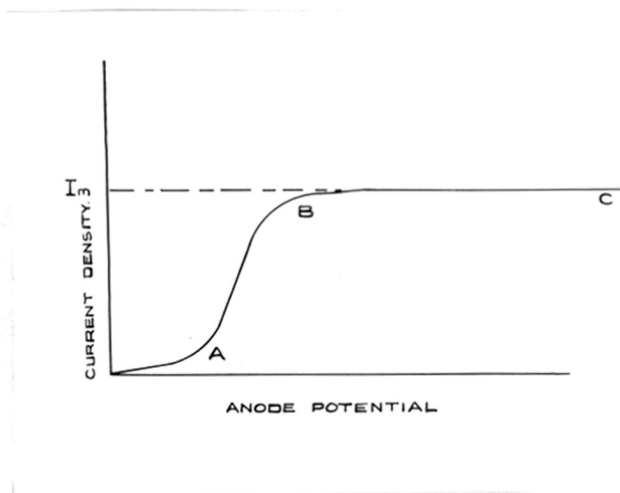


Fig.12.

Hence, a curve as shown in Fig.12 shows the type of anode potential-current relationship which we should expect when the overpotential is determined by the changes in the Cu^{++} concentration at the anode. The curves obtained experimentally (of which Fig.8 is typical) are of the same character and show that such a relationship in the range $I = 0$ to $I = I_{\text{max}}$ (ABC part of the curve) is given by equations (7) and (8).

The value of the current in the range BC is limited by the concentration gradient at the anode as given by equation (9), which expresses the maximum rate of dissolution of copper (maximum rate of diffusion into the bulk solution). If an attempt is made to increase the current still further, the maximum rate of metal dissolution is insufficient to satisfy its requirements and another process must occur simultaneously at the anode. This will be oxygen evolution commencing at the point C (Fig.8) and beyond this point, considerable current can flow with relatively little polarisation as shown by the part CD (Fig.8).

(iii) Factors Affecting the Limiting Current Density.

Experiments have been carried out to test the general accuracy of equation (9). Since the value of I_m as given by BC, defines the polishing range of copper, it was of

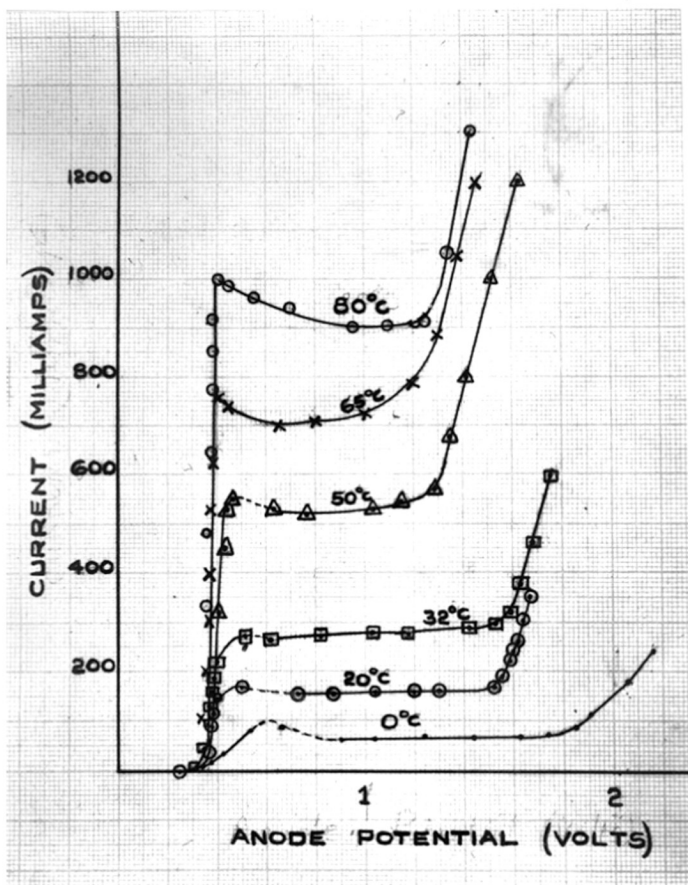


Fig.13.

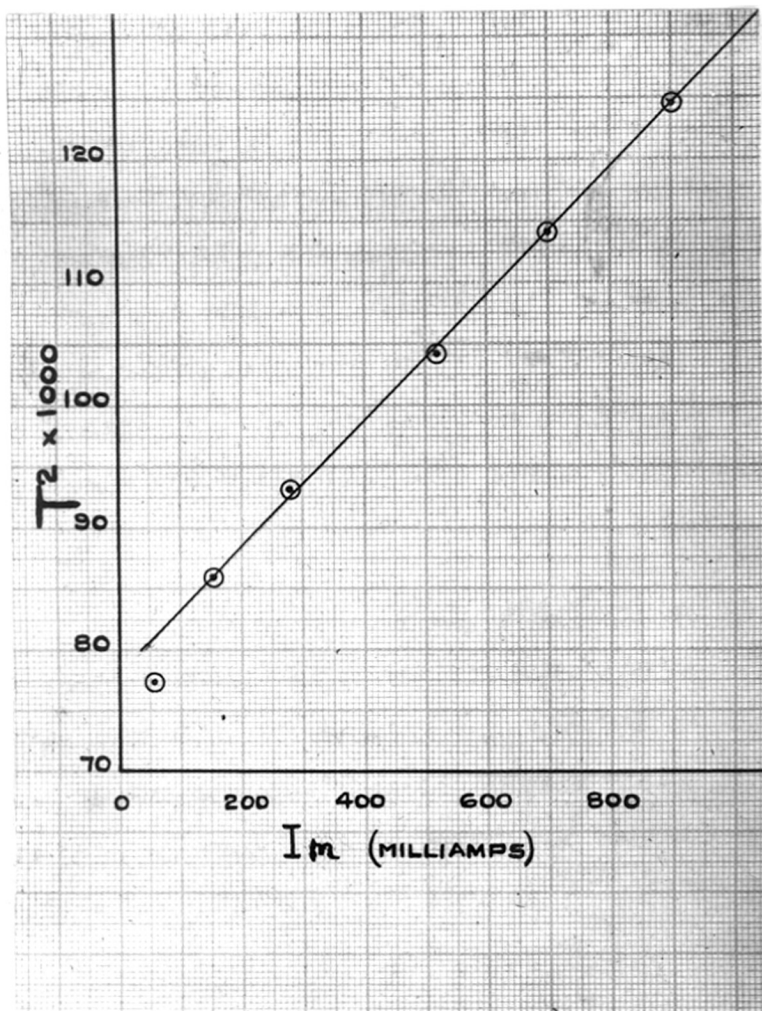


Fig.14.

special interest to investigate the effect of various factors on the value of the limiting current density, to elucidate the importance of the diffusion layer in electrolytic polishing, and to see how far the experimental results agreed with equation (9). These experiments will be discussed in the following order: (1) Effect of temperature of electrolyte. (2) Effect of the position of the anode. (3) Experiments with a rotating anode. (4) Experiments with very restricted diffusion. (5) Effect of the electrolyte composition.

1. Effect of Temperature.

Fig.13 shows the anode potential-current density curves for copper in orthophosphoric acid at 0°C., 20°C., 50°C., and 80°C. The limiting current density represented by the horizontal portion of the curve in each case is seen to increase with rise of temperature. This is to be expected from equation (9), since the diffusion coefficient D increases with rise of temperature.

Glasstone (1942) gives for the diffusion coefficient of an ion of equivalent conductance λ the relation $D = \frac{\lambda RT}{F^2}$

If we assume that λ is roughly proportional to T (Glasstone, 1942, p.61) and that $C_m - C_0/\delta$ remains almost constant, then $D \propto T^2$ and $I_m \propto T^2$ Fig.14 shows this

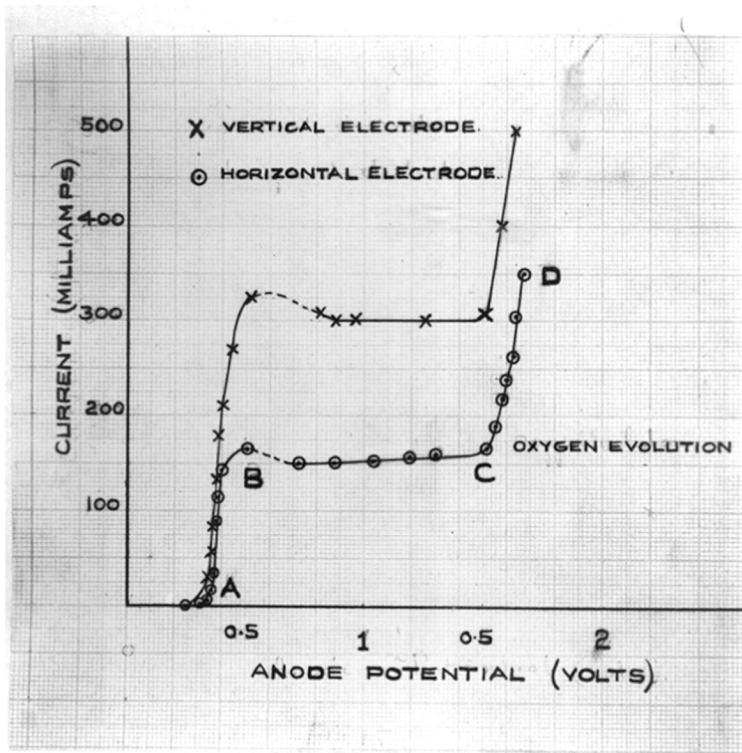


Fig.15.

to be true except for the very lowest temperature. This deviation is presumably due to the much higher value of $C_m - C_0/\delta$ at 0°C (in Fig.13). It should also be noted that the width of the horizontal portion of the curve decreases as the temperature is increased.

The surface was polished in all cases along the horizontal section, though the quality of polish (in a certain time) was better for lower temperatures.

2. Effect of the Position of the Anode.

The position of the anode has a very distinct influence on the value of I_m . Fig.15 shows the anode potential current density relations at 20°C . for a horizontal and a vertical copper anode. Whereas with the electrodes horizontal polishing occurs at a current density of 20 mA/cm^2 , no polishing was possible with a vertical anode until the current density had reached 37 mA/cm^2 .

This effect is to be expected from equation (9), since with a vertical anode the reaction products stream downwards from the electrode, and a higher current density is necessary to maintain a stable diffusion layer under such conditions of enhanced diffusion.

On the other hand the distance between the electrodes had a very negligible effect on the value of I_m . This

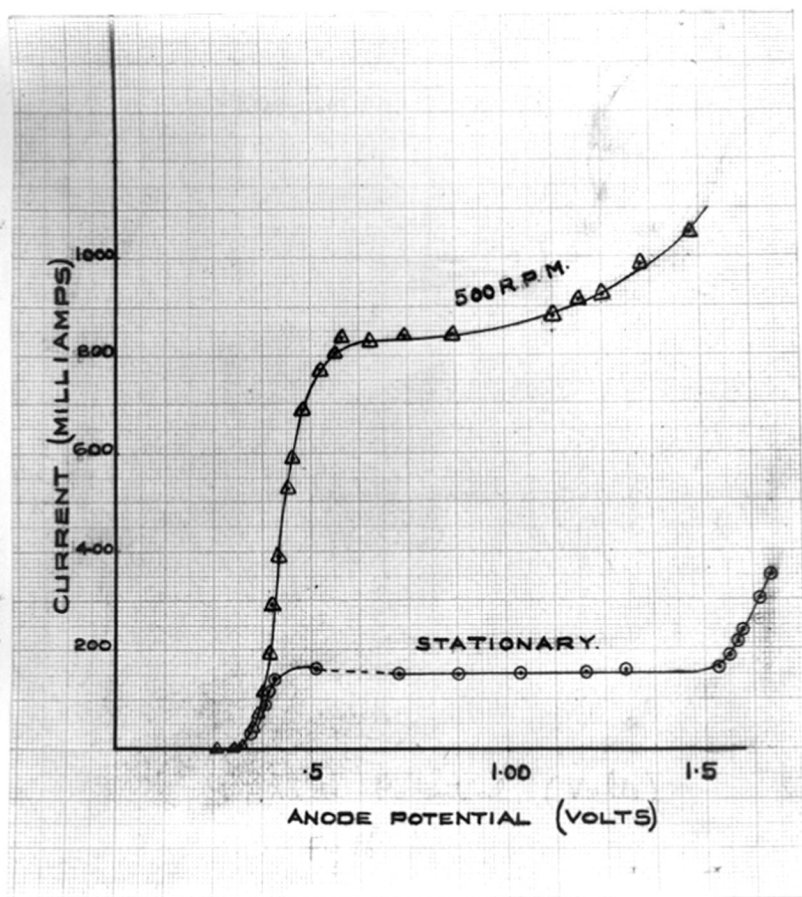


Fig. 16.

implies that the formation of the diffusion layer, as a result of the anode reaction is the condition most relevant for electrolytic polishing.

