THE SURFACE STRUCTURE AND SOME PROPERTIES OF ELECTRODEPOSITED METALS.

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INTRODUCTION.

The electrodeposition of metals has been applied on an industrial scale for more than a century and, so far as single metals are concerned, theory has advanced until the working of high concentration, commercial plating solutions has been explained.

The simultaneous deposition of two metals was first postulated by de Roultz in 1841. The two metals were copper and zinc and their co-deposition was later applied on an industrial scale for the decoration and protection of iron and steel articles. The appearance of brass could thus be achieved at a much lower cost than if the article were made of solid alloy. Because of this use, the only criterion of a successful plating solution was the "colour" of the deposit; the word colour implying all the surface properties controlling the appearance of the plate. It was found that the colour of electrodeposited brass was not necessarily the same as that of cast brass of the same composition, but the practice of specifying the plate by its colour only did not die out until quite recently, when the advent of a new application of electrodeposited brass led to a much closer control of plating conditions.

It was found that rubber could be satisfactorily bonded to 70/30 brass, and hence by using an interlayer of

of brass it could be bonded to any metal, especially iron and steel. The easiest method of obtaining this interlayer was by electrodeposition. Such rubber-metal units have found wide application in the suppression of vibration and in the flexible coupling of driving shafts. Rubber to metal bonding required a much closer control of the plating conditions in order to obtain economically a brass plate of the correct composition. This stimulated research into brass plating and in general into all alloy plating.

THEORY OF ELECTRODEPOSITION.

From thermodynamical reasoning, the potential set up between a substance and a solution of its ions is given by:-

$$E = \frac{RT}{NQ} \log \frac{P}{p}$$

where

P is the electrolytic solution pressure
N is the valence of the ion
p is the osmotic pressure of the ions
Q is Faraday's constant.

If e_h is the hydrogen overvoltage for a given system and P' and p' the solution and osmotic pressure of the hydrion, then the potential of hydrogen at the cathode will be given by:-

$$E' = e_h + \frac{RT}{Q} \log \frac{P'}{p'}$$

If $E' > E$ then only the metal will be deposited since its potential is reached first.

If $E > E'$ only hydrogen ions will be discharged at the cathode. In the special case when $E' = E$ both the metal ions and hydrions will be discharged together.

A generalisation of this to a solution containing more than one kind of metallic ion indicates the essential theory of the simultaneous deposition of two metals. It can be seen that to obtain this simultaneous deposition it is necessary for the potentials of the two metals in the mixed solution to be equal. Since these potentials are controlled by the osmotic pressures and the concentrations of the ions in the mixed solution, it is possible, in theory, to obtain this equality of the deposition potentials. In practice this is not so easy and is often impossible. Thus a solution containing both zinc and copper sulphates can be made up so as to obtain this equality, but the concentration of copper ions in it is only of the order of 10^{-38}N, which is not a practical concentration. In all alloy plating solutions that have been used, complex ions are employed. Such solutions often contain cyanide complexes as these are readily formed. The type of substance present in such a plating solution has the formula $R_xM(CN)_{x+n}$ where R is generally sodium (most used commercially) or potassium. The dissociation of this compound is regarded as taking place in two stages:-

(i) $Na_x M(CN)_{x+n} \rightleftharpoons M(CN)_{x+n}^{x(-)} + x\ Na^{+}$

(ii) $M(CN)_{x+n}^{x(-)} \rightleftharpoons M^{n(+)} + (x+n)\ CN^{-}$

The rate of dissociation of the complex ion $M(CN)_{x+n}^{x(-)}$ is never great and can be controlled to some extent by arranging for a second source of cyanide ions to be present to repress this dissociation. This is most conveniently done by arranging for an excess of sodium cyanide in the solution. The metal ion concentration is thus made very low and it can be seen that it should be possible to have such low metal ion concentrations present so that simultaneous deposition can occur.

The current is carried by the highly concentrated complex ions and thus high current densities are possible, an important factor in reducing the cost of plating.

The presence of so many complex ions makes the task of predicting any changes caused by altering one factor in the equilibrium very difficult and for that reason no comprehensive theory has as yet been made to account fully for the variations of cyanide alloy plating solutions. The working of such solutions in practice is largely empirical and many formulae for successful solutions with widely differing compositions have been put forward.

Complex ion solutions of only one metal are not fully understood, though several theories have been put

forward to explain their properties. One of the most striking of these properties is the extremely fine grain deposit that is obtained from them. The fine grain structure was originally believed to be due to cathode polarisation but Glasstone [1] working with silver cyanide showed that little or no polarisation occurred but that the deposit was still fine grained. Bancroft [2] stated that the crystal size in the deposit was decreased by (i) increased current density, (ii) lower temperatures, (iii) the presence of colloids at the cathode surface, and (iv) an increase in the cathodic potential difference. L.B.Hunt [3] enlarged on this in his theory and gave the following account of the process of electrodeposition. The crystalline structure of an electrodeposited metal will be governed by the relation of the metal ion concentration in the cathodic film to the concentration of the other constituents of that film. If the proportion of metal ions to inert particles is comparatively high, there will be little interference with crystal growth and a coarse grained deposit will result. If, however, this proportion is low due to a low degree of dissociation, (the case with complex ion solutions), or to the presence of colloidal matter, there will be considerable interference with crystal growth and hence the formation of many nuclei.

A metal ion on approaching the cathode will seek to enter the lattice as soon as possible and in order to do

this it must lose both the "ionic atmosphere" of inert particles and its water envelope. It is conceivable that the rate of deposition may be so high that the ion will enter the lattice still possessing part of either and that with such rapid deposition this impurity may be unable to diffuse out. O'Sullivan [4] found that colloidal hydroxides were so entrapped. The influence of the basis metal on the structure of electrodeposits has been the subject of much research. Huntington [5] first observed this influence with copper deposits upon a copper base. Blum and Rawdon [6] and Graham [7] continued this work and by observing the continuance of etching figures present on the basis metal drew the conclusion that the orientation of this was continued in the deposit. Wood [8] using X rays showed that the orientation of the basis metal may be copied by the deposit. The microstructure of the deposit was examined by Hothersall [9] who concluded that even with considerable difference between the lattice parameters of the substrate and the deposit, this microstructure could be continued through deposits as thick as 0.5 mm. Finch and Sun [10] using fine grained substrates found that the influence of the basis metal orientation ceased after deposits of only a few thousand angstroms had been deposited. Finch and Williams [11] using macrocrystalline substrates found that this result still held, though the influence in

this case continued to occur until a thickness of some twenty thousand angstroms had been deposited. Thus with deposits normally met with in commercial plating, the influence of the basis metal on the structure of the surface layers of the metal deposit is negligible.

The present research was started in order to study the surface condition of commercially plated brass surfaces used for rubber to metal adhesion. It was found that little work had been carried out previously on the structure of alloy deposits and the scope of the work was enlarged to study other alloy systems. The bonding of rubber to metal is essentially a surface phenomenon, this being indicated by the poor bond obtained when the surface has been fingered or otherwise contaminated. Electron diffraction has been used by many workers for studying surface conditions and it was considered to be the best method to employ in this case. A considerable amount of work had already been carried out on the structure of electrodeposits by this method [12] and in particular both Finch and Sun [10] and Finch and Williams [11] had used this method in their investigation of orientation effects. The usefulness of electron diffraction as a means of investigating thin films and the advantages it possesses over X-ray methods are dependent on the fact that the depth of penetration of electrons is so much smaller than that of X-rays of similar wavelength.

Thus high speed electrons, 50,000 e.v. energy, will only penetrate 10^{-6} cm. perpendicular to the beam, whereas the least penetration of suitable X-rays will reveal the structure of material to a depth of 10^{-3} cm.

INTERPRETATION OF ELECTRON DIFFRACTION PATTERNS.

In the experiments to determine the lattice dimensions of the alloy deposits only polycrystalline substrates, and therefore deposits, were used, so that the electron diffraction patterns had the same form as those obtained by X-ray diffraction using the Hull-Debye-Scherrer method.

The actual mechanism of electron diffraction by polycrystalline specimens is quite different from that of X-rays and is best approached by first considering the diffraction at a single crystal. Laue [13] has given the following equation for the diffraction of a beam of wavelength λ at a line grating of constant $\underline{a}$ representing interval and direction:-

$$h\lambda = \underline{a}.(\underline{s} - \underline{s}_o)$$

where $\underline{s}_o$ and $\underline{s}$ are unit vectors defining the directions of the incident and diffracted rays and h is an integer.

For a space lattice, or a three dimensional grating three similar equations must hold simultaneously, i.e.

$$h\lambda = \underline{a}.(\underline{s} - \underline{s}_o)$$
$$l\lambda = \underline{b}.(\underline{s} - \underline{s}_o)$$
$$k\lambda = \underline{c}.(\underline{s} - \underline{s}_o)$$

where $\underline{a}$, $\underline{b}$, $\underline{c}$ are vectors giving the directions and intervals in the space lattices and h, k, l are integers. These three equations are known as the Laue conditions for diffraction and h, k, l the Laue indices.

The penetration of the electrons is very small so that only a few atom rows in the direction of the beam will be effective in the diffraction. This means that the resolution of the line grating in the direction of the incident beam will be very poor and that one of the Laue conditions will be relaxed. The transmission of an electron beam through a single crystal is thus best regarded as a case of diffraction at a cross grating. It has been shown by Thomson [14] that the "reflection" type of specimen, in general, gives rise to a pattern due to the transmission of the electron beam through the thin projecting crystallites present on all but highly polished or other very smooth surfaces.

A polycrystalline substance can be regarded as a single crystal rotated so as to give all possible orientations with respect to the incident beam. The difference between diffraction at such substances by electrons or X-rays is thus due to the original difference between single crystal

diffraction by the two methods, i.e. cross grating as against space lattice. Thomson's initial experiments [15] showed that Bragg's Law, $2d\sin\theta = n\lambda$, developed for X-ray diffraction could be applied to electron diffraction at crystals. Thus for a set of crystal planes with Miller indices (hkl) the spacing d_{hkl} is given by the equation $d_{hkl} = \lambda/2\sin\theta$ for first order diffraction.

The crystal geometry necessary to arrive at the correct crystal structure of a polycrystalline substance giving rise to a diffraction pattern whose spacings have been found by the Bragg equation, is given below.
It is possible to show that:-

$$d_{hkl} = \frac{a_o}{\sqrt{f(hkl;\ a\bar{b}c;\ \alpha,\beta,\gamma)}}$$

where a_o, a,b,c and α, β, γ are constants of the unit cell of a crystal lattice giving rise to a diffraction pattern with Laue indices h, k, l. a_o is the length of the side of the cell, a:b:c the ratio of the lengths of the sides and α, β, γ, the angles between the axes of the unit cell.

ORIENTATION OF A POLYCRYSTALLINE SPECIMEN.

In many cases a polycrystalline film will possess orientation, i.e. one or two directions in the crystallites are fixed with respect to the substrate. One degree orientation is the more common; it is defined by stating the

Miller indides of the crystal planes that are parallel to the surface of the substrate or else the indices of the lattice row normal to it. This lattice row direction is called the fibre axis of orientation. It has been shown that with crystallites arranged at random, the ring pattern is due to the intersection of the cones of diffraction rays with the plane of the screen; when orientation occurs only certain parts of these conical surfaces will be present since the crystal planes giving rise to the diffracted rays will not be arranged at all angles to the incident beam but will occur only at specific directions. Thus the pattern appearing on the screen will consist of arcs of the rings only. The position of these arcs can readily be calculated for the different orientations possible, their length indicates the extent to which orientation has occurred.

Two degree orientation is equivalent to a single crystal giving no rotation at all. The pattern to be expected in this case will be similar to that obtained from a single crystal, though, unless the orientation is perfect, the spots will be drawn out into arcs. The simplest way of calculating the position of the arcs is to consider the pattern as due to the intersection of the Laue zone of reinforcement from the lattice row (uvw) parallel to the orientation axis with the ring hkl.

This reinforcement zone or layer line of order 1'

is given by:-

$$l' = uh + vk + wl$$

These layer lines are practically straight in electron diffraction with spacings $L/c'\cos\theta$ where the axis makes an angle θ with the direction of the beam, L is the camera length, and c' is the interval along (uvw).

In reflection specimens the orientation most commonly met with is such that one plane (uvw) is parallel to the shadow edge. An arc is formed at the intersection of any given layer line l' with the hkl ring, if the indices of one or more of the diffractions contributing to the ring satisfy the relation $l' = uh + vk + wl$.

The method of identifying the indices of the planes giving rise to the different diffractions was that described by A.W.Hull and W.P.Davey [16]. Logarithmic plottings of the spacings were matched on graphical charts of crystal plane spacing ratios plotted against different axial ratios for hexagonal and tetragonal lattices. Though limited to these types of lattice, the method was quite satisfactory.

The idnetification of the substance after the crystal structure was known was helped by using the reference books by Knaggs, Karlik and Elam [17] for cubic lattices, R.Wykoff [18] and Ewald and Hermann [19]. Further identification of substances suspected of being present or thought likely to be present on the surfaces of the specimens was furnished by a

list of the principal spacings for 1,000 substances collected by Hanawalt, Rin and Frevel [20] from X-ray data.

EXPERIMENTAL.

The research can be divided into two sections, A, the research on suitable plating solutions and the effects of various additions of salts to these on the resulting electrodeposited alloy, and B, the investigation of the structure of the alloy by electron diffraction and its subsequent behaviour when corroded in different atmospheres.

A.

Several types of solution were used; the bulk of the work was carried out on brass plating solutions, especially those made up to the formula recommended by H.P.Coats [21] for the electrodeposition of α-brass for the adhesion of rubber. The solution, as made up, contained 26.2 g./l. copper cyanide, 11.3 g./l. zinc cyanide dissolved in 45 g./l. sodium cyanide. This solution was made up with both commercial and pure salts; with the former a sludge was formed as soon as the cyanides were dissolved, but with pure salts the solution was clear at first. The experiments were carried out initially in a large glass tank 22 cm. x 10 cm. x 25 cm. deep, holding four litres of solution. This tank was kept in a water bath, the temperature of which was controlled by a gas thermostat.

The first sample of the brass plating solution to be used was taken from a commercial plating bath already in use for depositing α-brass on to steel and iron for subsequent rubber adhesion. This solution has had additions made in order to keep the composition, as analysed, to that given above. It had a high sludge content. This solution was known as Solution A. A fresh solution made with commercial salts in the laboratory to Coats' formula was known as Solution B.

A different type of plating bath was also tried, which was made up in the laboratory to the following formula:- 60 g./l. copper cyanide, 8 g./l. zinc cyanide, 90 g./l. sodium cyanide and 8 g./l. sodium hydroxide. This was known as Solution C.

The experiments carried out with Solution A were designed to increase the pH of the solution. Additions of calcium hydroxide were made in small quantities. To one sample of this solution additions of 0.3 g./l. were made and the pH measured after each addition until a total of 1.5 g./l. had been added. Specimens were plated throughout these additions, both for examination in the electron diffraction camera, described later, and for analysis, which was carried out as described below. A second sample taken on a different day from this Works bath proved to be buffered quite successfully, and even an addition of 2.25 g./l. of calcium hydroxide could only raise the pH by 0.1

Solution C was then tried. This was a new solution with part of the zinc present as sodium zincate, and experiments were carried out to find the ranges of the different variables over which the solution would plate brass. It was found that using mild steel as substrate, a minimum current density of 3.5 amps./sq.ft. was necessary. With considerable agitation of the cathode it was possible to plate up to a current density of 30 amps./sq.ft. It was noted that all the specimens, whether previously polished or not, had a dull surface after plating. A current density of 5 amps./sq.ft. and a temperature of 26°C. gave a deposit of 70% copper and 30% zinc; at higher temperatures a higher current density was required to get this composition. For example, at 40°C. only very poor deposits of a purple and black colour were obtained even at 7 amps./sq.ft. There was evidence that at these higher temperatures considerable gas evolution occurred, as several of the specimens plated at 40°C. showed vertical streaks on the surface, and this did not occur on specimens that had been agitated. The results of the experiments carried out on these two solutions are shown in Tables I and II.

Solution B was used to investigate the variation in the cathode potential and in the resistance of the solution with changes in the composition. The resistance was measured in a short conductivity cell with small platinized platinum electrodes 3 cm. apart and 2 cm. in diameter. Since only

variations of the resistance with composition were being investigated, the cell was not calibrated with a known solution. The solution B was always diluted one hundred times before measurements by drawing a 5 ml. sample in a pipette and transferring to a graduated 500 ml. flask and making up with so-called "conductivity water." This latter was made by distillation under reduced pressure so as to drive out dissolved gases that would otherwise increase its conductivity.

The resistance of this cell was measured in an A.C. bridge supplied from a 1,000 c.p.s. valve oscillator. The sensitivity of the balance point was increased by amplifying the out of balance current with a two stage amplifier before it was detected by headphones. Experiments were carried out to test the accuracy of these measurements. The cell was first filled with the distilled water to find out what the resistance of this was compared with the solution B, when diluted one hundred times. A 500 ml. sample of solution B was then taken and kept in a tightly corked bottle in the dark whilst tests were being carried out. 5 ml. samples of this solution were taken and diluted to 500 ml. in the standard way and repeated measurements taken of the resistance of the cell. All resistance measurements were taken at a constant temperature by immersing the cell in a constant temperature water bath and leaving it there for half an hour before taking a reading.

The results of these preliminary experiments showed

that the resistance of the cell filled with pure water was approximately one hundred times that of the cell when filled with diluted solution B and also that results obtained both by fresh dilutions and by repeated measurements of the same dilution agreed to within 3%. It was thus considered that this method was capable of showing comparative changes in the conductivity of the plating solution with variations in the composition.

The main variation that was investigated was the "uncombined cyanide" concentration. This was calculated as the difference between the total cyanide concentration (see later) and the sodium cyanide equivalent of the copper and zinc cyanide complexes present. These latter were calculated as corresponding to $Cu(CN)_3^{\ddot{}}$ and $Zn(CN)_4^{''}$. The uncombined cyanide concentration is an important quantity in the analytical control of the plating solution and its estimation is neither easy nor quick. It was hoped that this quantity would have a pronounced effect on the conductivity of the plating solution, since it controlled the dissociation of the complex metallo-cyanide ions. It was therefore thought that it could be rapidly estimated by suitable conductivity measurements.

Additions of varying amounts of sodium cyanide were made to one litre samples of Solution B, well stirred and allowed to react with the solution at the operating temperature,

30°C., overnight. The resistances of these samples were then measured as above and a chemical analysis carried out in order to determine the metal content and the total cyanide concentration, and hence to calculate that of the uncombined cyanide. As much as 10 g./l. of sodium cyanide was added to one sample of solution B; this amount caused all the precipitate to be dissolved and a clear solution was obtained. It proved impossible to plate with this solution on to steel surfaces at either high or low current densities; only hydrogen was evolved at the cathode surface. Even this quantity of sodium cyanide, which increased the uncombined cyanide concentration by 4 g./l., did not alter the resistance more than could be expected from any such increase in the total concentration of the ions present. It was also found by additions of copper and zinc cyanides and of sodium carbonate that the measurement was not sensitive to changes in the concentrations of these ions. The results of this investigation are shown in Table III.

METHOD OF ANALYSIS OF THE BRASS PLATING SOLUTIONS AND DEPOSITS.

The chief quantities necessary to specify the plating solution and permit of accurate control by analysis are:-

(i) the concentration of the copper and zinc salts present

(ii) the concentration of cyanide salts present, the total cyanide concentration,

(iii) the concentration of "free" or uncombined cyanide ions.

Two other quantities are often specified in addition to those above; these are the other metal ion concentrations, present as impurities, and the carbonate ion concentration. The deposit is only analysed to give the zinc/copper ratio of the brass.

The analysis was carried out by the methods recommended by H.P.Coats [21]. The deposit was analysed by electrochemical means. The brass plated steel blank was first weighed and then the brass removed by immersing in a solution of 75 g. of ammonium persulphate crystals in 335 ml. of ammonium hydroxide (Sp.Gr. 0.880) and 665 ml. of water. The steel blank was removed from the solution as soon as all the brass was dissolved, detected by inspecting the blank for colour change. This blank was dried and weighed again and hence the weight of brass and iron dissolved was known. The persulphate solution was reduced in volume by boiling gently until only half the bulk remianed. This destroyed the persulphate and any iron present was precipitated and then filtered out. The filter paper and precipitate were washed with dilute ammonia water to remove all the copper and zinc. The filtrate was transferred to an electrolytic

beaker, neutralised with 1 : 1 sulphuric acid and 10 ml. of excess acid added. Two to three ml. of nitric acid were then added, together with four to five grams of urea to destroy any nitrogen oxides present. The copper was then electrodeposited on to a weighed platinum electrode in the usual form of electro-analysis unit. This electrode with the copper deposit was washed carefully, dried in acetone and weighed. This gave the weight of copper in the brass; from this the weight of zinc was calculated by difference and hence the percentage composition of the brass. The weight of iron present, weighed from the precipitate filtered out, was very small and negligible. A test was made to check that all the copper had been deposited. A little distilled water was added to the electrolyte when the deposition was thought to be complete and the cathode inspected to see whether any copper was deposited on the platinum thus immersed. The bath was analysed for metal ion content in the following way:- 10 ml. of the solution to be analysed were taken and one gram of sodium cyanide added. The solution was then diluted and electrolysed, using the platinum electrodes and a current of 10 amps., until all the metals had been deposited, zinc being deposited last. To test the solution to see whether all the zinc had been deposited a small sample was taken, one drop of concentrated nitric acid and three drops of concentrated sulphuric acid

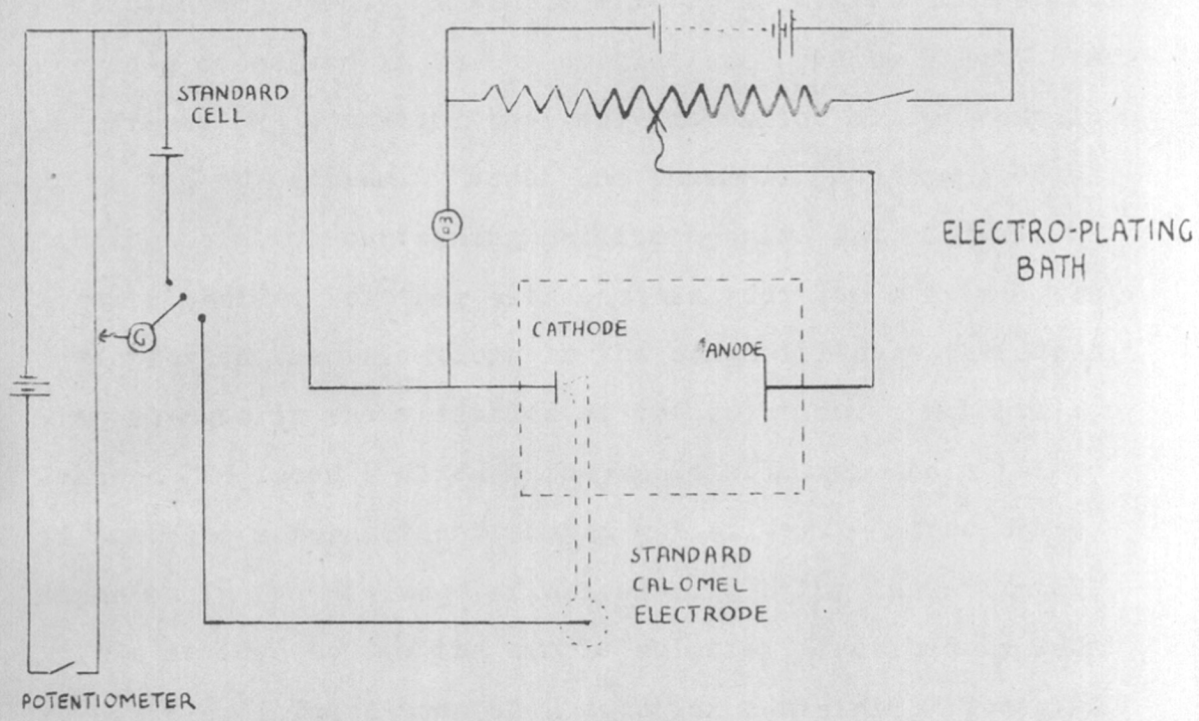
added and the solution boiled to remove hydrogen cyanide. The excess acid was neutralised with a drop of ammonium hydroxide and the excess of the latter boiled off. A solution of one drop of Tropaeolin 00, one drop of 10 : 1 sulphuric acid and two drops of potassium ferricyanide was made and then added to the other solution. If no green coloration was then seen within three minutes the electrolysis was complete. The cathode was then washed, dried in acetone and weighed; this gave the total weight of metals in the solution. The deposit was then dissolved off the platinum in the minimum amount of pure nitric acid, three grams of urea were added and the solution warmed. 10 ml. of concentrated sulphuric acid were added and the solution electrolysed as before, but with a current of only five amperes. The copper was deposited and the electrode dried and weighed as for the deposit analysis. The weight of zinc was found by difference. The weight of copper present multiplied by 140.8 gave the concentration in grams per litre of copper cyanide, CuCN, in the solution. The weight of zinc multiplied by 179.5 gave the weight of the zinc cyanide, $Zn(CN)_2$ present.