3. Experiments with a Rotating Anode.

The effect of using a revolving anode instead of a stationary one was investigated. Fig.16 shows that with a speed of 500 rotations per minute, the limiting current density is much higher. This is to be expected from equation (9), since the thickness of the diffusion layer must necessarily decrease when the electrolyte is stirred. In investigating the effect of higher speeds of rotation, the measurement of anode potential presented some difficulty and uncertainty. The voltage across the cell was measured instead and the resulting current-voltage curves are shown in Fig.17. The anode was in these cases a small cylinder of copper (diameter 1 cm., length 1 cm.) screwed to the axis of the motor which was protected with anti-acid paint. The copper cathode was a sheet of 200 sq.cm. surface area.

The anode was always polished along the horizontal portions and also at the very high current densities. However at the very high speeds, the rapid streaming of the electrolyte past the anode caused unevenness in the equality of polish; few streaks were observed. At moderate speeds, 200 - 500

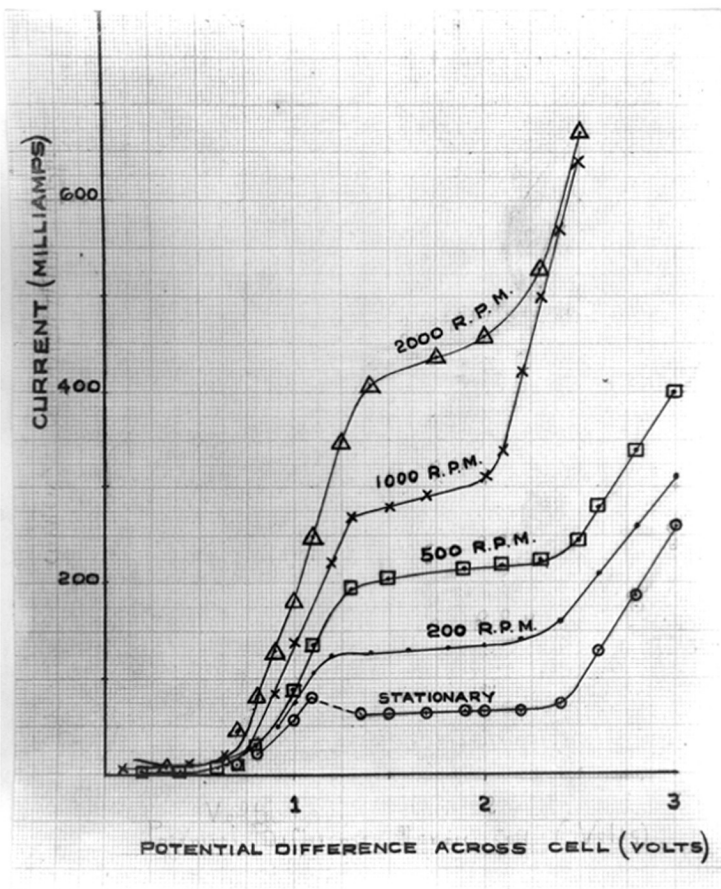


FIG. 17.

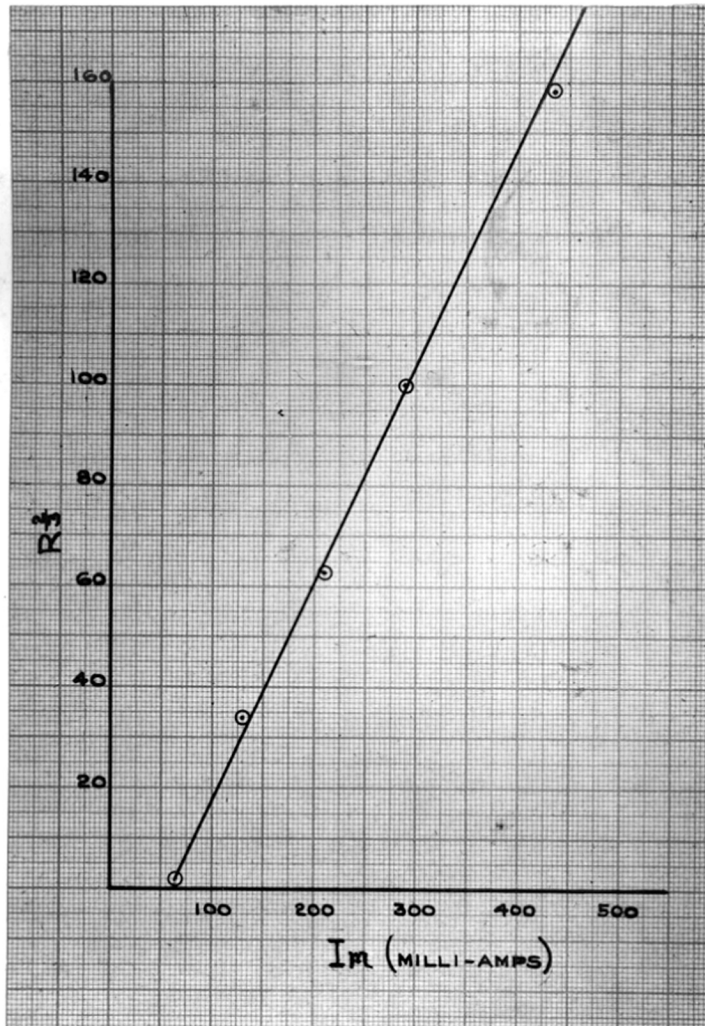


Fig.18.

the polished surface presented a very good and even appearance. The high current density used permitted a more speedy polishing. It is therefore seen that whereas no advantage is gained from using a high temperature for polishing, a moderate speed of rotation is advantageous in bringing about a good polish in a short time.

From Fig.17 it can be seen that:

- (i) The shape of the curve becomes less ideal as the speed of rotation is increased.
- (ii) The instability of the hump disappears with a reasonable speed of rotation.
- (iii) The width of the horizontal portion of the curve decreases as the speed of rotation is increased.

In discussion of the diffusion phenomena in electrolysis, Glasstone and Hickling (1935) state that from the results of various authors on electrolytic oxidation and reduction, it appears that the thickness of the diffusion layer is inversely proportional to the two-thirds power of the rate of rotation "R" of the electrode. If this relation is applicable to the electrolytic polishing of copper, then from equation (9), I_m would be proportional to $R^{2/3}$, all other variables being kept constant. This relation is plotted in Fig.18, and within the limits indicated by the experimental points, it holds quite satisfactorily. (For the stationary

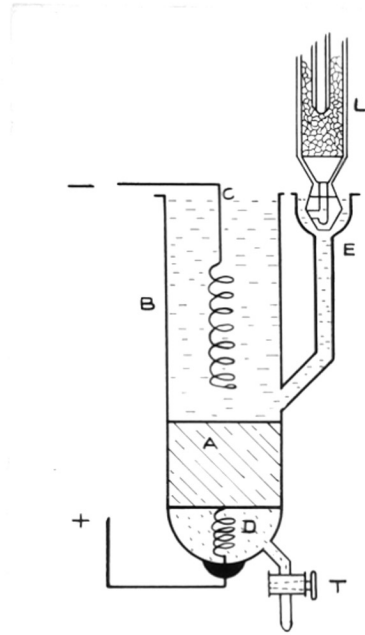


Fig.19.

electrode, R is considered to be unity).

When the speed of rotation was increased even to 10,000 r.p.m. the anode could still be polished at a very high current density of 2 amp./sq.cm. It thus appears that the diffusion layer cannot be completely eliminated but it tends to reach a limiting minimum value below which it cannot be reduced. It might then probably be identified with a liquid layer very strongly adsorbed to the anode surface.

4. Experiments with a very Restricted Diffusion.

In contrast with experiments with a very high speed of rotation, it was thought of interest to conduct some experiments where the rate of diffusion of the anode dissolution products into the bulk of the electrolyte is as low as possible. For this purpose a simple apparatus as shown in Fig.19 was used.

The anode A is a short cylindrical rod of copper which fits very tightly into the glass tube B , so that only the upper base is exposed to the electrolyte and lateral diffusion of the anode dissolution products from the inter-electrode region is impossible except for a very slow seepage (about 1 cc. in 14 hours). Electrical connection to the external source of E.M.F. is effected through a copper spiral S passing through a small hole in the bottom closed by picein

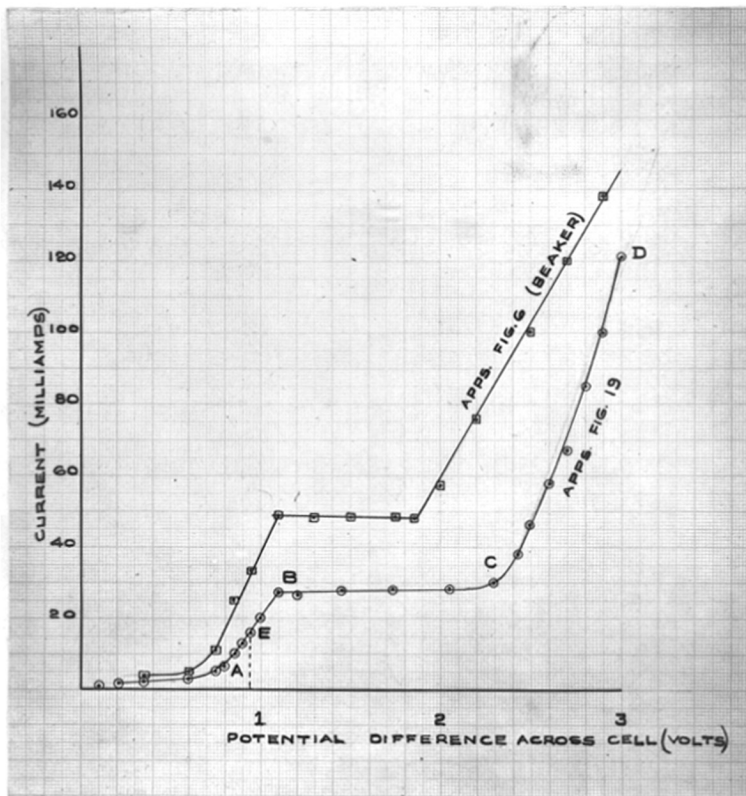


Fig. 20.

wax. Through the bottom there is a narrow tube with a stopcock T. The anode dissolution products which are heavier than the phosphoric acid seep very slowly down along the sides of the tube and collect in the space D whereby it can be discharged through T, for conductivity and viscosity measurements (see later, p.73). The side tube E which emerges just at the surface of the anode ends with a cup where a Cambridge type calomel electrode L serves to measure the anode potential. The cathode C is a long copper spiral with a surface area three times that of the anode. When no current was flowing, the electrolyte remained perfectly colourless over a period of two days, and thus the attack of the copper is negligible.

Fig.20 shows the electrical relationships when the anode is protected as compared with a current-voltage curve of the same electrodes similarly disposed in an open vessel. It is clear that with the restricted rate of diffusion, the limiting current density is much lower. This, again, is in accordance with equation (9) since the thickness of the diffusion layer δ is greater and a lower value of I_{M} is expected.

Moreover, if the diffusion layer is allowed to build up very slowly and undisturbed, electrolytic polishing can even be accomplished under conditions where the surface is

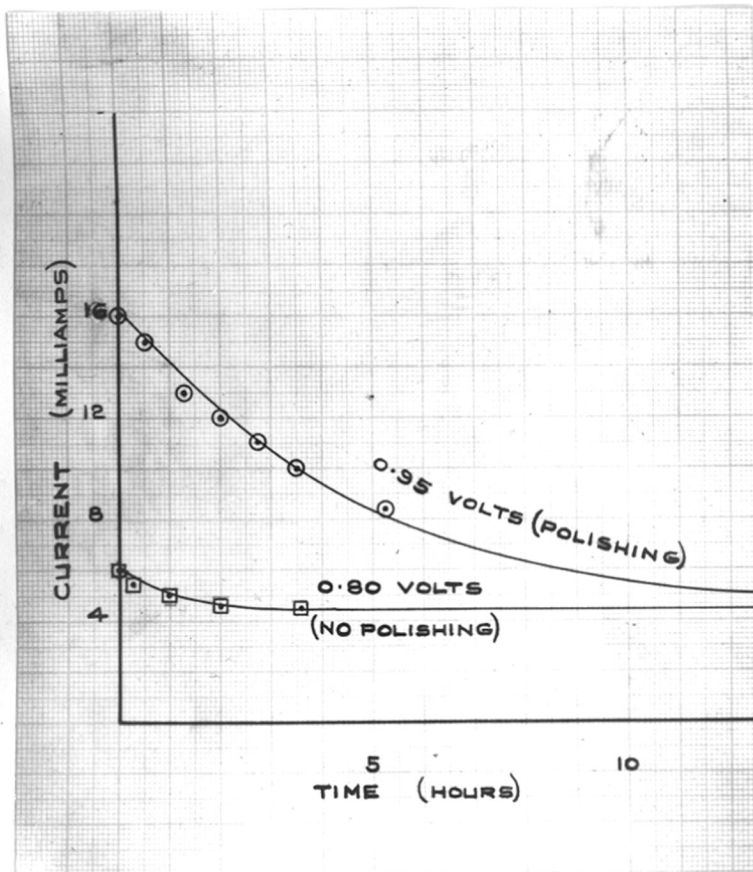


Fig. 21.

normally etched, e.g. at a point "E" on the ascending part AB of the curve. Thus, when the potentiometer resistance was set to a value whereby the voltage across the cell is 0.95 volt, the equilibrium reading of the current (after about 5 minutes) is 16 milliamps. With the gradual building up of the diffusion layer, the value of the current continued to decrease slowly with time as shown in Fig.21 and after 14 hours was constant at 4.5 ma., while the voltage remained practically constant. This experiment was repeated several times and the anode was examined after definite lapses of time. It was found that at this value of applied voltage (0.95 volt), the anode remained etched for just over one hour from the moment the circuit was closed. At any time after an hour and a quarter had elapsed the anode was found to acquire a high degree of polish. It is of interest to note that a measurement of anode potential after the 14 hours with the current still passing gave a reading of 0.567 volts and with the current off but the anode in contact with an almost saturated copper solution (thick diffusion layer) the potential was 0.410 volts. These values are to be compared with Fig.8 where the anode potential of copper rises during electrolytic polishing from 0.50 to about 1.50 volts at a constant current density.