The total cyanide concentration was determined by distillation of available hydrogen cyanide into caustic soda solution. Twenty five ml. of 10% sodium hydroxide solution were placed in a beaker and the tip of the adapter of an

Allihn condenser adjusted to dip below the surface of the liquid by a small amount. This condenser was attached to a distilling flask fitted with a side neck in which was placed a dropping funnel filled with a solution of 12.5 ml. of hydrochloric acid in 200 ml. of water. Five ml. of the solution to be analysed were placed in the flask and the acid run in. The liquid was then distilled until about 70 ml. remained in the flask. The condenser was disconnected and washed through with distilled water, the washings being collected in the beaker. Three ml. of a 10% solution of potassium iodide were added to this solution in the beaker, which was then titrated against standard decinormal silver nitrate solution until the first permanent turbidity was observed. The volume of silver ~~cyanide~~ nitrate used, multiplied by its normality multiplied by 27.6 gave the total cyanide concentration expressed as grams per litre of sodium cyanide. The uncombined cyanide figure was thus expressed as grams per litre of sodium cyanide.

Solution B was also used to measure the variation in the cathode potential with composition. Since there is a distinct variation of the cathode potential with current density due to polarisation effects, precautions had to be taken to ensure that this was kept constant throughout the experiments. The backs of the specimens were varnished with an inert cellulose lacquer and the faces of the specimens

arranged parallel to the anode surface. The surface finish of these mild steel specimens were kept constant by abrading them all with 000 emery as a final finish and cleaning them by rubbing with cotton wool moistened with approximately normal sodium cyanide solution. This constant finish was employed in order to obtain as near as possible a constant effective surface area of cathode. The potential was measured between a standard saturated calomel electrode and the cathode; the connection between the former and the cathodic film of electrolyte was made by a siphon tube filled with a jelly of potassium chloride set in agar agar. The end of this tube was drawn into a jet and fixed about a millimetre from the cathode surface (Figure 1). The potential difference was measured by a Cambridge potentiometer standardized with a Weston cell and accurate to one millivolt. The results of this investigation are listed in Table IV. No definite trend in the cathode potential with increase in uncombined cyanide or metal ratio was observed. It was found that there was a variation from specimen to specimen that was as great as any variation with composition. The structure of specimens whose cathode potential had been measured was investigated as described later, and three specimens were measured whose area was two and a half times that of the standard specimen. Due allowance was made so that the current density remained constant and the cathode potential was measured. These larger specimens were



CATHODE POTENTIAL MEASUREMENTS.

figure 1.

employed so that enough brass could be plated for analysis as above.

The deposition of silver cadmium alloys was next studied. This alloy was first deposited as early as 1891 by S.O.Cowper Coles [22] and since then many different methods have been employed. A simple mixture of silver and cadmium cyanides dissolved in sodium cyanide was used by Faust, Henry and France [23], however they only deposited alloys containing up to 10% of cadmium. Stout and Thummell [24] prepared a plating solution containing cadmium cyanide and silver argenticyanide, together with certain addition agents; they investigated the variations in the composition of the deposit with changes in the variables of the solution. Mathers and Johnson [25] used a mixed thiocyanate solution and obtained in one case a deposit containing 69% silver. Since only deposits in the α-range of alloys were being investigated, it was decided to use the simple solution described by Faust et al [23]. Two litres of a solution containing 17.4 g./l. cadmium oxide, 12.4 g./l. silver cyanide, 66 g./l. sodium cyanide and 2 ml./l. of ammonium hydroxide (Sp.Gr.0.880) were made. The cadmium oxide and the silver cyanide were first dissolved separately in parts of the sodium cyanide solution and afterwards mixed. This solution was allowed to settle overnight and then decanted. The experiments with this solution were carried out on a smaller scale than with the

brass solutions; only one litre of solution was used, contained in a large beaker, and only a limited amount of cathode was employed. Mild steel specimens were used, as before, and these were polished with grades of emery paper down to 000 and then stored in approximately semi-normal sodium cyanide solution until they were required for plating. This solution etched them very slowly and even after a week in it the specimens retained their original finish. In general the specimens plated from this silver cadmium alloy solution were a matt white colour, but on lightly polishing with "Bluebell" metal cleaner on cotton wool they became a bright silver colour. The silver-cadmium deposit was analysed gravimetrically. A steel specimen was dried in acetone and weighed. It was plated at a set current density for one hour and then washed, dried and weighed, the weight of the deposited alloy thus being known. This deposit was dissolved off the steel with 1:1 nitric acid, care being necessary to prevent much iron being dissolved. As soon as the colour of the specimen changed in the acid it was quickly hooked out by a glass hook, washed and dried as before and then weighed. The amount of iron dissolved was thus known. To the solution of the alloy in the nitric acid was added slowly 0.1N hydrochloric acid until no further precipitate was caused. This solution was then warmed to coagulate the precipitate and was filtered through a previously weighed

TABLE 1.

Experiments to increase pH of Solution A.

Temperature °C.	Additions g./l.	pH
33	none	9.8
32	0.8	9.9
32.5	1.0	10.2
31.5	1.3	10.4
29	none	9.7*
31	1.8	9.7*
30	2.2	9.8*

* Second sample of Solution.

TABLE II.

EXPERIMENTS CARRIED OUT ON SOLUTION C.

TEMPERATURE °C.	pH	CURRENT DENSITY	ANALYSIS OF DEPOSIT % COPPER
28	11.3	2.5	31
26	11.3	5	69.1
		8	92.5
		10	83.2
29	11.3	15	88.7
32	11.1	5	63.5
		13	89
		21	91
29	11.05	5	80
		20	89
40	11.0	3	gas evolution
		7	black coloration

TABLE III.

ELECTRICAL RESISTANCE OF SOLUTION B.

ADDITION g./l.	TOTAL CYANIDE g./l.	UNCOMBINED CYANIDE g./l.	COPPER/ZINC RATIO AS CYANIDES	RESISTANCE ohms.
None	72.2	14.33	2.74	50
None	73.3	12.30	2.74	45.5
None	75.0	17.8	2.37	49.5
3 NaCN	78.1	16.8	2.84	49.9
7 NaCN	89.5	16.6	2.56	45.3
8 NaCN	79.8	18.0	2.50	45.47
10 CuCN	71.1	1.15	7.29	60.0
5 $Zn(CN)_2$	73.0	7.83	2.02	60.1
8 Na_2CO_3	74.4	17.3	2.38	42.2
2 NaOH	75.3	18.3	2.47	47.3

TABLE IV.

CATHODE POTENTIAL MEASUREMENTS ON SOLUTION B.

ADDITIONS g./l.	ANALYSIS			CATHODE POTENTIAL millivolts
	TOTAL CYANIDE g./l.	UNCOMBINED CYANIDE g./l.	COPPER/ ZINC	
None	72.2	14.33	2.74	1807, 1720, 1905.
3 NaCN	78.1	16.80	2.84	1906, 1849.
7 NaCN	89.5	16.60	2.56	1911, 1835, 1803, 1821, 1803, 1867, 1839.
10 CuCN	71.1	1.15	7.29	1805.
5 $Zn(CN)_2$	73.0	7.83	2.02	1881.

sintered glass crucible. It was washed with cold 0.01N. hydrochloric acid and finally with distilled water. It was then dried at 160°C. in an air oven and weighed as silver chloride. In some cases the preliminary weighing of the steel blank was not carried out and it was necessary to estimate the amount of iron dissolved in the nitric acid solution. This was carried out by precipitating the iron as ferric hydroxide. To the filtrate obtained after removing the silver was added ammonium hydroxide solution (one part water to one part 0.880 ammonia) until a slightly alkaline solution had been obtained. The precipitate was then filtered and washed with hot water. It was redissolved in 1:1 hydrochloric acid and then reprecipitated with ammonium hydroxide in the presence of macerated filter paper to coagulate the precipitate. This was then refiltered on to an "ashless" filter paper and washed with a two per cent solution of ammonium nitrate. The precipitate was ignited and heated to redness in a porcelain crucible and weighed as ferric oxide.

B.

The electron diffraction camera used throughout this research was that described by Finch and Wilman [26] and is shown in Figure 2. The technique of obtaining

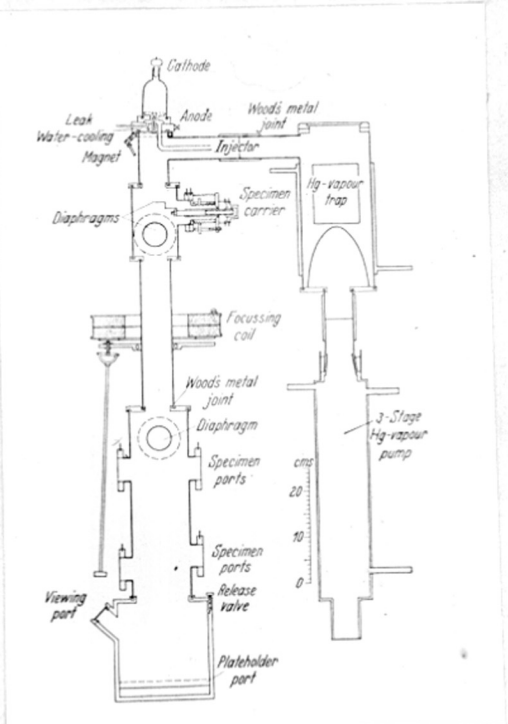

Cathode
Anode
Woods metal joint
Leak
Water-cooling
Magnet
Injector
Hg-vapour trap
Specimen carrier
Diaphragms
Focussing coil
Woods metal joint
Diaphragm
3-Stage Hg-vapour pump
Specimen ports
cms
20
10
0
Specimen ports
Viewing port
Release valve
Plateholder port

figure 2

diffraction photographs from both transmission and so-called reflection specimens has been well described by these and other workers [26,27] and does not require repetition here.

The essential need of a precision electron camera, such as the Finch type, is a beam of electrons of constant velocity, a "monochromatic" beam. This entails the use of a very constant high potential to accelerate the electrons and an absence of stray varying electrostatic or magnetic fields in the body of the camera. The whole camera with the exception of the discharge tube was constructed of drawn brass tubing with soldered permanent joints, the whole being at earth potential. There was thus no likelihood of electrostatic fields being present. The absence of any ferromagnetic substance in the construction of the camera and the specimen holders minimised the risk of stray magnetic fields being present. If, however, iron or steel specimens were examined it was found necessary to demagnetise them immediately before examination.