It should be noted, however, that the value of 0.95

volts across the electrode was the minimum that could be applied to bring about electrolytic polishing. With an applied voltage of 0.8 volts, corresponding to 6 ma. (Fig.21) the anode was not polished even after 15 hours. In this case apparently the anode dissolution products are formed at a slower rate than that with which the slow rate of diffusion can cope so that no appreciable building up of a stable diffusion layer is possible. On the other hand, the application of a higher voltage for a considerable length of time resulted in the precipitation on the anode of a blue-green crust of copper phosphate. In this case the anode dissolution products diffuse at a much slower rate than that at which they are formed and thus accumulate in the anolyte until it is supersaturated and crystallisation of the salt takes place.

5. Effect of the Electrolyte Composition.

Two different kinds of experiment were carried out to investigate this effect. In the first series of experiments colourless phosphoric acid at different dilutions, in the second, phosphoric acid containing an excess of copper ions was used.

The composition of the four aqueous phosphoric acid solutions used in the first series are shown in the following table.

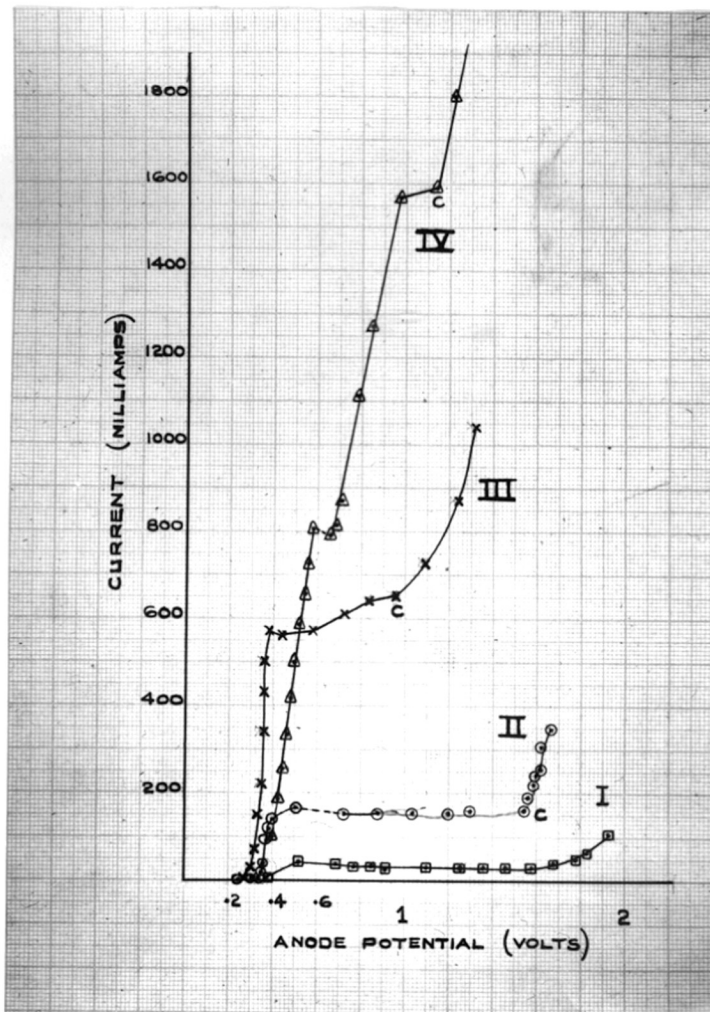


Fig.22.

Solution No.	m.l./litre of the syrupy acid Sp.Gr. 1.75	Sp.gravity of the solution at 20°C.	Weight in gm./litre of H_3PO_4
I	1000	1.75	1572
II	666	1.516	1048
III	400	1.315	628
IV	166	1.135	262

The anode potential-current density relations at room temperature are shown in Fig.22. In all four cases oxygen evolution occurred at the point C. Satisfactory electrolytic polishing was obtained with solutions II and III. With a solution I a good polish could be obtained but a longer time was required owing to the low conductivity of the solution. With solution IV the whole surface was etched over most of the current range. At current densities much higher than C, only the edges of the specimen showed signs of polishing.

Fig.22 also showed the shape of the curve becomes less ideal as the dilution increases and shows almost no horizontal plateau in the more dilute solutions. It is also seen that the value of the limiting current density increases with dilution. This is to be expected from equation (9) since two factors contribute to this increase in I_m . Firstly, the decrease in the phosphate ion concentration with dilution results in an increase of the copper ion

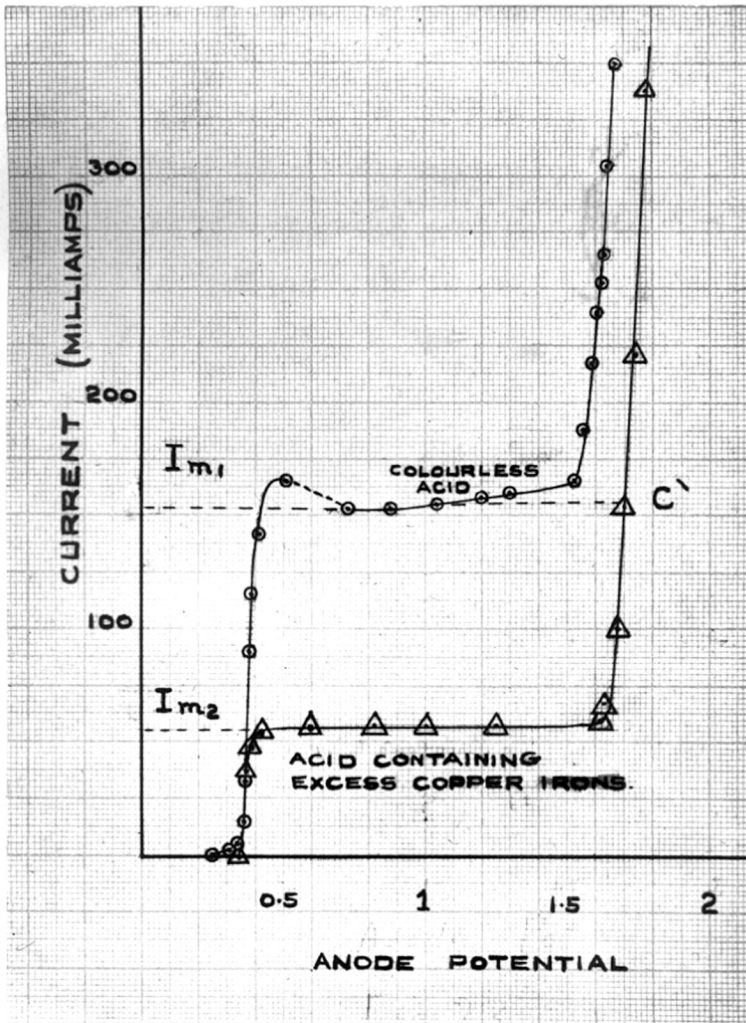


Fig.23.

concentration C_m according to the solubility product principle. This is true whether a simple copper phosphate is the final result of the anodic dissolution or whether the copper ions take part in a complex ion formation. Secondly the dilution of the electrolyte results in a decrease of viscosity and hence an increase in the diffusion coefficient D . An increase in C_m and D will result in an increase of I_m as can be seen from equation (9).

The object of the second experiment was to start with a solution already rich in copper ions. This was achieved by dissolving copper carbonate in the phosphoric acid electrolyte of Sp.Gr. 1.516 until the solution was almost saturated (copper content 95.6 gms./litre). According to equation (9), C_0 is now very large and I_m should subsequently decrease. This was verified experimentally as shown in Fig.23. The increase in viscosity of the solution might also account for the decrease in the value of the limiting current density due to a decrease in D . The metal was perfectly polished along the horizontal plateau.

This result is of great technical importance. The electropolishing solutions used in industry are generally divided into two types, finite and infinite. In finite solutions the anode dissolution products are not precipitated and are difficult to eliminate so that the solution has a

finite life and must be discarded at the end of it. Solutions in which the contaminating salts precipitate out or the metals can be deposited on to a cathode have a much longer life.

It will be seen from equation (9) and from Fig.23 that in solutions of the first type when C_0 increases (contaminated solutions), successful electrolytic polishing could still be effected at the lower current density (I_{m_2}). If electrolytic polishing is tried at the usual current density for uncontaminated solutions I_m , oxygen evolution will occur (at C^v) with probable pitting of the surface.

If the industrial electropolisher adjusts his working current density thus from time to time as the concentration of the contaminating salt increases, then the life of the so-called finite solutions could be much prolonged and the process would thus prove more economical.

(iv) The Electron Diffraction Results.

Interpretation of Electron Diffraction Patterns.

The condition for diffraction of a monochromatic beam of wavelength λ by a line grating of constant a , is given by the equation

$$a(\cos \alpha - \cos \alpha_0) = n\lambda$$

where θ and θ' are the angles between the lattice row and the directions of the incident and reinforced beams respectively and h is an integer. With a three dimensional grating or a space lattice, three such simultaneous equations (Laue conditions) must be satisfied. The resolving power of a line grating depends upon the number of its scattering centres and upon its inclination to the incident beam, being greatest for a given length when the grating is normal and least when parallel to the beam.

In electron diffraction, the penetrating power is so low that the length of the atom rows in the direction of the beam is greatly restricted and the resolving power of the corresponding line grating is accordingly greatly reduced. In other words the third Laue condition is virtually relaxed. In transmission through an exceedingly thin single crystal of mica for example the pattern consists of a large number of well defined spots as would be expected from a two-dimensional grating.

In the light of the above considerations, we can consider the diffraction of electrons by reflection from single crystal surfaces. Consider the three cases shown in Fig.24.

(a) The crystal surface is etched. This gives a typical cross grating pattern which is caused by electrons passing through projections on the surface (the process being really

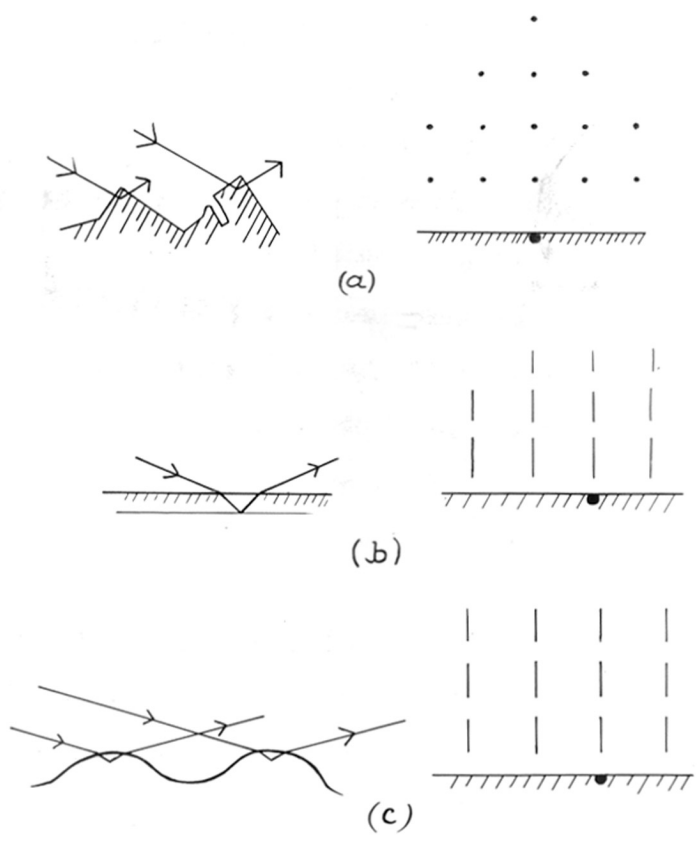


Fig.24.

much more of the character of transmission).

(b) The crystal surface is an atomically smooth and flat net plane. Here the pattern is modified (1) by the limited penetration of the electrons below the crystal surface and (2) their refraction on entering and leaving the potential region of the crystal lattice. The first factor results in a low resolving power of the atom row normal to the surface, i.e. an appreciable broadening of the Laue zones parallel to the shadow edge of the specimen. The circular well defined spots will therefore be replaced by spots elongated in a direction normal to the shadow edge. The second factor, namely the refraction of the electrons at the crystal boundary may be said to cause a shift of the diffraction pattern towards the shadow edge. The amount of shift at any point in the pattern from its position if no refraction had occurred increases rapidly with its closeness to the shadow edge.

(c) The surface is smooth though slightly undulating.

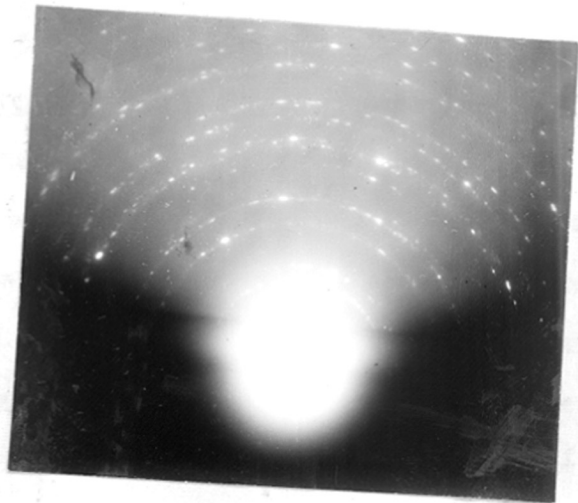
In such a case, the projections are too thick for true transmission to take place. Instead, refraction at the tips of the projections takes place. Since the beam hits different crests, there will be more than one effective shadow edge and thus quite long elongated spots could still be found at relatively long distances from the undeflected spot.



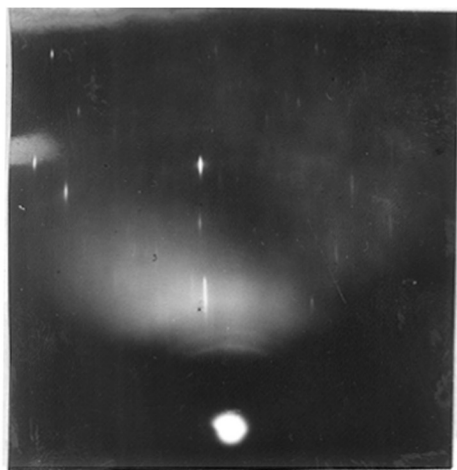
Fig.25
Macrocrystalline Copper

X 120

Fig.26
Pattern from Macro -
crystalline etched
Copper.



A 7162



(a) A7601



(b) 8001

Fig.27 Patterns from Electropolished Macrocrystalline Copper
(without oxygen evolution)

a and b represents different parts of the same specimen.

The Preparation of Copper Specimens for Electron
Diffraction Examination.

Single crystals of copper and polycrystalline copper specimens were examined after electrolytic polishing by electron diffraction. A macrocrystalline copper specimen which on etching gave the normal Debye-Scherrer rings, gave also a ring pattern after electrolytic polishing. In order to see clearly the effect of the electrolytic polishing on the degree of smoothness of the surface, it was thought best to use macrocrystalline copper specimens. The macrocrystalline specimens were obtained by heating the (2x2 cm.) copper specimens in air at about 1000°C. followed by annealing at 500°C. and quenching in air. The oxide layers were removed by heavy etching in dilute nitric acid followed by electrolytic polishing. Microscopic examination of the surface after electrolytic etching (along AB, Fig.8) gave the microphotograph Fig.25, and electron diffraction examination gave the pattern Fig.26. After electrolytic polishing (along BC, Fig.8) the electron diffraction patterns given by different parts of the surface were those in Figs.27a and b). Electrolytic polishing (along CD of Fig.8) with oxygen evolution produced a surface that gave the pattern Fig.28. Measurements of the radii of the rings in Fig.27a and 28 proved these to be copper rings. No trace of oxide rings were detected. The elongation of the

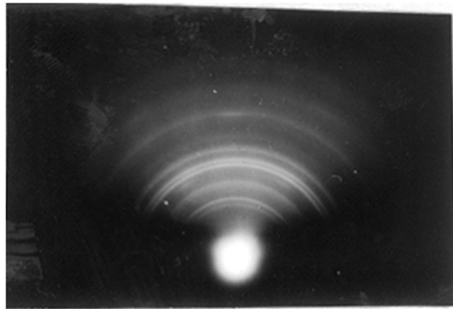


Fig.29

A7675

Sulphide films formed on
an etched copper surface.

spots towards the shadow edge is very marked and indicative that the electropolished surface was extremely, i.e. atomically smooth though slightly undulating.

It must be stressed however that the treatment of the surface after leaving the electrolytic polishing bath is of great importance. The following procedure was always adopted. After the specimen was withdrawn from the bath, it was washed under running water, then several times with distilled water and finally with alcohol, and then transferred to the electron diffraction camera under absolute alcohol. This treatment was quite satisfactory to avoid contamination of the specimen with oxide or sulphide films by the laboratory atmosphere when the specimens were examined by the camera of Fig.5. The establishment of a high vacuum in the camera Fig.3 took a relatively longer time, and in most cases the copper pattern was accompanied by cuprous oxide rings. When the specimen was not transferred under alcohol, through the laboratory atmosphere to the camera, or when sulphur containing compounds such as plasticine were present near the specimen, the copper pattern was usually accompanied or even replaced by that of a copper sulphide (as shown in Fig.29). The elimination of such contaminations was however possible by introducing the specimen into the electron diffraction camera bathed, after the absolute alcohol, with a liquid of much lower vapour



(a)

A 8000

Fig. 30

Electropolished Copper
Single crystal

(a) Camera length 25 cms.

(b) " " 49 "

arbitrary direction of
electron beam.



(b)

A 7069

pressure, e.g. amyl alcohol, which protected the metal surface inside the camera for a longer time.

It seems most likely therefore that the cuprous oxide patterns obtained by previous investigations from electrolytically polished surfaces were due to atmospheric and not to anodic oxidation.

Single crystals of copper electropolished with or without oxygen evolution gave patterns similar to those of Fig.30 a and b. The Kikuchi lines indicate the high degree of lattice perfection and the elongated spots show the extreme smoothness of the surface. Electrolytic polishing of either single crystal or polycrystalline copper even along CD (Fig.8) with brisk evolution of oxygen gave electron diffraction patterns free from any oxide rings. It is hardly probable therefore that any oxide film is present on electrolytically polished copper, unless such a film is monomolecular and escaped electron diffraction. The latter possibility is ruled out completely by the following argument. If the oxide film is monomolecular, it must be so coherent and adherent that it could not allow any further growth of the oxide. Under such conditions, it will render the metal passive, and almost stop its anodic dissolution. Since copper quantitatively dissolves in phosphoric acid according to Faraday's laws, it is evident that a monomolecular protecting film cannot be present. A

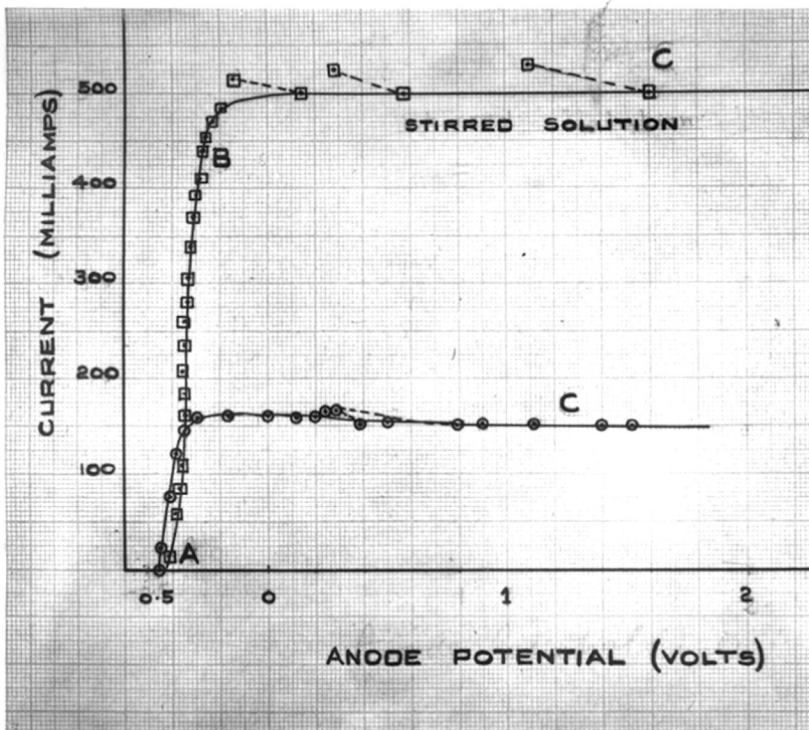


Fig. 31.

porous film, a few molecules thick, could have been easily detected by electron diffraction on the smooth surfaces obtained.

It is, therefore, safe to conclude that an electrolytically polished copper surface, when protected from atmospheric contamination, represents a clean crystalline metal surface with no amorphous or oxide layers.

2. The Electrolytic Polishing of Silver.

Anode Potential Measurements.

The electrolyte used for the electrolytic polishing of silver was a potassium cyanide solution in which silver cyanide was dissolved. The composition of this solution, which contained an excess of free cyanide ions was as follows:

KCN	43.5 gm./litre
AgCN	30 gm./litre.

The results of the anode potential-current measurements are shown in Fig.31. When the solution was stirred by a stream of CO₂-free air, the limiting current density was raised. The mechanism of the electrolysis of complex argenticyanide solutions is complicated and the views put forward to explain it are conflicting (Glasstone, 1935). For our purpose, however, since we are not concerned with the cathodic process,

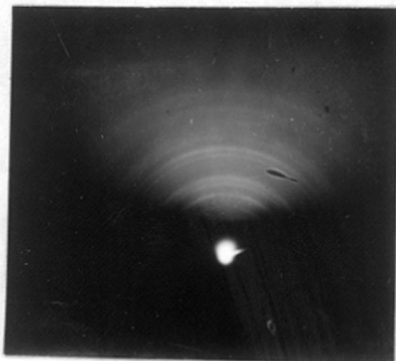


Fig.32.

A 7720

Pattern from the brown compound
formed on a silver anode in the
electropolishing bath at 1.2 volts.
(Ag CN).

it is convenient to regard the maximum rate at which the anode can dissolve to form $[\text{Ag}(\text{CN})_2]^-$ ions depends on the maximum rate at which the cyanide ions diffuse to the anode from the bulk of the solution. In this case, when the limiting current density is reached, the concentration of CN at the anode has fallen to zero. By the same treatment as was adopted in the discussion on the anodic treatment of copper, we can arrive at the two equations:

$$\Delta E = \frac{RT}{nF} \log_e \frac{k C_0}{k C_0 - I} \dots\dots\dots (8a)$$

and

$$I_m = \frac{DnF}{t\delta} C_0 \dots\dots\dots (9a)$$

where C_0 is the concentration of the free CN ion in the bulk of the solution.

The Mechanism of Electrolysis.

At low current densities, the anode dissolves normally with the formation of the argentocyanide (ascending part AB of the curve). The anode surface is etched. As the current density is increased (when the curve starts to bend at B) a brown film starts to form on the anode. As the electron diffraction pattern Fig.32 and the measurements in the following table show, this film is AgCN and is formed as

Identification of the Compound that gave
the pattern Fig.32.

$$L = 49 \text{ cms.}$$

$$\lambda = .05356 \text{ \AA.}$$

Observed Data

Literature (A.S.T.M. 1945)

Intensity	r(cms.)	$d = \frac{\lambda L}{r}$	d	Intensity
m.s.	0.712	3.68	3.7	0.8
v.s.	0.87	3.01	3.00	1.00
m.s.	1.12	2.34	2.33	0.5
m.	1.406	1.88	1.84	0.24
m.s.	1.51	1.73	1.73	0.12
-	-	-	1.57	0.06
-	-	-	1.5	0.10
-	-	-	1.383	0.02
v.f.	2.07	1.25	1.266	0.02
-	-	-	1.230	0.01
v.f.	2.30	1.15	1.158	0.01
-	-	-	1.36	0.01

L = camera length

r = ring radius

d = lattice spacing

λ = wavelength of the electrons

f = faint

m = medium

s = strong

v = very

a result of the decrease of CN at the anode, and in the meantime the increase in the Ag^+ concentration. The $AgCN$ is apparently formed more quickly than it can be dissolved by the KCN solution. This film was thought by Hedges (1926) to be an oxide film. The onset of this film was marked by a rise in anode potential after which a series of oscillations started (represented by the dotted lines on the curves). The anode surface displayed alternate brown and white flashes, sometimes the alternation was so quick as to resemble a twinkling. During these fluctuations the anode became more and more bright. When the applied voltage was increased, there was often a tendency for the brown film to become permanent (point C on the curve). This film immediately dissolved, however, in the electrolyte when the current was cut off, and the anode was then highly polished if the electrolysis had been continued for 5-10 minutes. When the applied voltage was increased beyond what corresponds to B, the anode potential increased while the current slightly decreased. A gray black film then covered the anode, and at higher potentials still, gas evolution took place. Although this film is presumably an oxide of silver, it was not possible to obtain a sufficiently clear electron diffraction pattern to identify it, since it was rather rough.

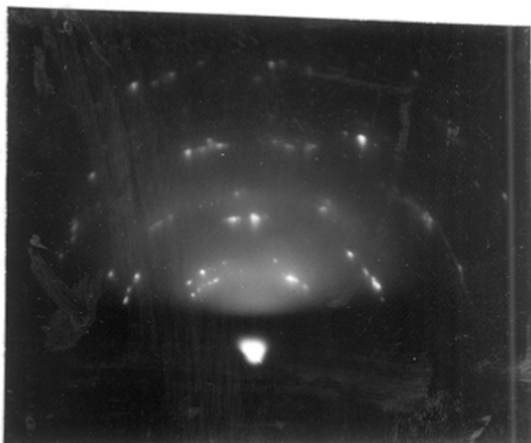


Fig. 33

Macrocrystalline Silver

X 5

Fig. 34.
Pattern from
Macrocrystalline
electro-etched silver.