The high tension unit used to supply the necessary negative voltage of the order of fifty kilovolts was the same as that described by Finch and Wilman [26]. It was designed to give a very constant current of approximately one hundred kilovolts with respect to earth. This arrangement was used in the following way to give a constant accelerating potential to the electron beam. A constant electrical resistance was

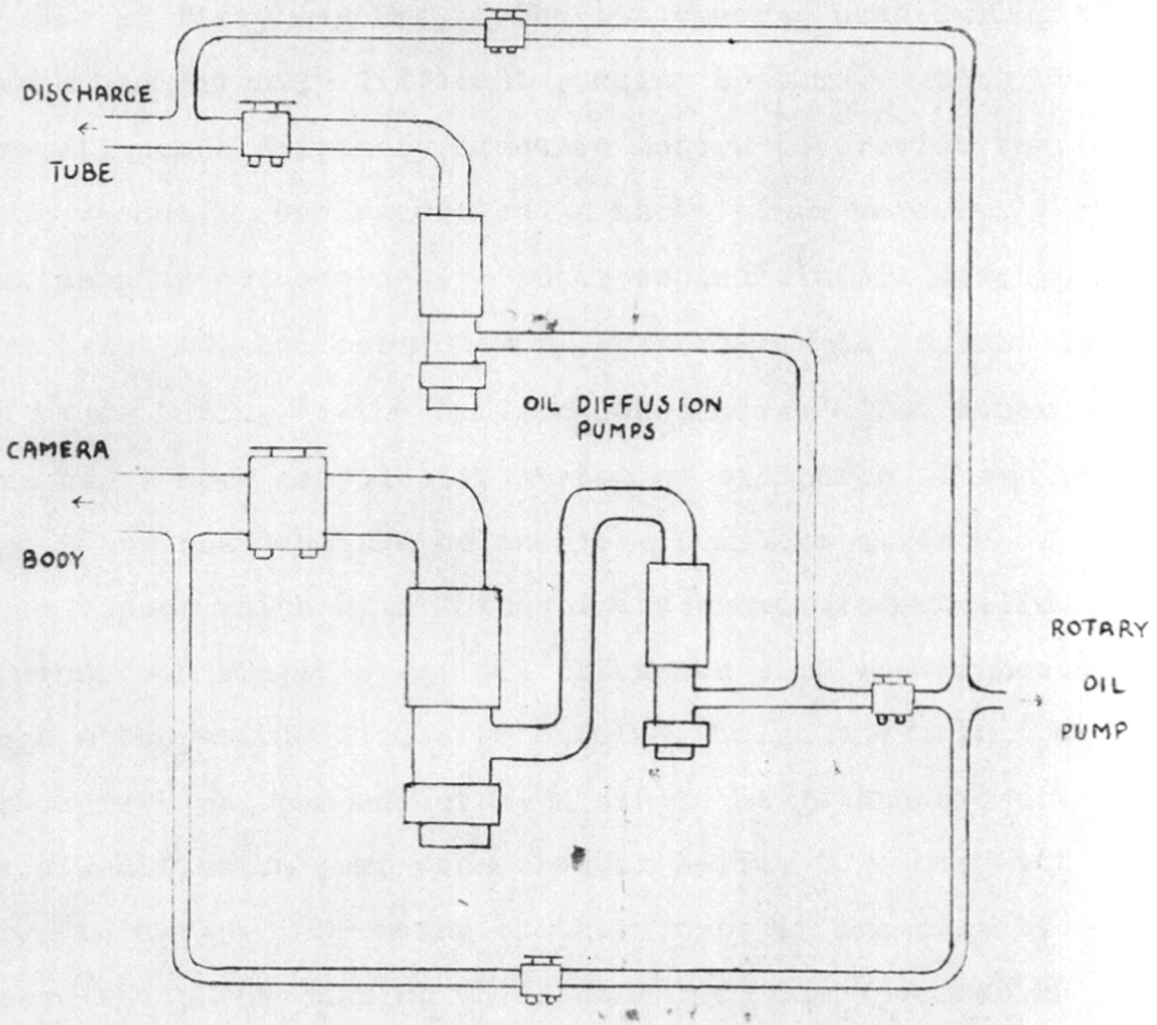
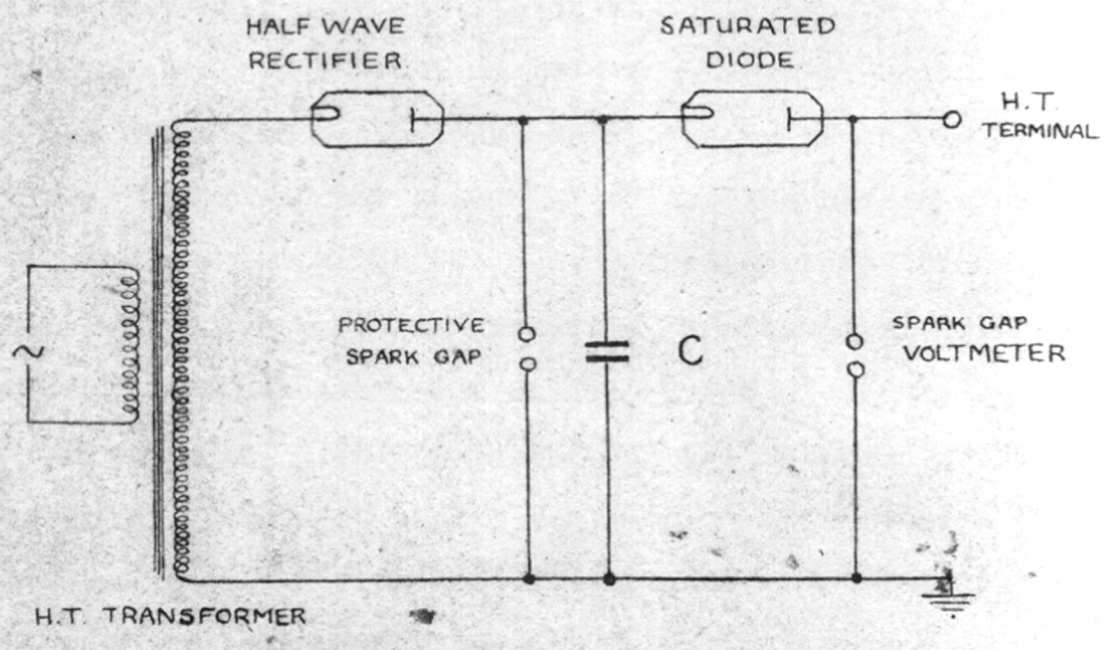

DISCHARGE
TUBE
OIL DIFFUSION PUMPS
CAMERA
BODY
ROTARY OIL PUMP

figure 3

created across the discharge tube of the camera by means of a regulated leak so that as much air was let into the discharge tube as was pumped out by the vacuum pumps in the same time. This kept a constant pressure in the discharge tube and thus created a constant electrical resistance of the order of fifty megohms. The two cameras used during the research had slightly different pumping systems. Both had rotary oil pumps driven by electric motors to provide the backing vacuum. One camera had a three stage mercury diffusion pump connected by a water cooled tinfoil mercury vapour trap and then connected by a short length of wide bore, drawn brass tubing to the diffraction camera. The other camera had a more complicated system of oil pumps, shown in Figure 3 and was designed to ensure a complete absence of mercury vapour which might otherwise contaminate metallic specimens. A single stage oil diffusion pump was connected through a tap to the discharge chamber whilst the main body of the camera was pumped out by a single stage and a double stage oil diffusion pump connected in series together with a large bore tap. By means of these taps it was possible to leave the pumps running whilst changing the specimen. This proved a great time saver and more than doubled the rate at which specimens could be examined.

Since so much of the precision of the camera depends on the constancy of the wavelength associated with the electron beam, the factors influencing this were investigated.



H.T. CIRCUIT

figure 4.

The high tension circuit is shown in Figure 4. A transformer supplied from the 230 volt A.C. mains and delivering at the secondary, a maximum of 120 kilovolts was connected to a half wave rectifying valve V_1, and a smoothing condenser of 0.045 microfarads capacity. This latter was protected against surges in the mains supply by a spillover spark gap set at 110 kilovolts and having a high water resistance in the earth lead. The smoothed current was then fed into a suitable diode, V_2, run under saturated conditions. This valve was a Philips K.125 diode having a water cooled anode. It can be seen from the characteristic of this valve, Figure 5, that a very steady anode current will be furnished whatever load is applied. The filament current of this valve could be varied by a resistance in the primary circuit of the filament transformer, and thus by altering the emission from the filament, different anode currents could be used. It was usual to keep the current low whilst making a preliminary survey of the specimen in order to conserve the polish on the cathode, which soon deteriorated if a high current was employed. When a photograph was taken the highest current was used, as this increased the intensity of the electron image and hence reduced the time of exposure. An approximate analysis of the high tension circuit was made in order to ascertain the regulation achieved. It was assumed to start with that the

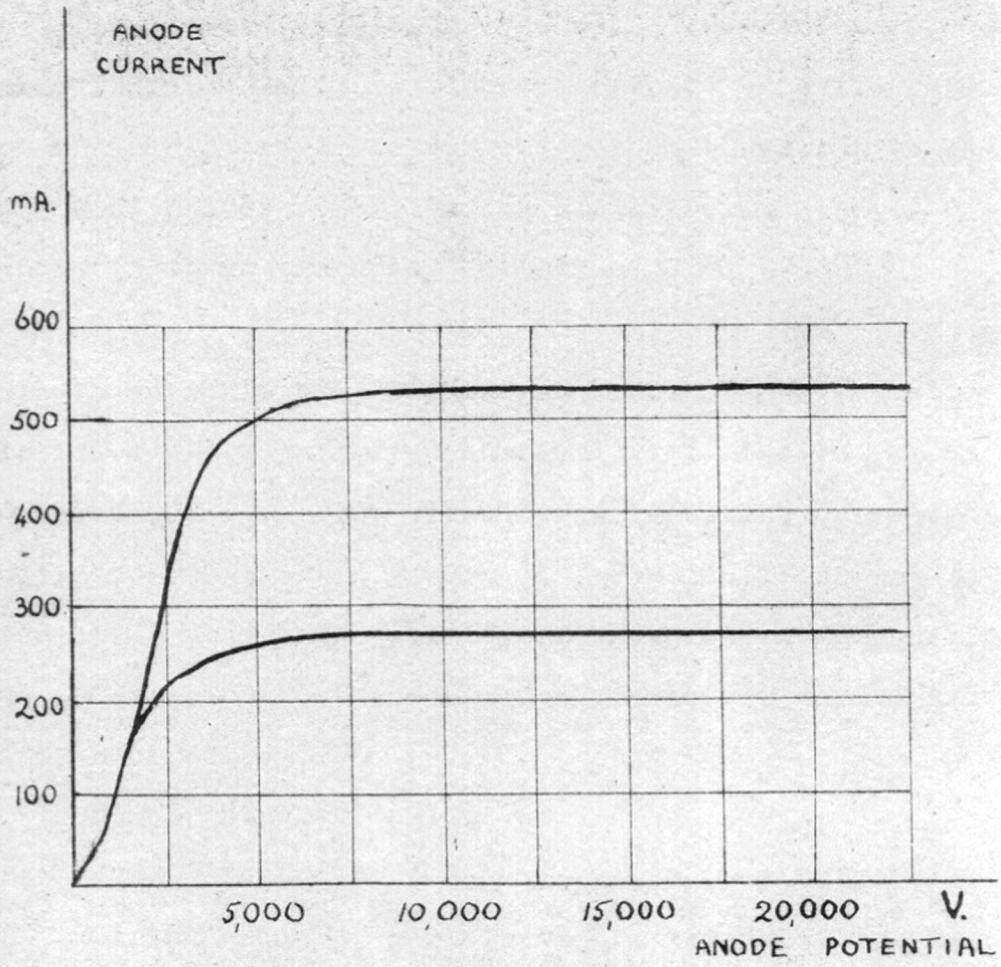

ANODE
CURRENT
mA.
600
500
400
300
200
100
5,000
10,000
15,000
20,000
V.
ANODE POTENTIAL

figure 5.

output of the transformer was sinusoidal though actually owing to the variation in the impedance offered by the rectifying valve this cannot be so. The rectifying valve used, Philips K.220, was chosen so that at no time during the cycle did the anode current reach saturation value; the three halves power law could therefore be applied and hence, if i_a is the anode current

$$i_a = kV_a^{3/2}$$

This is approximately a straight line so that the diode rectifier was regarded as an ideal rectifier in series with a resistance R_o. The circuit and resulting currents and voltages are shown in Figure 7. The rectifier was conducting from time t_1 to t_2 as shown in the graph Figure 8. For the remainder of the time the rectifier was regarded as an open circuit.