H 19

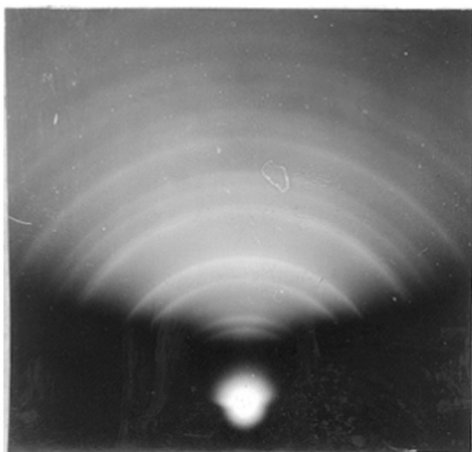


Fig.36.
Silver deposited on
copper from a cyanide
bath
(15,000 Å⁰)

A 7739

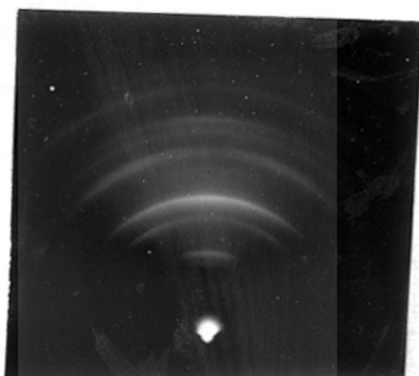


Fig.37.
The silver deposit
of fig.36 electropolished

A 7741

Electron Diffraction Results.

The pure silver sheet as supplied by Messrs Johnson Matthey and Co., London, was macrocrystalline. Fig.33 shows a photomicrograph of the surface after electrolytic etching along the ascending part of the curve. The electron diffraction pattern given by this electroetched surface is shown in Fig.34 and after electrolytic polishing the same surface gave the pattern Fig.35. The elongation of the spots and their displacement from their normal positions towards the shadow edge illustrate clearly the effect of refraction and show the extreme smoothness of the surface.

Silver was also deposited from a cyanide bath on a mechanically polished copper surface at a current density of 4 amps./sq.dm. The deposit, of average thickness 15,000 Å. gave the electron diffraction pattern Fig.36 and after electrolytic polishing gave the pattern of Fig.37. Both show the surface to be crystalline silver.

3. The Electrolytic Polishing of Aluminium.

The Electrical Relationships.

The electrolyte used for the electrolytic polishing of aluminium was prepared by gradually and slowly adding from a separating funnel two volumes of acetic anhydride to one

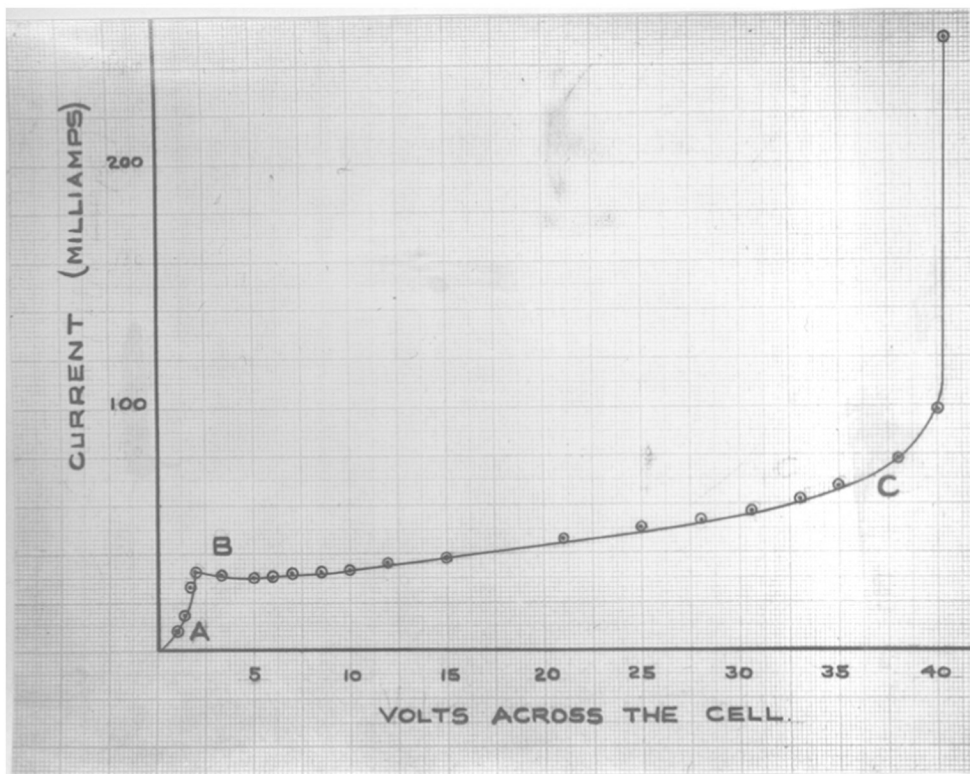


Fig.38.

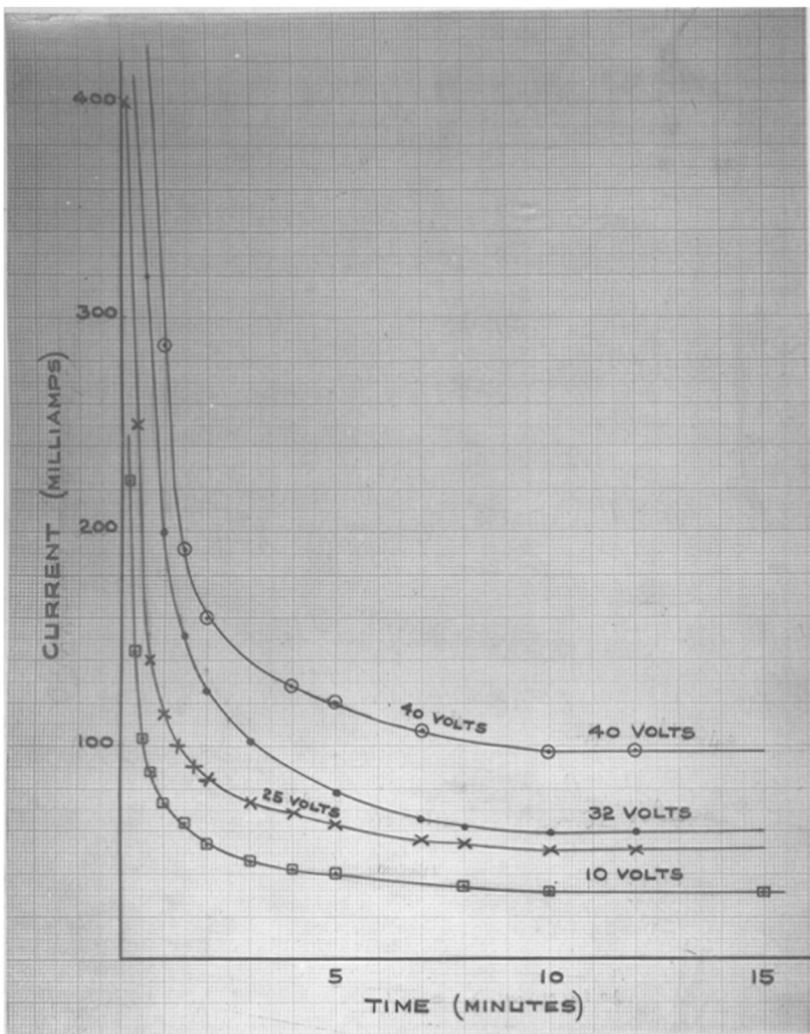


Fig. 39.

volume perchloric acid (60%). The latter was kept cold by a stream of running water, and the temperature was not allowed to exceed 15°C.

The results of the voltage-current measurements at 15°C. are shown in Fig.38. Although Jacquet (1943,a) found two horizontal plateaux for electrolytic polishing in the region between 15 and 30 volts, this was not found in the present work. The curve had the usual form with a comparatively large voltage range where electrolytic polishing was possible. (4-35 volts). Throughout that range, however, the current density did not remain practically constant but showed very slow increase with increase of the applied voltage (BC). A better polish in a shorter time was always obtained in the voltage range between 20-25 volts, at temperatures not exceeding 20°C. When the applied voltage was adjusted at e.g. 25 volts, and then the anode immersed in the electrolyte, the current was initially rather high but immediately decreased with time, until after about 5 minutes, it remained almost constant. Fig.39 shows the rate of change of current with time at different values of the applied voltage. The anode after electrolytic polishing was usually covered with a very viscous brown layer, and for electron diffraction examination was not allowed to come into contact with water. It was therefore immediately immersed in dry acetone and the surface

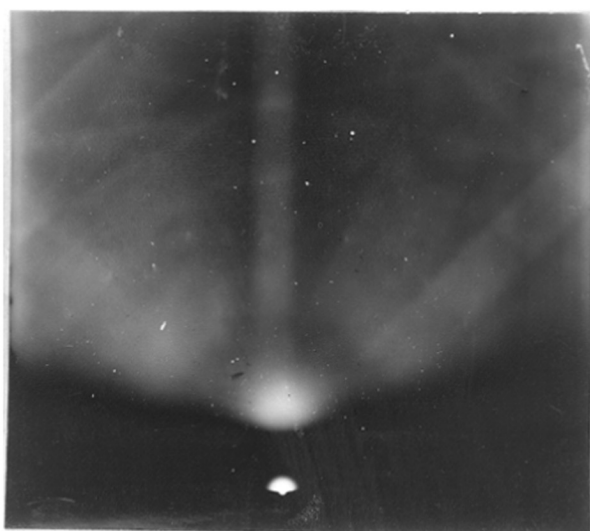
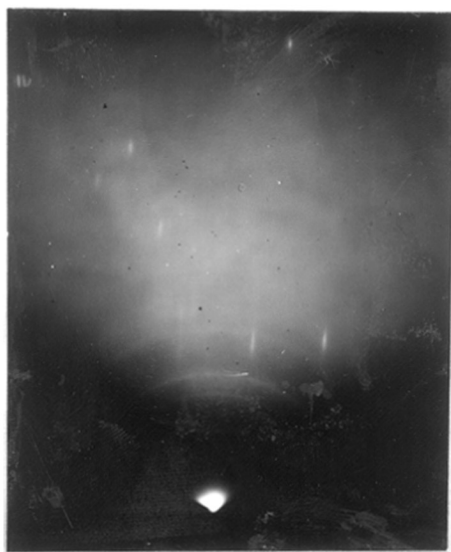


Fig.40.

A7785

Electropolished Aluminium
Single crystal (cube face.)



A7762

Fig.41.

Macrocrystalline Electropolished
Aluminium.



(a)

A7763



(b)

A7938

Fig.(42) Macrocrystalline electropolished aluminium (a and b
represent different parts of the specimen.

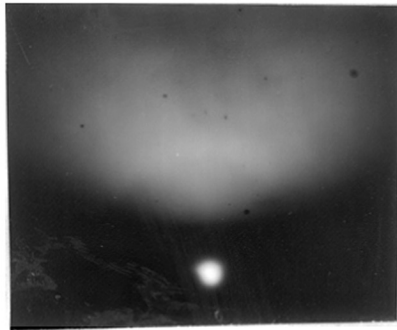


Fig.43.

Amorphous oxide film formed on
aluminium single crystal exposed
to air for two days.

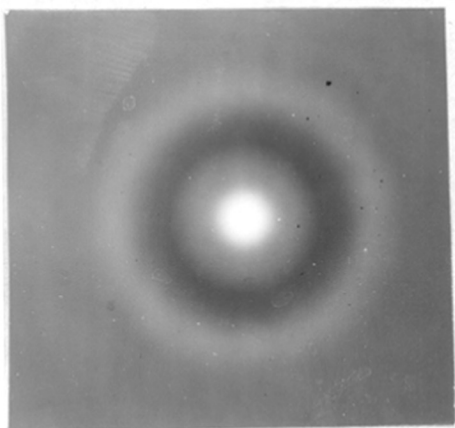
wiped with cotton wool. Repeated washing in acetone was necessary before the specimen was taken (under pure acetone) to the electron diffraction camera.

Electron Diffraction Results.

Fig.40 shows the diffraction pattern obtained from an electrolytically polished aluminium single crystal (cube face). The Kikuchi lines indicate that the crystal face had a high degree of lattice perfection. Fig.41 shows the pattern given by macroscopically electropolished aluminium and Figs.42 a and b also show patterns given by different parts of another macrocrystalline specimen with much bigger crystals (average size of crystal about 1 sq.cm.). Measurement of the ring radii in Figs. 41 and 42 showed them to be aluminium rings and the elongation of the spots indicate the extreme smoothness of the surface. Anodic polishing of aluminium therefore produces a smooth oxide-free metal surface.

All the 99.99% aluminium specimens used in the present work were kindly supplied by Dr.P.Lacombe of the Vitry Laboratory (C.N.R.S.), Paris.

When the aluminium single crystal which gave the pattern Fig.40 was kept in a Petrie dish for two days, the Kikuchi line pattern disappeared, and only a halo characteristic of the air-formed amorphous oxide film was obtained, as shown in



A 7957

Fig.44.

Transmission pattern of aluminium
oxide film stripped from aluminium
anodized in 8% oxalic acid.

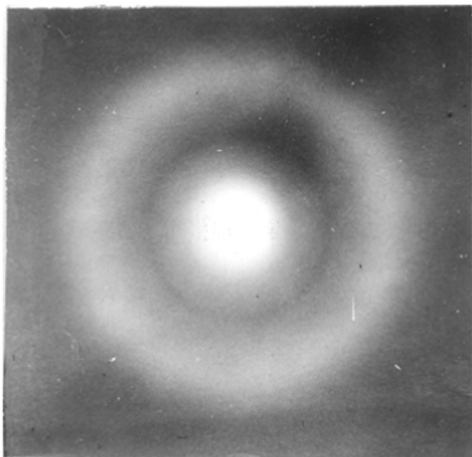


Fig.45

The stripped aluminium oxide
film of fig.44 boiled in
water for 5 minutes

A 7962

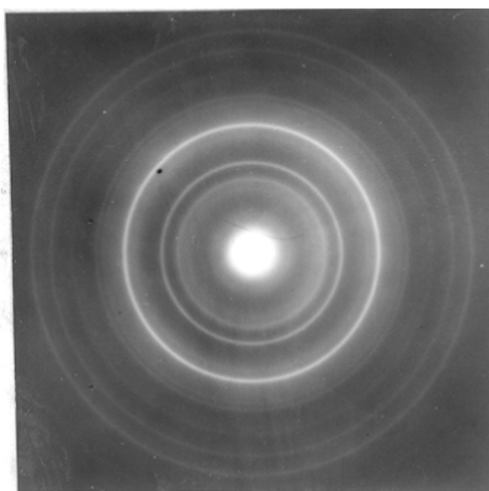


Fig.46

Pattern from the same
film after igniting
for 1 minute

A 7965

Fig.43. Lacombe and Beaujard (1945) have developed a new technique for the stripping of anodic oxide films from aluminium. The method is electrochemical, and consists in using the anodized sheet as anode in the normal electrolytic polishing bath (perchloric acid-acetic anhydride). When a high potential of about 90 volts is applied across the electrode the oxide film is detached from the underlying metal. The detachment of the film is rendered much easier by scraping the edges of the specimen with a penknife. This technique was used in the present work to strip oxide films from anodized aluminium for electron diffraction examination (by transmission). The anodizing solution was 8% oxalic acid, and an oxide film was formed on the single crystal for 3 minutes at 8 volts. The stripped oxide film gave the halo pattern shown in Fig.44, which shows the film to be amorphous. After boiling in water for 5 minutes the film was still amorphous as shown in Fig.45. The film crystallised, however, into α - Al_2O_3 when it was heated on the nickel gauze in the non-luminous flame for 1 minute, as shown in Fig.46 and the following table.

Although Fig.44 is in agreement with the results of Harrington and Nelson (1940), Fig.46 contradicts their results. These authors failed to obtain a crystalline pattern from anodized aluminium heated in air for 160 hours at 650°C. On the other hand they found that boiling in water for 30 minutes crystallised the film. Miss S.B.Roche Lynch in this laboratory is at present investigating this problem in further detail.

Identification of the Compound which gave the
Pattern Fig.46.

L = 49 cms.

 $\lambda = 0.05356 \text{ \AA}$.

Observed data.			Literature (A.S.T.M. 1945)	
Intensity	r(cms)	$d = \frac{\lambda}{r}$	d	Intensity
v.f.	0.760	3.45	3.47	0.5
s.	1.02	2.57	2.55	0.75
v.f.	1.107	2.37	2.37	0.30
v.s.	1.262	2.08	2.08	1.00
f.	1.501	1.74	1.74	0.5
v.s.	1.674	1.57	1.59	1.00
-	-	-	1.54	0.05
-	-	-	1.50	0.05
-	-	-	1.402	0.4
m.f.	1.926	1.36	1.37	0.5
f.	2.104	1.24	1.233	0.2
-	-	-	1.186	0.1
-	-	-	1.144	0.05
-	-	-	1.122	0.05
-	-	-	1.095	0.05
f.	2.422	1.08	1.080	0.05
-	-	-	1.040	0.08
-	-	-	1.015	0.05
v.f.	2.691	0.98	0.995	0.05

L = camera length; λ = wavelength of electrons; r = ring diam.;
d = lattice spacing; f = faint; s = strong; m = medium; v = very

COMPARISON OF ELECTROLYTICALLY AND MECHANICALLY
POLISHED SURFACES.

1. Introduction.

The electron diffraction results obtained in the present investigation show that the electropolished metal surface is crystalline. On the other hand, previous work in this laboratory by Finch and his collaborators (1934, 1935, 1937), has shown that mechanical polishing produces an amorphous "Beilby layer" formed by a surface flow of amorphous, vitreous like or liquid material. The mechanical polishing introduces heat effects, deformation and undoubtedly strains the surface. It often produces polishing pits; moreover the presence of abrasive particles embedded in the surface is not uncommon.

Such a difference in structure, between the mechanically and electrolytically polished surfaces, is of great interest from a scientific as well as an industrial point of view. The fact that electrolytic polishing removes the projections without causing any surface distortion gives this technique an advantage over and a preference to the mechanical method for many purposes.

Thus, electrolytic polishing was, immediately after its discovery, applied to the micrographical examination of metals. Apart from the gain in time, ease of execution and the

production of a surface completely free from any strain and which represents the true structure of the metal, there are other important advantages (Jacquet, 1947; Pellisier, Markus and Mehl, 1940).

Elmore (1937, 1938a and b) used the electrolytic polishing method for the study of the magnetic powder patterns of iron and cobalt. He found that the mechanical polishing had a marked effect on the nature of the pattern. Boas and Honeycombe (1944) have applied the electropolishing technique to produce a satisfactory surface on metals such as Cd, Sn and Zn for a study of the process of plastic deformation. Vernon and his associates (1939) studied the oxidation of zinc by heat using an electropolished surface. It was necessary for their investigation to avoid the production of a flowed or disturbed surface and at the same time to be free from possible objections to chemical etching, notably the risk of traces of reagent remaining in crevices produced by the etching process.

In a study of the optical constants of copper, Lowery, Wilksinson and Smare (1936) found that the reflecting power of the electropolished surface was higher than that of the mechanically polished surface under the best of conditions. Similar conclusions on aluminium and zinc were also obtained by Capdecemme (1937, 1941) and Jacquet (1938c).

Miss S.B.Roche Lynch (1948) in this laboratory has carried out an investigation of the anodic oxidation of aluminium, its oxidation by air at different temperatures as well as the growth of deposits on it, using an electropolished aluminium single crystal. Electrolytic polishing has proved invaluable for imparting to single crystals the satisfactory state of surface required for the study of many physico-chemical properties of metals. Single crystals have certain advantages over polycrystalline aggregates for such studies but they are much more sensitive to mechanical work; hand polishing distorts the structure to an appreciable depth, hence the necessity of polishing electrolytically.

2. Electrodeposition and Substrate Effects.

In the field of electrodeposition, electrolytic polishing has provided a new tool for the study of the problems of crystal growth and substrate effects. Since there exists an unsaturated field of adsorbing forces on or near a substrate surface, it is to be expected that the arrangement of the atoms in the initial thin layers of the deposits will be largely determined, under favourable conditions, by the atomic or ionic arrangement of the substrate surface. This problem was extensively investigated, using electron diffraction, by different workers under the direction of Professor Finch in this laboratory. Thus Finch and Sun (1936)

found that the first thin layers of electrodeposits growing on random polycrystalline substrates in general also showed random polycrystalline structure. On one-degree orientated substrates, parallel growth of the deposit was observed when its lattice dimension was nearly the same as that of the substrate. With a mechanically polished surface, Finch and Sun could observe the dissolution of the first thin layers of the deposit in the amorphous Beilby layer. Thus, on a crystalline copper surface, zinc gave its crystalline pattern after 30 seconds of deposition, whereas 3 minutes under the same conditions were necessary for the production of a zinc crystalline pattern when the substrate was mechanically polished copper. The random polycrystalline structure of thin deposits usually produced on the mechanically polished substrates is due to the random deposition of the atomic groups in the surface of the substrate. Such irregular groupings act as the equivalent of small crystal nuclei.

Finch, Wilman and Yang (1947) have used an electrolytically polished (100) cube face of a copper single crystal as a substrate, to study the nature of the growth of the first layers of cathodic deposits. Copper, from an acid bath, was deposited on this crystal face, and the surface examined by electron diffraction. When the deposit was about 200 Å. thick, the electron diffraction pattern showed that it had

continued closely the structure of the substrate both in crystal orientation and in lattice perfection. The spots on the pattern were, however, no longer elongated, indicating that the smoothness of the original electropolished surface was not maintained. Thus, although the deposits had extended the crystal lattice of the substrate, crystal outgrowths were formed on the surface. An increase in the deposit thickness to about 500 A., produced an even rougher surface. Although the continuity of the substrate lattice was still maintained, the Kikuchi lines became much fainter suggesting that the diffraction pattern was almost due to the transmission of the electron beam through crystal outgrowths. The results of Finch, Wilman and Yong clearly show that, in the primary stages of electrodeposition the deposit continues faithfully the crystal lattice of the substrate surface, though with gradual increase of surface roughness.

Thirsk (1939) in this laboratory has investigated deposits of the order of a few thousand angstrom thickness on single crystals of copper and iron. When the lattice spacings in parallel directions in the contact plane of the substrate and deposit were nearly equal, lattice continuation has been observed.

Jacquet (1937b) has shown, by microscopic examination, that there is a continuity in crystalline structure between an electropolished copper substrate and a deposit of copper.

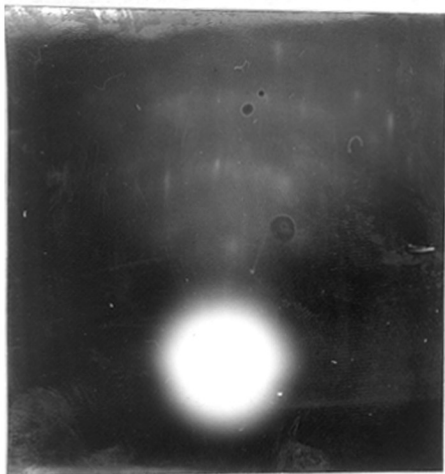
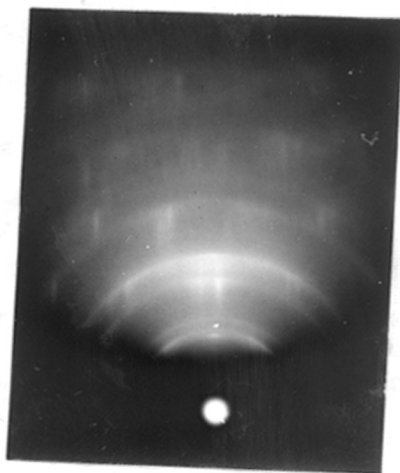


Fig.47

Silver deposited on
macrocrystalline electro-
polished copper (fig.28)
by chemical displacement
from a cyanide bath for
5 seconds.

A 7606

Fig.48
Silver electrodeposited
on Macrocrystalline
electropolished copper
from cyanide bath(200 A⁰)



A 7600

No such continuity was observed when the substrate was mechanically polished. Similar results were obtained by Pray and Faust (1940) when they plated nickel on polished steel. In this connection, however, it must be noted that Finch and Williams (1937) have shown that conclusions based on microscopic methods as to the retention of crystal size and orientation of the basis metal by an electrodeposit should be treated with reserve unless confirmed by electron diffraction.

Fig.47 shows an electron diffraction pattern of Ag deposited on an electropolished macrocrystalline copper (Fig.27a) by a simple displacement for 5 seconds from a cyanide bath. Fig.48 shows an electron diffraction pattern of silver electrodeposited on macrocrystalline electropolished copper at a low current density (deposit 200 Å. thick). Both patterns show that the deposit continues the substrate structure in crystal size and orientation.

3. Comparison of the stress in Electrodeposits on Mechanically and Electrolytically Polished Surfaces.

The tension under which metals are deposited on a substrate has been studied by Mills (1877), Stoney (1909), Kohlschutter and Vuillumier (1918), Macnaughton and Hotherhall (1928), Marie and Thon (1931), Jacquet (1932), Hume-Rothery (1943), Soderberg and Graham (1947) and Wyllie (1948).

The method used in the present investigation to measure and compare the stress in deposits on mechanically and electrolytically polished steel was that due to Stoney. According to this author, if a thin steel rule of uniform thickness d and length l is varnished on one side and coated with a metal deposit of small thickness t on the other side, then the stress within the deposit will cause the rule to bend in the form of an arc of radius r . If the modulus of elasticity of the steel strip is E , then the stress P , i.e. the tension per unit area of section on the metal film is given by the equation:

$$P = \frac{1}{6} \cdot \frac{E}{r} \cdot \frac{d^2}{t} \dots\dots\dots (10)$$

assuming that the deposit is much thinner than the steel rule.