Now by Kirchoff's laws:-

during conduction:- $i_b = i_c + a$ ..... (i)

during blocking period:- $i_c + a = 0$ ..... (ii)

The potential across condenser was equal to supply voltage e_s less the drop through the resistance R.

Hence during conduction:-

$$i_c = \frac{d}{dt}(e) = \frac{d}{dt} e_s - i_b R_o$$

Now the value of $i_b R_o$ was small compared with e_s so that the current flowing through the condenser could be regarded as due to the supply voltage.

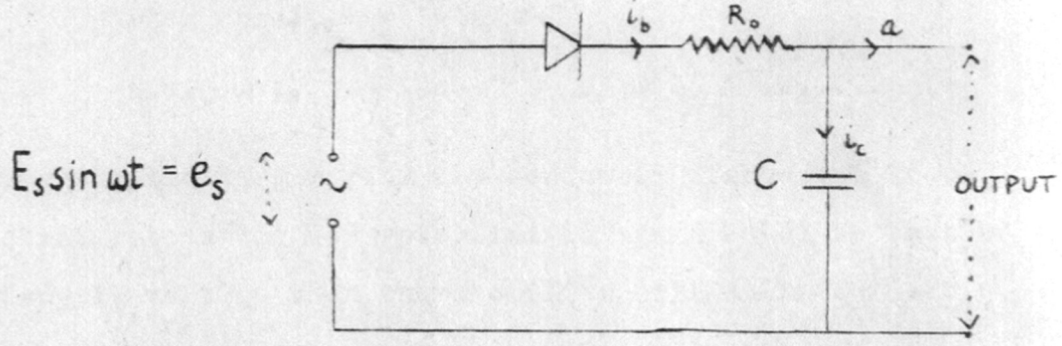


figure 7.

i.e. $i_c = CE_s \cos \omega t$

then from (1) $i_b = CE \cos \omega t + a$ ..... (iv)

At the end ofmthe period of conduction $t = t_2$, $i_b = 0$

Then substituting in (iv)

$$0 = CE \cos \omega t_2 + a$$

$$\text{when } \cos \omega t_2 = - a/\omega CE_s$$

$$\text{i.e. } \omega t_2 = \cos^{-1} - a/\omega CE_s \quad \ldots\ldots\ldots \quad (v)$$

During the blocking period the condenser discharges at a constant rate until its potential is again equal to that of the supply voltage when the rectifier will again conduct, i.e. at point $(2\pi + \omega t_1)$ in the cycle.

The supply voltage at $(2\pi + \omega t_1)$ is $E_s \sin(\omega t_1 + 2\pi)$

The potential of the condenser is equal to $E_s \sin \omega t_2$, the maximum value to which it rises, less the drop during the period ωt_2 to $2\pi + \omega t_1$. This latter is equal to

$$a/\omega \; C \left(2\pi + \omega t_1 - \omega t_2\right)$$

Hence $E_s \sin (2\pi + \omega t_1) = E_s \sin \omega t_2 - a/\omega \; C \left(2\pi + \omega t_1 - \omega t_2\right)$

i.e. $E_s \sin \omega t_1 + a/ \; C \; t_1 = E_s \sin \omega t_2 - a/\omega C (2\pi - \omega t_2)$

Substituting the value of ωt_2 from (v)

$$E_s \sin \omega t_1 + \frac{a}{\omega C} \; t_1 = E_s \sin\left(\cos^{-1} - a/\omega CE_s\right) + \frac{a}{\omega C} \; 2\pi - \cos^{-1} a/\omega \; CE_s$$

The right hand side of the equation is therefore a constant K, and writing $\omega t_1 = x$ the equation reduces to:-

$$E_s \sin x + a/\omega C \; x = K \quad \ldots\ldots\ldots\ldots\ldots \quad (vi)$$

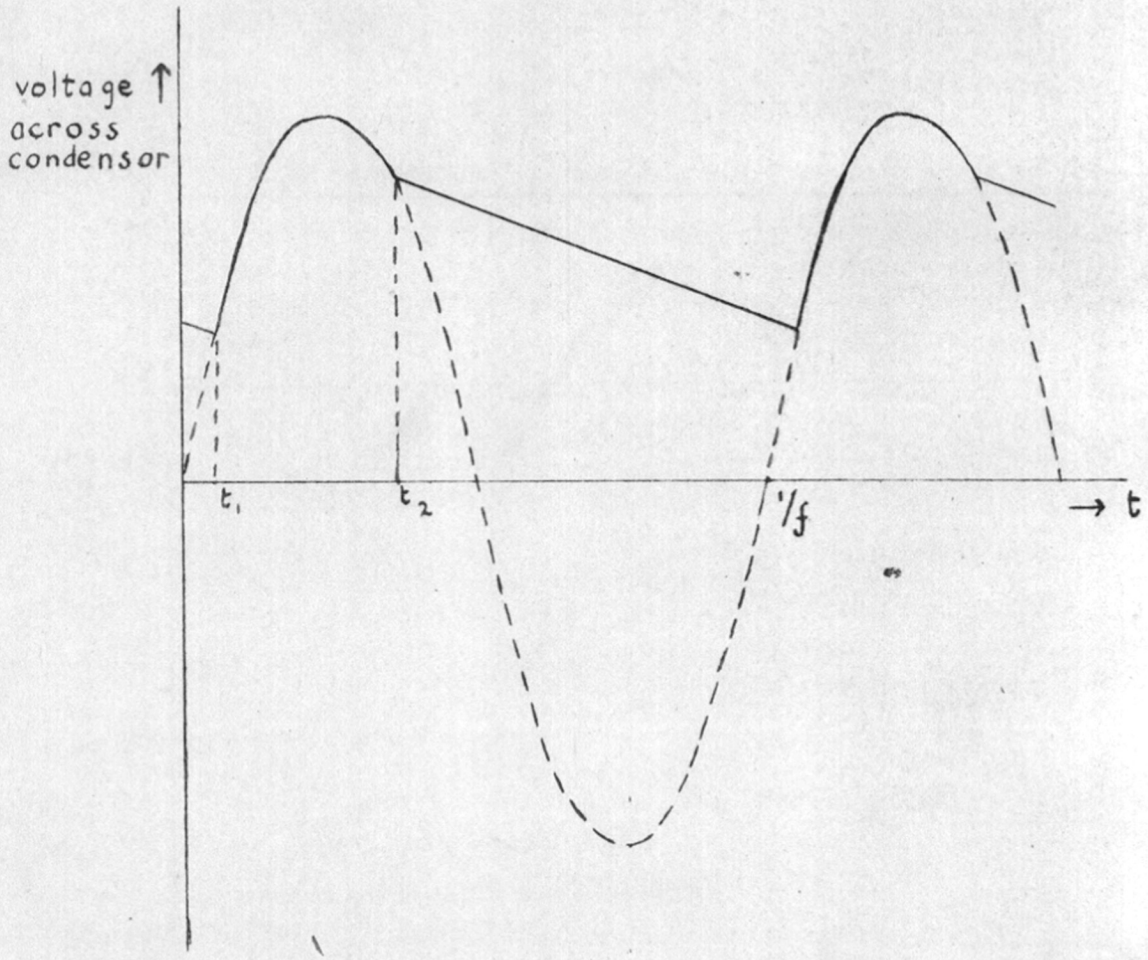


figure 8.

TOTAL VOLTAGE AND CURRENT VARIATIONS IN SATURATED DIODE

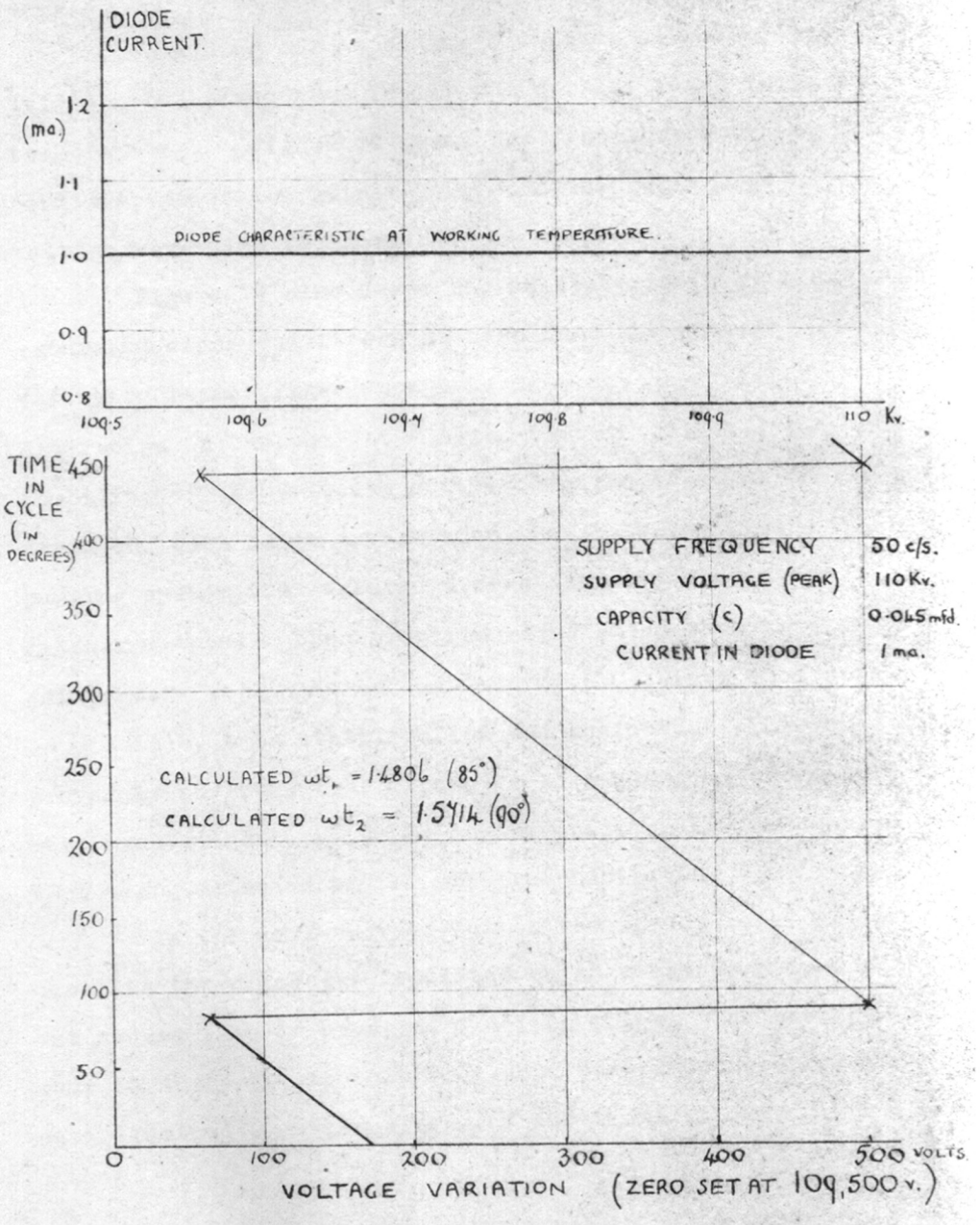


figure 10.