If the curvature is measured by the deflection z of the rule in a length l (measured at one end while the other end is rigidly fixed), then:

$$r = \frac{l^2}{2z} \dots\dots\dots (11)$$

and putting in this value of r in equation (10) we have:

$$P = \frac{1}{3} \frac{E d^2 z}{t l^2} \dots\dots\dots (12)$$

In the present work strips of equal length l and the same thickness d and the same modulus of elasticity E were used. For deposits of the same thickness t , the relative

magnitude of the stress P in the deposits will then be directly proportional to the deflection z of the free end of the steel rule. The nickel deposits caused a tensile stress since the rule was bent so that the varnished side became convex.

Steel rules $1/80$ inch thick and of standard gauge of $\frac{1}{8}$ " width were used as the substrate. These rules were cut into strips of 12 cms. each. For a mechanically polished substrate the strip was polished on a buff wheel with rouge and then thoroughly degreased. For the electrolytically polished substrate, a perchloric-acetic anhydride bath was used (Jacquet and Rocquet, 1939). The amount of anodic attack was adjusted so that the mechanically and electrolytically polished specimens gave the same thickness, d .

One side of each strip was completely varnished and on the other side the varnish covered 2 cms. at one end leaving 10 cms. length for deposition. While the varnish was still wet, a thin, stout glass fibre about 3 cms. long was stuck at the extreme (free) end of the strip. This served as a pointer whose movement could be followed by a vernier microscope recording up to 0.01 mm. After drying the strips were weighed. (The modulus of elasticity of the different strips of equal length and thickness were compared by clamping each one firmly at one end and measuring the deflection caused

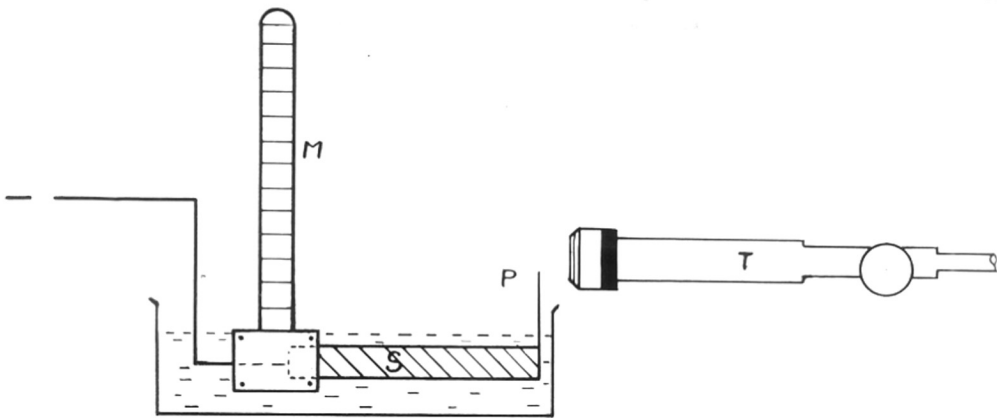


Fig.49

by hanging a weight of 2 grams at the other end. Only strips which gave nearly the same deflection (within 2%) and hence the same modulus of elasticity were chosen).

Fig.49 shows the experimental set up. The electrolytic cell was a rather shallow vessel of about 600 cc. capacity. The bath was of the nickel-sulphate-boric acid type. The steel strip S was held in a horizontal position by a varnished clamp M, with the unvarnished side towards the nickel anode (not shown in the Fig.). Most of the length of the glass pointer p was outside the electrolyte and its tip was above the wall of the cell, so that its deflection could be followed by the travelling microscope T after definite lapses of time. The increase of tension with time of deposition is plotted graphically in Fig.50 for electropolished and mechanically polished substrates. The two steel strips were exactly identical as regards length, width, thickness and modulus of elasticity. The current in each case was 20 milliamps., and the bath was at room temperature.

If the stress within the deposit on mechanically polished steel after a definite length of time is P_m and that within the deposit on the electropolished steel after the same time is P_e , then according to equation (12), everything else being the same:

$$P_m/P_e = z_m/z_e$$

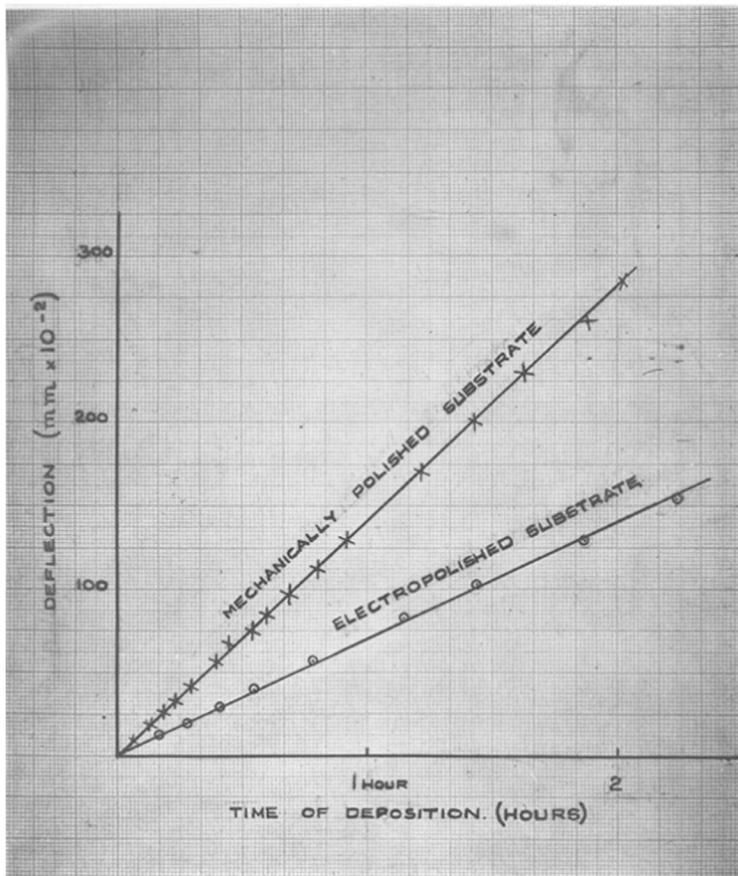


Fig.50.

It is clear from Fig. 50 that e.g. after two hours the stress P_m is almost twice as much as P_e .

No clear cut explanation of the stress in electrodeposits has yet been offered. Whatever might be the cause, it is known that in electrolytic polishing the metal is removed without accompanying mechanical work that introduces heat effects and strains the surface, and thus after electropolishing the substrate presents its true crystal structure to the depositing metal. The deposit can then continue the crystal structure of the substrate as long as their lattice constants will permit, and the bond zone between them would be as little strained as possible. Early work by Blum (1923) has shown that in those cases where the crystals of the deposit represent a continuity of the substrate crystals almost perfect adhesion is obtained.

4. Comparison of the Dissolution Potentials of Electrolytically and Mechanically Polished Metals.

If the electropolished metal represents a clean, unstrained, crystalline and oxide-free metal, it should have a dissolution potential identical with a clean etched metal. On the other hand, straining the surface layers of the metal by mechanical polishing raises its free energy and therefore should shift the potential to a less noble direction, i.e. less affinity for electrons. In other words the electrode

potential of a mechanically polished metal should be more negative than the value given by the electropolished one. Experiment has shown this to be true. A long copper rod $1/4$ square inch in cross section was cut into four shorter rods. The first was mechanically polished on the buff with rouge, the second electrolytically polished in phosphoric acid, the third simply etched in potassium cyanide and the fourth heated in air to form an oxide film. The dissolution potential of each rod in saturated potassium chloride was measured against a saturated calomel electrode at 20°C .

The results were as follows:

Mechanically polished copper	-0.104 volts
Electropolished copper	-0.092 volts
Etched Copper	-0.092 volts
Oxide coated copper	-0.044 volts.

The oxide film shifts the potential to the noble direction, i.e. greater affinity for electrons.

The dissolution potential results thus confirm the electron diffraction results that the electropolished metal surface is crystalline and oxide-free. The lower dissolution potential of an electropolished metal (as compared with the mechanically polished one) makes it of special advantage for industrial purposes since it is more resistant to corrosion.

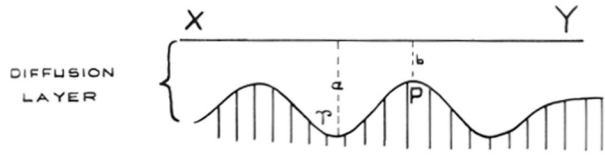


Fig. (2)

THE THEORY OF ELECTROLYTIC POLISHING.

1. Discussion of the Jacquet and Elmore Mechanisms.

The simple mechanism put forward by Jacquet (1936) and previously given on page 11 and Fig.2 is not at all satisfactory. In a personal interview with Dr. Jacquet in 1946, the present writer pointed out to him the objections to such an explanation, to which Jacquet definitely agreed and later outlined in a paper to the International Conference on Electrodeposition (Sept. 1947). Reproducing Fig.2 we can point out the two most important objections. These are (1) The recessed parts undergo themselves a micropolishing effect becoming very bright. (2) Under certain conditions (e.g. high speed of rotation of the anode) where the diffusion layer is too thin for the Ohm's law resistance effect to intervene to any great extent, electrolytic polishing could still be observed. As a matter of fact it is now fully recognised that electrolytic polishing tends to remove submicroscopic roughness rather than grosser irregularities, and the resistance effect does not indeed explain polishing on the submicroscopic scale, for it is not very likely that a difference in thickness a-b of the order of a micron can produce an effective supplementary resistance. This resistance effect might be, however, responsible

for the "rounding off" of grosser irregularities when electrolysis is continued for a moderate length of time.

The explanation put forward by Elmore (1939, 1940) namely that the diffusion of the dissolved anode material plays the important role, is not much more satisfactory. He maintains that the presence of a concentration gradient in the vicinity of the anode (with a saturated solution at the anode surface) is responsible for the levelling effect, since this gradient, which is proportional to the current density is higher at the "hills" and lower at the "valleys".

There are certain objections to the Elmore hypothesis.

- (1) He assumes that all the metal ions are removed from the vicinity of the anode by diffusion only and not by migration. This assumption cannot be considered as a very exact one.
- (2) The second objection of explaining the polishing solely on the basis of diffusion is as follows: the diffusion layer is more or less present in almost every case of irreversible anodic dissolution of a metal in different electrolytes. Presumably there is a concentration gradient, higher at the hills in all these cases, yet only certain electrolytes can bring about the polishing effect. Even in an electrolyte like phosphoric acid, which polished copper normally under certain conditions, fails to do so under others, e.g. when it is too dilute, or when its temperature is rather high,

although in both these cases a constant current density, limited by the diffusion of copper from the diffusion layer, is attained.

(3). The main objection to the Elmore hypothesis, however, will be evident from the following argument. The thickness of the diffusion layer as observed by Jacquet is of the order of 0.05 mm. The projections on a lightly etched metal surface are of the order of a fraction of a micron, which is almost negligible compared with δ , the mean thickness of the diffusion layer. It is difficult to believe that a difference in the concentration gradient of $C_e - C_0/.005 - C_e - C_0/.0049$ or even less would cause a preferential dissolution of the peaks on a submicroscopic scale. It is reasonable however to assume that the diffusion mechanism and the stagnant conditions in the recesses might be responsible (together with the Ohm's law effect previously mentioned) for the rounding off of the grosser irregularities.

In conclusion, although the diffusion hypothesis, as modified and elaborated by the present writer, could explain the electrical relationships of the anode reaction, as illustrated by the tests to which equation (9) was put, it was felt that simple diffusion alone cannot represent the whole explanation of the polishing effect. It was necessary to consider the electrical forces at the anode-diffusion layer

interface and thus the probability of a given metal ion being thereby removed together with the effect of the shape of the surface upon this probability. Before doing this, however, it was considered essential to investigate in more detail the properties of the diffusion layer.

The Isolation, Properties and Artificial Preparation of the Diffusion Layer.

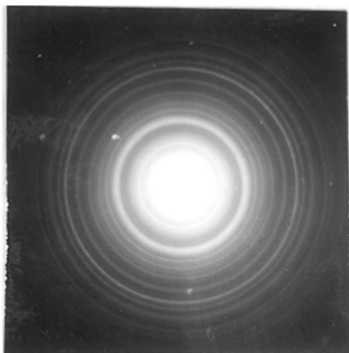
Using the apparatus shown in Fig.19, the anode dissolution products collecting in the space D (later referred to as solution A) were discharged through the stopcock T for further examination. Since the theoretical development leading to the deduction of equation (9) was based on the reasonable assumption that the concentration of copper ions at the anode represents saturation, it occurred to the writer to prepare a saturated solution of copper phosphate in phosphoric acid (later referred to as solution B). Phosphoric acid of Sp.Gr. 1.516 at 20°C. and containing 1048 gms. H_3PO_4 per litre was used for the preparation of both solutions A and B so that the results might be comparable. Solution B was prepared by adding to the phosphoric acid copper carbonate very gradually and slowly at room temperature until the solution was saturated. This was shown by signs of turbidity due to the precipitation of copper phosphate. The solution used for the measurements, obtained by decantation after standing for 24 hours, was clear dark blue.

Measurements of the conductivity and relative viscosity were carried out in a thermostat adjusted at 25°C.; a micro conductivity cell and an Ostwald's viscometer of a suitable capillary were used. The results are shown in the following table.