~~Figure 9 shows $E_g \sin x$ and $a/\omega C$ x plotted against values of x.~~

By adding corresponding ordinates as shown, equation (vi) can be solved graphically and a value found for x and therefore t_1. Figure 10 gives the final graph of condenser potential gainst time, and the full range of the voltage variation is shown.

Figure 10 also shows the characteristic of the saturated diode and it can be seen that the voltage variation is not great enough to make any appreciable alteration in the current flowing through this valve. The stability of the velocity of the electron beam was therefore dependent to a large extent upon the stability of the pumping system that ensured a constant pressure in the discharge tube. When properly adjusted so that the vacuum joints were well made and as few movable joints incorporated as possible, this stabilisation was achieved. This was proved by the fact that exposures of as long as one minute were made without any shift in the position of the central spot being detected on the photographic plate.

In the work carried out on the structure of alloy deposits the alloy was deposited on to metal specimens about one square inch in area and 1/4 inch thick. No attempt was made to strip the deposit from this base and the specimens were examined by using a beam of electrons at grazing

incidence, the so-called "reflection" type of specimen. The surface of the basis metal was smoothed by rubbing with fine emery paper (000 grade) until a bright flat surface was obtained. It was found essential to use these flat surfaces since the angle of incidence of the electron beam was so low, less than five degrees, that the innermost diffraction rings would be cut off by the shadow of the irregularities of the surface. By making these surfaces flat the amount of diffuse, inelastic, scatter of the electrons was much reduced and a greater contrast obtained on the plates.

No attempt was made to produce a polish layer on the surface. The smoothing was carried out by fixing the emery paper over a piece of plate glass and rubbing the specimen on this. The specimen was then cleaned and degreased by washing in a sodium cyanide solution which had a very slight etching action. The difference between specimens so prepared and ones prepared by the commercial cleaning method of acid etching lay only in the general contrast of the electron diffraction patterns. In no case was any difference between the lattice constants of deposits plated on either flat or rough specimens observed. The results of these electron diffraction experiments are given in Tables V - XV and typical patterns are shown in Figures 11 - 25.

ELECTRON DIFFRACTION MEASUREMENTS.

In all the following tables the following abbreviations are used throughout.

R radius of ring, measured on the plate.

d_{hkl} Crystal plane spacing calculated from R.

I Relative intensities estimated from the photographic plate as:-

VVW	Very very weak.
VW	Very weak.
MW	Medium weak.
W	Weak.
MS	Medium strong.
S	Strong.
VS	Very strong.
VVS	Very very strong.

a_o lattice constant, the calculated length of the unit cell.

TABLE V.

ELECTRON DIFFRACTION MEASUREMENTS

OF α -BRASS.

Plate No. A.5409

R mm.	d_{hkl} A	I	f.c.c. index.	a_o A
11.44	2.06	S	111	3.57
13.27	1.78	W	200	3.56
18.76	1.26	VS	220	3.57
21.92	1.08	VVS	113	3.59
22.96	1.03	VVW	222	3.57
28.95	0.815	MW	133	3.54
29.90	0.790	W	240	3.53
32.53	0.725	VW	224	3.55

Average value of lattice constant a_o = 3.56 A.

TABLE VI.

ELECTRON DIFFRACTION MEASUREMENTS OF ELECTRODEPOSITED α - BRASS.

Plate No. A.5288.

R mm.	d_{hkl} A.	I	c.p.h. index.	f.c.c. index.	a_o A.
11.09	2.16	VW	100		
11.69	2.05	VVW	002	111	3.49
				200	
19.15	1.25	MW	110	220	3.54
			200		
22.41	1.06	MW	112	113	3.52
			004	222	
27.40	0.87	VVW		400	3.48
29.57	0.81	VVS	120	133	3.53
38.24	0.72	VVW		224	3.53

Average value of lattice constant a_o = 3.52 A.

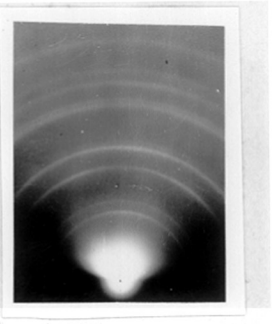


figure 11
α- brass
(cast)

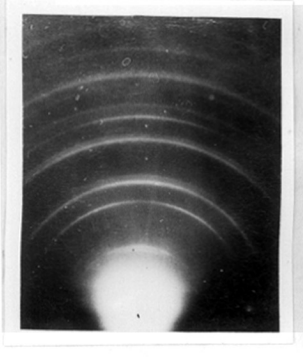


figure 13
α- brass
(e-deposit)

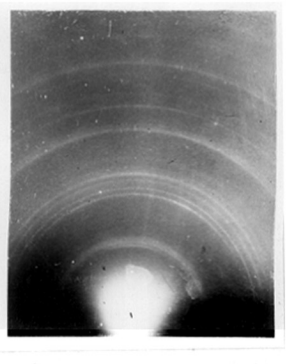


figure 14
α-brass + graphite

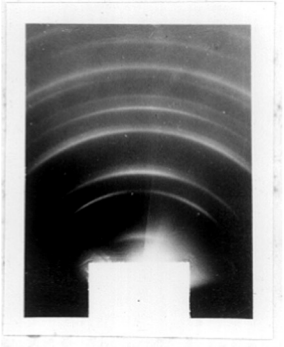


FIGURE 12a

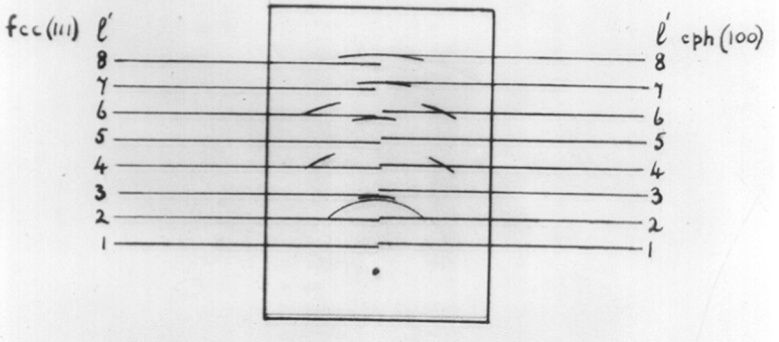


figure 12b.

1. Brass.

The majority of the specimens examined had a composition of approximately 70% copper and 30% zinc. In the cast metal this has been shown to be within the limits of the α-phase [28]. A specimen of cast brass similar in shape to the plated specimens and given similar surface treatment (e.g. smoothed with emery papers) was examined. Figure 11 shows the pattern obtained and Table V gives the measurements and the net plane spacings derived from the pattern, from which it can be seen that the structure was of the face-centred cubic type. Of the plated specimens Figures 12 - 14 show the patterns obtained from brass of composition about 30% zinc. Orientation was observed in some cases, the rings being arced, as indicated in Figure 12.

In many cases, although the measurements of the pattern obtained could be fitted to the face-centred cubic structure, certain extra rings and the absence or comparative faintness of the ring due to the (200) planes cast doubt on the correctness of this decision. This pattern is shown in Figure 13 and measurements are given in Table VI. The table shows that the pattern could equally well be attributed to a close-packed hexagonal structure of axial ratio 1.63 A. Again certain rings normally strong in the close-packed hexagonal structure were absent or only appeared faintly. Thus neither structure seemed to be the complete answer.

In order to get a better interpretation it was decided to obtain a more accurate determination of the lattice constants of the substance giving rise to this pattern. This was carried out by dusting the surface of the specimen with fine graphite dust (particle size less than 4 μ) with the idea of obtaining a composite pattern due both to graphite and to the unknown substance. The specimen was tapped to remove the surplus graphite but when the specimen was examined by electron diffraction only a pattern due to graphite was obtained. Even the small amount left, though not visible, was too much to allow the electron beam to penetrate it. The specimen was then hung in the neck of the flask of a reflux distilling apparatus and petroleum ether distilled in the apparatus so that the specimen was washed by hot, pure petroleum ether. This was the method adopted for degreasing specimens and proved effective in this instance for removing the graphite from the specimen. By adjusting the time of washing it was found possible to obtain the required double pattern as shown in Figure 14. By adopting this method errors in the measurement of the voltage, i.e. the electron wave length, and in that of the camera length were eliminated, since the spacings of the crystal planes in the unknown substance could be calculated by interpolation from those of graphite, whose net plane spacings are known with great accuracy from X-ray data. The only measurements it was necessary to make were those of the ring radii on the

TABLE VII.

ELECTRON DIFFRACTION MEASUREMENTS OF COMPOSITE PATTERN OF GRAPHITE AND ELECTRODEPOSITED α -BRASS.

Plate No. A.5446

R mm.	d_{hkl}* graphite	$d_{hkl} \times R$ calc.	d_{hkl} α-brass calc.	c.p.h. index.	a_o A.
11.47			2.205	002	2.705
19.64			1.292	110	2.593
20.71	1.227	25.45			
20.95	1.150	24.31			
22.99			1.103	112	2.521
30.18			0.841	120	2.640

Average value of lattice constants of close-packed hexagonal structure :- $c/a = 1.63$; $a_o = 2.590$ A.

* d_{hkl} graphite obtained from X-ray data [20].

Table VIII.

ELECTRON DIFFRACTION MEASUREMENTS OF ELECTRODEPOSITED β - BRASS.

Plate No. J.961.

R mm	d_{hkl} A.	I	b.c.c. index	a_o A.
11.46	2.11	VVS	110	2.98
16.37	1.48	W	200	2.96
19.92	1.21	VS	112	2.96.
23.00	1.05	VW	220	2.96
25.74	0.940	MS	130	2.97
28.22	0.857	MS	222	2.97
30.41	0.795	S	123	2.97
34.58	0.702	VVW	114	2.98

Average value of lattice constant a_o = 2.97 A.

photographic plate. This was carried out by using a good travelling microscope reading to 0.01 mm. with the optical system reversed so that an image of the cross-wires was focussed on the photographic plate. This method enabled even very poor contrast plates to be measured.

The measurements of such a composite pattern are given in Table VII from which it was possible to calculate the lattice constants of the structure as $a_0 = 2.64 \pm 0.03$ A and $c/a = 1.63$. These constants do not correspond to any substance listed in Wyckoff [18] or in the Strukturbericht [19]. Some further explanation of this pattern had to be found. This is attempted later (see page 58).

The plating solution C gave quite a different deposit whose electron diffraction pattern (Figure 15) was entirely different from that of α-brass. An analysis of the deposit carried out on a larger specimen plated at the same current density showed that it contained 63% copper and 37% zinc. This composition, in the cast metal, lies within the β-phase with a body-centred cubic structure [29]. The pattern was so interpreted with the lattice constant of the body-centred cubic structure $a_0 = 2.97$ A. Table VIII gives the ring radii, the spacings calculated from these and the theoretical spacings based on the structure already mentioned.

Although most specimens were examined immediately after plating, occasionally one would be left for some hours

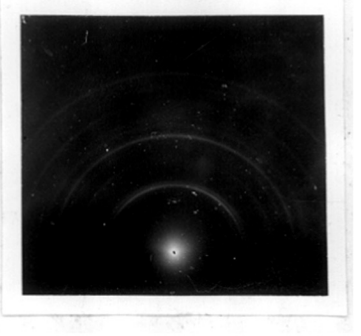


Figure 15

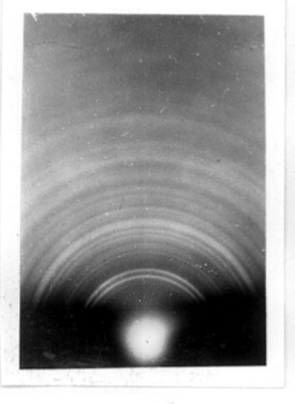


Figure 16

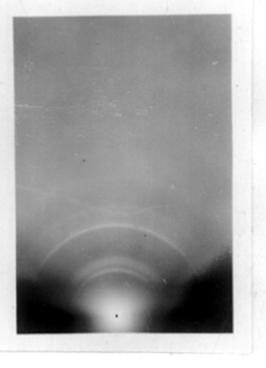


Figure 17

TABLE X.

ELECTRON DIFFRACTION MEASUREMENTS OF

AN OXIDISED BRASS SURFACE.

Plate No. A.5424.

R mm.	d_{hkl} A	I	c.p.h. index	calc. spacings ZnO, a_0 = 3.25A
7.55	3.25	VS	-	-
8.94	2.75	VW	100	2.78
9.15	2.68	VW	002	2.60
15.08	1.63	W	110	1.62

TABLE XI.

ELECTRON DIFFRACTION MEASUREMENTS OF

AN OXIDISED BRASS SURFACE.

Plate No. K.745.

R mm.	d_{hkl} A	I	c.p.h. index	calc. spacings ZnO, a_0 = 3.25A
8.51	2.79	VS	100	2.78
9.53	2.49	VVS	101	2.48
12.62	1.88	VW	102	1.91
14.68	1.62	VS	110	1.62
16.05	1.48	W	103	1.48
17.42	1.36	S	112	1.38
21.40	1.11	VVW	203	1.09

TABLE XII.

ELECTRON DIFFRACTION MEASUREMENTS OF ELECTRODEPOSITED BRASS HEATED IN EVACUATED TUBE.

Plate No. J.967

R mm.	d_{hkl} A	I	f.c.c. index	calc. spacings Cu_2O, a_o = 4.26A
10.15	2.45	VVS	111	2.46
11.80	2.11	S	200	2.13
16.81	1.48	VS	220	1.51
19.41	1.28	W	113	1.28
20.62	1.21	W	222	1.227
23.21	1.075	VW	400	1.065
25.38	0.98	W	331	0.977

TABLE XIII.

ELECTRON DIFFRACTION MEASUREMENTS OF ELECTRODEPOSITED BRASS HEATED IN ATMOSPHERE OF H_2S.

R mm.	d_{hkl} A	I	f.c.c. index	calc. spacings Cu_2S, a_o = 5.59A
6.08	3.89	S	110	3.95
7.41	3.20	VS	111	3.21
8.68	2.72	S	200	2.69
10.32	2.29	W	112	2.29
11.95	1.98	W	220	1.98
14.15	1.67	VW	113	1.68
18.35	1.29	W	331	1.28

exposed to the atmosphere and on examination in the electron diffraction camera such specimens gave rise to patterns shown in Figures 16 and 17. Tables IX and X give the ring radii measurements and calculated lattice plane spacings for two such patterns. As can be seen from the Tables these were identified as oxide films. Such films were of the same type as those previously found on cast brass surfaces [30].

Certain specimens were plated, examined by electron diffraction as above and afterwards treated in a special way. A further electron diffraction examination was then made. This sequence was carried out to find what surface films were detrimental to the adhesion of rubber to brass. The two treatments carried out were (i) dipping the plated specimen for a known time in an aqueous solution of sodium cyanide or solutions of certain acids and alkalis; (ii) heating the specimen in different atmospheres to about 400°C. Some were heated in vacuo, others in dry air and a few in dry hydrogen sulphide. The results of these many experiments are listed in Tables XI - XIII and typical electron diffraction patterns obtained during the experiments are shown in Figures 18 - 23.

The pattern shown in Figure 18 was very frequently obtained from specimens examined immediately after plating and washing in distilled water. Figure 19 shows that the pattern was considerably simplified after the specimen had been dipped in sodium cyanide solution and then washed.

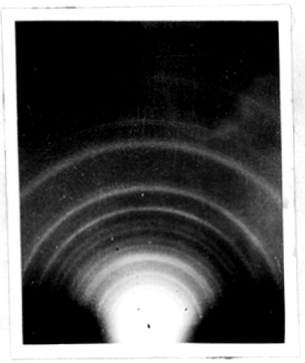


figure 18

figure 19
specimen as fig. 18
washed in N-NaCN soln.

It was discovered on measurement that Figure 18 was an identical pattern to that shown in Figure 13, identified as the pattern due to α-brass deposits. The extra rings present on Figure 18 were then attributed to a substance present on the brass surface and insoluble in water but soluble in sodium cyanide solution. When acids and alkalis were used it was found that strong solutions were necessary to remove the substance and this removal was effected mainly by their etching action on the brass, since after treatment films of the corresponding salt of zinc or copper were found present. The identification of this substance proved difficult as it had not been previously studied. It was discovered that this substance was most often co-deposited on specimens plated from "older" brass solutions, i.e. solutions that had already been in use for some time, and it was considered likely that the film consisted of included ions or colloidal particles which became present in the plating bath as a result of use. Research was carried out to isolate colloidal particles present in the plating solution and substances were found which gave similar electron diffraction patterns. Chemical analysis showed that these colloids were complex sodium zinc ferrocyanides [31].

Heating the specimen in air produced a film whose electron diffraction pattern is shown in Figure 20. This pattern, Table XI, was identified as a modified form of zinc

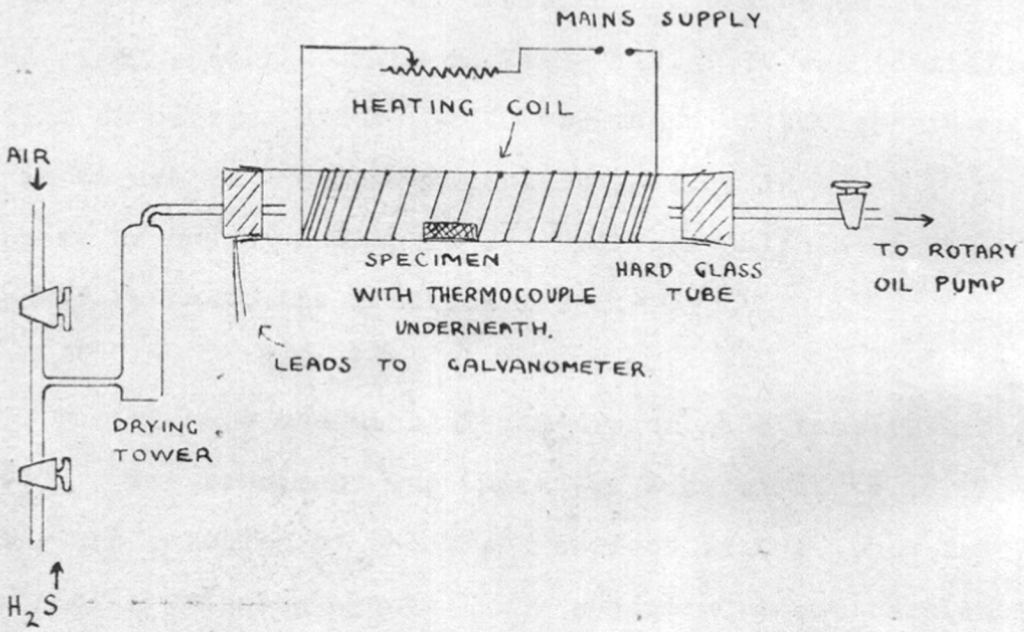

MAINS SUPPLY
HEATING COIL
AIR
SPECIMEN
WITH THERMOCOUPLE
UNDERNEATH.
HARD GLASS
TUBE
TO ROTARY
OIL PUMP
LEADS TO GALVANOMETER
DRYING
TOWER
H_2S

figure 22.

oxide previously identified by Lamchen [30]. When a Hyvac rotary oil pump was used to evacuate the tube in which the specimen was heated a different pattern was obtained. This is shown in Figure 21 and the measurements and calculated crystal plane spacings given in Table XII. It was identified as a film of cuprous oxide [32]. By means of the apparatus shown in Figure 22 a specimen could be heated in an atmosphere of hydrogen sulphide. Hydrogen sulphide is decomposed by heat, the reaction being:-

$$H_2S \rightleftharpoons H_2 + S$$

The mixture contains 5 % hydrogen at a temperature of 400°C. The treatment was therefore equivalent to studying the reaction of the brass surface with sulphur in the presence of a reducing agent. The specimen became tarnished and subsequent electron diffraction examination revealed the presence of a sulphide layer - Cu_2S. Figure 23 shows the pattern obtained and Table XIII the measurements and calculations. Identification was helped by electron diffraction photographs of copper sulphide already obtained in this laboratory and from the results of [33].

The heating experiments carried out on the brass deposits did not show any marked difference in results from those obtained by other workers on cast brass surfaces. it would be expected that the greater volatility of zinc would render the surface film more rich in copper when heated in

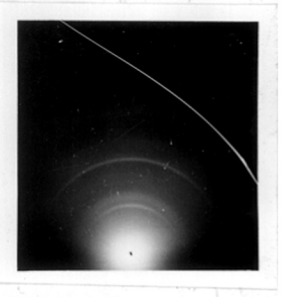


figure 20

figure 21

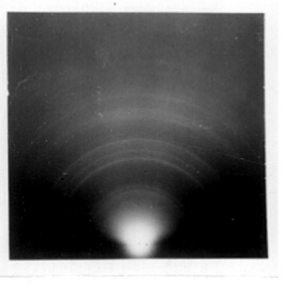


figure 23

vacuo, and hence lead to the presence of copper oxide films. The more stable zinc oxide film, however, could be expected to predominate in the surface film on heating the brass in air. Similarly, copper sulphide, being more stable than the corresponding zinc compound, would be expected on brass surfaces heated in a hydrogen sulphide atmosphere.

In one or two cases, the oxidised specimen was etched lightly in acid, washed in distilled water and dried. It was then re-examined by electron diffraction. The light etching removed the surface film and exposed the brass surface. The examination showed that a true face-centred cubic structure was present, not the modified form present before the heating. On further etching the brass deposit the same result was obtained showing the the change occurred throughout the deposited brass.

2. Silver-Cadmium Alloy.

In these experiments alloys containing not more than 20% cadmium were investigated. This limit is within the α-phase for the cast alloy which had been shown to have a face-centred cubic structure [34]. The solution used did not give bright deposits and after deposition on bright steel specimens a white matt surface was obtained. The diffraction pattern obtained from these specimens is shown in Figure 24

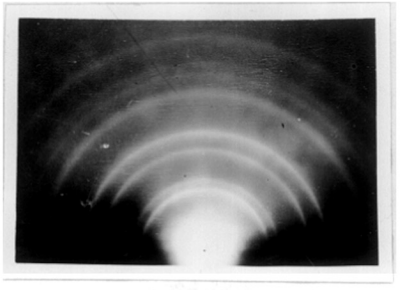


figure 24
(e deposited Ag-Cd.)

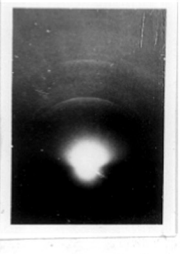


figure 25
(e-deposited Ag-Cd oriented)

and the ring radii measurements and calculated spacings are given in Table XIV. These results show that the electrodeposited alloy was structurally the same as the cast metal, unlike the brass sdeposits the majority of the specimens showed a complete face-centred cubic pattern. Figure 25 however shows a different type of pattern obtained in a few cases. This indicates orientation of the deposit ~~and the measurements, Table XV,~~ and shows ~~the~~ resemblance to the brass structures. As can be seen clearly from the diffraction pattern (Figure 24) no traces of any other structure can be deduced.

OTHER EXPERIMENTAL METHODS.

In order to estimate the value of previous experiments on electrodeposits, a short review of the experimental methods used by other investigators is given.

A. Micrographic.

The most obvious examination of electrodeposits that can be carried out is that of inspecting them with the eye. For a long while this was the only test employed in the production of plated articles. Brass plate, in particular, was inspected for colour and freedom from stains. Solutions were sought that gave bright, even deposits so that subsequent finishing for decorative purposes was reduced to a minimum. This criterion of electrodeposits is important

in commercial practice and so this simple inspection is still used. However, until something more was known about the mechanism of the processes involved in deposition, all attempts at improving the efficiency of the process and the appearance of the plate was entirely empirical. For that reason chemical analysis of the deposit and a rigorous determination of its physical properties were introduced.