	Colourless H_2PO_4	Solution A (electrolytic)	Solution B (chemical)
Sp. Gravity at 25°C.	1.512	1.600	1.630
Copper content (gm ions/litre)	-	100.5	110.6
Specific conductance (ohm ⁻¹)	0.145	0.087	0.078
Coefficient of relative viscosity (water = 1)	13.8	27.2	29.8

The above data show clearly that solutions A and B are almost identical, as revealed by analysis, specific gravity, conductivity and viscosity measurements, although they suggest that solution A collected from the apparatus (Fig. 19) does not seem to represent exactly the composition of the diffusion layer. It had been inevitably contaminated with a less concentrated solution from the immediate vicinity of the diffusion layer.

The salt present in both solutions A and B was in each case precipitated by diluting the solution and boiling it.



K1841

Fig.51

Copper phosphate deposited from
the anode dissolution products
collecting in space D fig.19

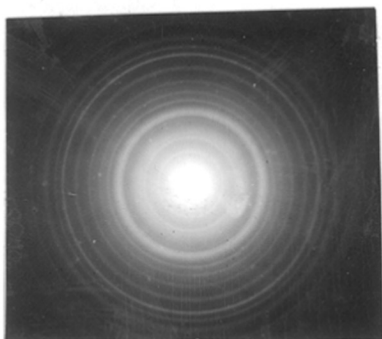


Fig.52

Copper phosphate deposited
from a chemically prepared
solution in phosphoric acid.

H46

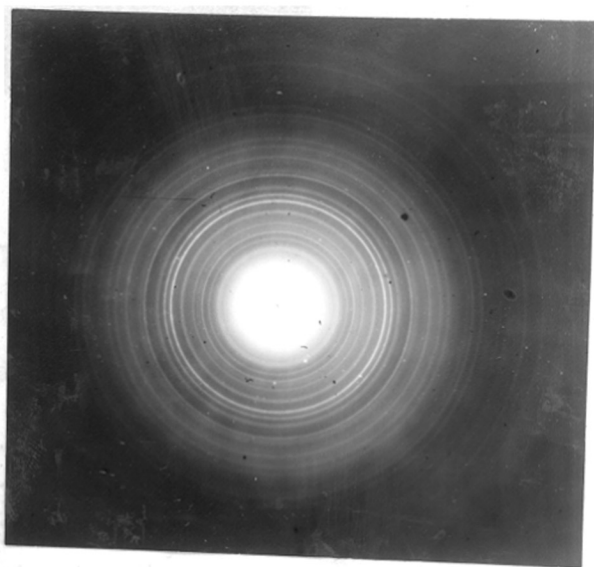


Fig.53

Pattern obtained from
the copper phosphate
deposited on the anode
fig.19 when a high
voltage is applied.

K 1000

A blue green precipitate was obtained in each case. This was filtered and washed repeatedly with distilled water to eliminate the last traces of phosphoric acid. A transmission pattern in the electron diffraction camera was then obtained in each case. These, as shown by Fig.51 and 52 respectively, are identical. To ensure that no change took place in the composition of the salt during its precipitation by boiling, a third specimen was obtained (without boiling) for electron diffraction examination. This was prepared by passing a relatively high current through the apparatus (Fig.19). This caused the salt to be precipitated on the anode. After washing with water it gave the electron diffraction pattern Fig.53, which is identical with both Fig.51 and 52. The pattern, as shown by the measurements given in the following table, shows the precipitated salt to be identical with libethenite ($4\text{CuO P}_2\text{O}_5 \text{H}_2\text{O}$).

Identification of the Compound which gave the Pattern Fig. 51.

L = 47½ cms.

 $\lambda = 0.05356 \text{ \AA}$.

Observed data			Literature (A.S.T.M. 1945)	
Intensity	r(cms)	$d = \frac{\lambda L}{r}$	d	Intensity
s.	0.427	5.95	5.85	.9
f.	0.523	4.86	4.81	1.00
m.s.	0.606	4.19	4.11	0.10
f.	0.686	3.71	3.69	0.70
s.	0.858	2.96	2.92	0.90
m.f.	0.945	2.69	2.63	1.00
m.s.	1.005	2.53	2.55	0.5
v.f.	1.062	2.40	2.40	0.6
f.	1.102	2.30	2.30	0.6
m.s.	1.196	2.11	2.07	0.4
m.f.	1.240	2.05	2.02	0.2
m.s.	1.281	1.98	1.965	0.2
m.f.	1.343	1.90	1.91	0.6
-	-	-	1.86	0.4
m.	1.419	1.79	1.80	0.2
m. (diff)	1.492	1.72	1.71	0.7
v.f.	1.525	1.66	1.66	0.5
-	-	-	1.615	0.6
s.	1.608	1.58	1.577	0.7
-	-	-	1.545	0.6
v.f.	1.656	1.52	1.527	0.3
m.s.	1.700	1.50	1.502	0.4
-	-	-	1.474	0.6
v.f.	1.752	1.45	1.451	0.7
-	-	-	1.431	0.4
m.f.	1.826	1.39	1.391	0.4
m.f.	1.837	1.38	1.371	0.4
m.f.	1.903	1.34	1.344	0.4
-	-	-	1.315	0.6
-	-	-	1.284	0.6
m.s.	2.008	1.26	1.262	0.6
f.	2.035	1.25	1.251	0.4
f.	2.100	1.21	-	-
f.	2.207	1.15	-	-
m.f. sharp	2.276	1.12	-	-
f.	2.459	1.03	-	-

The electron diffraction results as well as the data of the previous table show that the saturated solution of copper phosphate prepared from the carbonate is identical with the diffusion layer at the anode. Since this solution can be easily prepared in comparatively large quantities, future study of the diffusion layer will be much easier. The results presented in this work are by no means complete, and it is intended in future to extend the study of the diffusion layer to other metals and in different electrolytes and to investigate the effect of temperature, dilution, addition agents, etc. on such properties of the diffusion layer as density, viscosity, conductivity, dielectric constant and transport number of the constituent ions. It is hoped then that such results may throw further light on the nature and mechanism of the anodic reactions leading to the production of highly polished anode surfaces.

However, the viscosity results obtained are of some interest. The fact that the viscosity of the diffusion layer is 30 times that of pure water and more than twice as much as that of the bulk of the electrolyte, seems to suggest that this factor plays some role in the mechanism of the polishing process.

A Suggested Mechanism of Electrolytic Polishing.

Before attempting to develop a satisfactory mechanism of electrolytic polishing, it is necessary to adopt a suitable

view of anodic reactions generally. Some electrochemists believed in the direct passage of the metal from the surface layer of the crystal lattice into solution. This is represented by



where z is the valency of the metal. (The solvation of the ions is neglected for simplicity of representation).

Others believed that the discharge of the anions is the primary reaction



where n is the valency of the anion. The discharged anions may then evolve as a gas (e.g. O_2 at carbon or platinum anodes) or may attack the anode forming a salt, M_nA_z which is completely ionised.

In the case of soluble anodes it may be convenient to embrace both views in the following statement on the lines advanced by Evans (1924). The external E.M.F. brings about a continual suction of electrons from the metal-electrolyte interface at the anode, and drives the anions towards the interface, resulting in the pairing of metal ions and anions to form a chemical compound.

In the case of copper, dissolving in phosphoric acid e.g. there is no reason to argue whether copper ions cross the interface in one direction, or whether the phosphate ions

cross it in the other; the mere assumption of relative motion between the copper and phosphate is enough. It is however necessary for the phosphate anions which carry the current to the highly polarised anode to cross the diffusion layer (of average thickness δ) before they arrive at the double layer. In crossing the very highly viscous diffusion layer, the phosphate ions aiming at hills on the surface would have a shorter distance to travel than their companions which have to reach the valleys.

When a phosphate ion of velocity u moves through an electrolyte of viscosity η , under the influence of a force f (potential gradient), then according to Stokes Law:

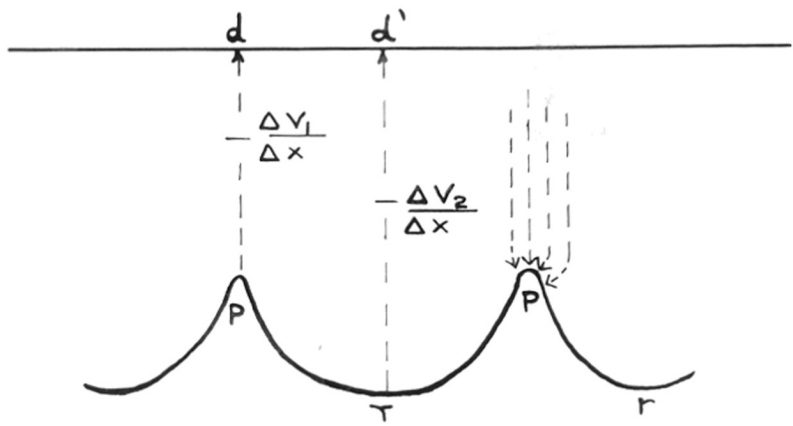
$$f = 6\pi\eta bu$$

where b is the radius of the ion.

It is quite clear from this relation that due to the very high viscosity of the diffusion layer, the ions move more slowly in crossing it than they do in moving through the bulk of the phosphoric acid, and indeed very much slower than they would do in a dilute solution.

Again, Stokes Law shows that the ionic velocity is higher the higher the potential gradient.

When the anode surface (Fig.54) is non-homogeneous, containing projections p and recesses r , there will be local differences of electric field intensity corresponding to these



FIELD INTENSITY AT "P" $I_1 = \frac{\Delta V_1}{\Delta x}$

" " " "r" $I_2 = \frac{\Delta V_2}{\Delta x}$

$I_1 \gg I_2$

Fig.54.

non-homogeneities and the electrical density will be much greater on the projections. It follows, therefore, that the potential gradient across the diffusion layer (in a direction normal to the mean surface) is much higher at the projections than at the recesses or

$$\frac{\Delta V_1}{\Delta X} \gg \frac{\Delta V_2}{\Delta X}$$

The existence of a higher potential gradient along pd means a higher velocity of phosphate ions moving in this direction. The higher intensity of the field at p , moreover, results in an attraction of a certain fraction of anions which would normally have been discharged at r , were the field normally distributed. This fraction which is deflected from its normal path is higher, the smaller the momentum or the velocity of the ion. As shown above, this damping down of velocity is achieved through the existence of the highly viscous diffusion layer. The net result is a preferential accumulation of phosphate ions at the projections and thus a relatively high probability of copper ions being detached from the lattice and going into solution. The dissolution of the projections results in a levelling effect eventually leading to a highly polished surface.

The above mechanism is supported by many experimental facts. Some of them are listed below:

1. Most of the electrolytes used for electrolytic

polishing are very viscous, ensuring the formation of a highly viscous diffusion layer. Examples of these are phosphoric acid, perchloric-acetic anhydride, conc. sulphuric acid, glycerine phosphoric acid ... etc.

2. Electrolytic polishing of copper in phosphoric acid is not possible if the viscosity of the electrolyte and diffusion layer falls below a certain critical limit either by dilution or rise of temperature. On the contrary, even if the diffusion layer is much reduced in thickness (anode rotating 10,000 r.p.m.) polishing is still possible as long as the diffusion layer remains highly viscous.

3. Yang (1948) has found that when Fe, Co or Ni were deposited on a cathode, in the presence of a magnetic field, there was a pronounced tendency of the deposits to grow along the direction of the field when this latter was normal to the cathode surface. This has been explained as due to the existence of a more concentrated field at the projections which guides the paramagnetic ions of Fe, Co or Ni resulting in an enhanced crystal growth at the projections.

VI. SUMMARY.

A review of the history and development of electrolytic polishing has shown the hitherto the mechanism of the process is not sufficiently clarified and also that the nature of the electropolished surface is not decisively elucidated.

The electron diffraction results obtained in the present work with single crystals, and polycrystalline copper, aluminium and silver specimens showed that an electropolished metal surface when protected from atmospheric contamination, represents a clean crystalline metal surface with no amorphous or oxide layers.

The anodic behaviour of copper in phosphoric acid was studied in detail to investigate the influence of various factors on the polishing process. An expression for the limiting current density of the process was derived. This was based on the reasonable assumption that the diffusion of the anode dissolution products into the bulk of the electrolyte is the slow rate determining process in the electrode reaction. This expression was in fair agreement with the experimental results.

The properties of electrolytically and mechanically polished surfaces have been compared. In electrodeposition on polished metal surfaces, the stress produced within the deposit was found to be less in the case of electropolished

substrates. An electropolished metal also gives the same dissolution potential as etched metal whereas the mechanically polished one is more anodic.

The diffusion layer at the anode has been isolated and its specific gravity, metal content, electrical resistance and viscosity were determined.

Finally a mechanism for electrolytic polishing is suggested. On reaching the diffusion layer from the bulk of the electrolyte, the anions are accelerated and deflected towards the projections on the metal surface where there is a much higher electrical field intensity or potential gradient (as compared to the recesses). The number of anions deflected from their normal path towards the projections increases as their velocity decreases. According to Stokes law, this decrease in velocity is brought about by the very high viscosity of the diffusion layer. The result of this anion accumulation is a higher rate of metal dissolution at the projections and hence a levelling effect leading eventually to a highly polished metal surface.

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