With the advent of good metallurgical microscopes and the devlopment of the technique of taking photographs of the enlarged image, the beginnings of a most important method of examination were made by Hughes [36] and others. By careful preparation, including polishing and etching, it is possible to obtain photomicrographs, both of a normal view of the deposit and of its cross section. Such photographs show the grain size and the shape of the grain for all but the finest deposits. From the cross section micrographs, it is possible to determine the way in which the structure of the deposit is built upon the basis metal. This method of examination has been a very powerful means of elucidating some of the problems of electrodeposition. Blum and Rawdon [6] and Graham [7] used such methods in showing that, in certain circumstances, the structure of the basis metal was continued throughout the deposit. The former based a successful theory of deposition upon their results which was later upheld by other experimenters [39]. McNaughton and Hothersall [9] gave

a review of the work of previous investigators on the microstructure of electrodeposits. This work, they said, did not generally incorporate control of enough of the variables and so lost much of its value; for instance Hughes [36] did not control the pH and the presence of impurities was seldom recorded. Already in 1913 Kohlschutter and Schact [41] had shown that the presence of even very small amounts of colloidal impurity in silver plating baths resulted in considerable differences in the grain size of the deposit. McNaughton and Hothersall considered that care was necessary in interpreting the results of photomicrographs. Later the interpretation of such micrographs was made more difficult by the discovery by Finch and Williams [11] of a hitherto unexpected phenomenon. X-ray and electron diffraction had given an independent method of determining the grain size, and in the experiments carried out by Finch and Williams a complete disagreement between the results obtained by electron diffraction and those from photomicrographs was found. Since the former are dependent on more fundamental theory, it appears certain that caution is necessary in interpreting photomicrographs and results should be checked by other means.

The fundamental problem in microscopy is to increase

the useful magnification as much as possible. This entails an increase in the receiving power of the instrument. The minimum distance of separation of two points, h, is given by the equation :-

$$h = \frac{.61\lambda}{n \sin U}$$

where n sin U is the numerical aperture of the objective lens and λ is the wavelength of the illuminating radiation. Such great advances have been made in the design of optical microscopes that the limit of the resolving power has almost been reached. With the verification of De Broglie's wave mechanics a much higher frequency source became available. A beam of high speed electrons (50,000 electron-volts energy) has an associated wavelength of less than 0.1 A. and it is possible to construct electrostatic and electromagnetic lenses to focus such a beam. Many designs of electron microscopes have been suggested and it has already become a standard instrument. Since the absorption of electrons by atomic structures is so very high, a special technique has had to be devised in order to prepare specimens that are not opaque to the beam.

B. X-ray Diffraction Methods.

The application of X-ray diffraction to the study of metals and alloys soon followed the discovery of diffraction effects in the early twentieth century by Friedrich and Knipping [42]. Neuberger [43] published in 1928 a catalogue of the results of investigations on the structure of most alloys that had been determined by X-ray diffraction. Stout and Stillwell [44] used this method in investigating the structure of silver-cadmium alloys. The experiments of Kersten [45] in his investigation of the effects of colloids on the structure of electrodeposited copper illustrate the accuracy obtained by this method even with quite simple apparatus. The advantages of the method are :-

(i) it is a non-destructive test.

(ii) the structure can be determined with great accuracy.

(iii) the method gives a fuller analysis of the structure than micrographs, for both grain size and orientation of the crystallites can be found.

The disadvantages of the method are the need for high voltage equipment and the long time that the exposure of a plate takes. For the purpose of investigating the structure of thin films that are backed by a more massive substrate, it also suffers from the disadvantage of the great penetration of X-rays which means that the substrate will give rise to the bulk of the diffraction.

Of recent years, X-ray diffraction has been used extensively to obtain the phase diagrams of alloy systems and, in particular, the work of Bradley, Sykes and Lipson [46] at Cambridge has utilised X-ray methods almost exclusively in very exhaustive analyses of the constitution of ferrous and non-ferrous alloys.

C. Miscellaneous Physical Measurements.

Several other measurements can be made on electrodeposits, among them being thickness of deposit and hardness.

The thickness of the deposit is of great importance in assessing the efficiency of the plating process and also the evenness of the deposit. The most direct method of measuring the thickness is that whereby the plated specimen is stripped, the weight of plate determined gravimetrically and from a calculation of the area of the specimen, the average thickness determined. It is of much more use however, to determine the local thickness since with anything but a plane electrode the current density will vary across the surface. A test has been devised whereby the time taken for a standard stream of solution to corrode through the deposit is found and from this and charts of thickness of deposit against time to corrode, the thickness can be determined [47]. The test is not extremely accurate,

but it has important uses in verifying calculations on the throwing power of different solutions.

Many workers have verified that the surface hardness of metals is correlated with their structure [48] and this applies still to electrodeposited metals [9]. Two methods of determining the hardness exist; one, the scratch test, is not very suitable as it does not yield results which are independent of the instrument employed, and this latter, in consequence, needs careful calibration. The other, the indentation method, has much more widespread use, and one particular form, the Brinell test, is extensively used in industry. In this method a small, hard steel ball is pressed on to the surface under test by means of a large static load and the radius of the dent measured.

However, in measuring the hardness of thin coatings on massive substrates, the influence of the latter must be known or eliminated. Moore [49] has shown that the Brinell method gives results that are independent of the hardness of the basis metal, if the thickness of the coating is seven times the maximum depth of indentation. McNaughton and Hothersall [9] used this method, employing a ball 1 mm. in diameter loaded with a 10 kg. weight, when a depth of indentation of 0.0319 mm. (Brinell number

100) could be expected. By depositing about 0.01 inch thickness of metal, results independent of the hardness of the basis metal were obtained.

They showed that the hardness could be directly correlated to the structure of the electrodeposit as revealed by cross sectional photomicrographs.

DISCUSSION OF RESULTS.

In considering the results obtained from the experiments described in Part A, it is seen that the cyanide plating solution is not simple and has many interdependent variable factors affecting its efficiency. In running a plating solution for commercial use, the economics of the plant involved are of primary consideration and so it is necessary to ensure that the maximum control of conditions is obtained. The experiments on the pH range of a typical commercial plating bath (Table 1) show the difficulties involved. It is not possible when dealing with gallons of solution to achieve the perfection possible with laboratory experiments.

In laboratory practice, the subject of the complex cyanides is difficult and an enormous literature has arisen dealing with the various aspects of the subject [50]. In commercial plating equipment, large quantities of solution are exposed to the atmosphere and many subsidiary reactions take place, in addition to the main reactions mentioned on page 4. In particular, carbon dioxide is readily absorbed by cyanide solutions.

$$NaCN + H_2O \rightleftharpoons NaOH + HCN$$

$$NaOH + CO_2 \rightleftharpoons NaHCO_3$$

The cyanide is thus driven off and the carbonates are included in the solution. These will act as buffering agents in that the ions present will take up equilibrium as below :-

$$2\,H^+ + CO_3'' \rightleftharpoons H_2CO_3$$

$$2\,Na^+ + CO_3'' \rightleftharpoons Na_2CO_3$$

$$\frac{[H^+]^2\,[CO_3'']}{[H_2CO_3]} = K_1$$

$$\frac{[Na^+]^2\,[CO_3'']}{[Na_2CO_3]} = K_2$$

with the usual notation, $[H^+]$ representing the molar concentration of the ion, and K_1 and K_2 the equilibrium or dissociation constants. K_1 is very small compared with K_2 so that any variation in the hydrogen ion concentration of the solution will have little nett effect on the pH. Such reactions would amply account for the buffering experienced with solution A (page 14).

The addition of sodium cyanide to a plating solution in equilibrium demonstrates the difficulties of using a theoretical approach to the analysis of plating bath reactions.

The dissociation of a complex cyanide can be described quantitatively in terms of the equilibrium constant K_6, given by

$$K_6 = \frac{[\,Cu(CN)_3^{''}\,]}{[Cu^{++}][CN^{'}]^3}$$

The influence of the cyanide ion concentration can thus be seen to be very great and the metal ion concentration $[Cu^{++}]$ very dependent upon it. A further effect is mentioned by Thompson [50]; an increase in the cyanide concentration can lead to a rise in the co-ordination number of the metal ion e.g. a change of $Cu(CN)_2^{'} \rightarrow Cu(CN)_3^{''}$, $Cu(CN)_3^{''} \rightarrow Cu(CN)_4^{'''}$. This change results in a decrease in the corresponding ion mobility and solubility so that the cathode efficiency is decreased. Thus, by adding a quantity of sodium cyanide to the solution, the immediate result of which is to increase the sodium and cyanide ion concentrations, a complete alteration in the solution equilibrium will occur.

The carbonate ion concentration is given by the relation

$$K_2 = \frac{[Na^+]^2 [CO_3^{"}]}{[Na_2CO_3]}$$

where K_2 is the dissociation constant for sodium carbonate. The equilibrium expression involves the square of the sodium ion concentration and hence the dissociation of carbonate is very dependent upon the sodium ion concentration. An addition of sodium cyanide will therefore markedly alter the carbonate ion concentration.

Further, zinc in solutions of moderately high pH readily forms zincate ions $ZnO_2^{"}$ [51]

$$Zn(CN)_4^{"} + 4OH' \rightleftharpoons ZnO_2^{"} + 4CN' + 2H_2O$$

Thompson [50] mentions that where such ions are formed deposition may occur from them.

$$ZnO_2^{"} + 2H_2O + 2\theta = Zn + 4OH'$$

Zincate ions are present according to the equilibrium :-

$$Na_2ZnO_2 \rightleftharpoons 2Na^+ + ZnO_2^{"}$$

$$K_4 = \frac{[Na^+]^2 [ZnO_2^{"}]}{[Na_2ZnO_2]}$$

so that the concentration of sodium ions present will appreciably affect the deposition of zinc, causing a change

from deposition from cyanide to deposition from zincate ions.

The presence of impurities in the plating solution cannot be ignored and these will give rise to further alterations in the equilibrium. In particular where steel and iron objects are brass plated for subsequent rubber adhesion the drag in of iron salts from pre-plating cleansing processes is considerable. The effect of ferrous ions in the solution is to cause a drop in the zinc ion concentrations. Robins [31] has shown that insoluble complex ferrocyanides are formed, the chief one being zinc hexamine zinc ferrocyanide which is extremely insoluble and hence rapidly diminishes the zinc cyanide ion concentration.

Two other effects of this impurity were noticed by the same worker; the analysis of the solution for uncombined cyanide was very unreliable when much of this ferrocyanide was present and secondly, because the compound formed a finely dispersed colloidal precipitate which was negatively charged, it existed in higher concentration around the anode causing a reduction in pH and therefore a lowering of the anode efficiency.

For a quantitative estimation of the effects of changes in the ion concentrations it is necessary to know

the dissociation and equilibrium constants at the working temperature. The measurement of these constants has been attempted by several experimenters using different methods and some agreement has been reached between them. Britton and Dodd [52] published some comprehensive figures and outlined the difficulties experienced in measuring such quantities. It is necessary to use dilute solutions to evaluate the constants and even within that range of concentrations Britton and Dodd found that the dissociation constant for potassium zinc cyanide was very dependent on potassium cyanide ion concentration as shown in Table XVI.

Table XVI.

$$2KCN + Zn(CN)_2 \rightleftharpoons K_2Zn(CN)_4$$

$[K_2Zn(CN)_4]$ x 10^{-3}	$[KCN]$ x 10^{-3}	K x 10^{-2}
9.09	3.74	2.47
2.91	36.17	37.0

Since commercial plating solutions have concentrations of 1-2 gr.mols/litre the use of the values of the dissociation constants quoted above would lead to incorrect conclusions.

The effect of temperature changes on the equilibrium can be considered in terms of the temperature

coefficients of the various dissociation constants. Since these coefficients will be different and may even be of opposite sign, temperature changes will profoundly affect the equilibrium. In addition the general effect of temperature rise in causing increased diffusion and high ionic mobility must be considered. The conflicting results mentioned by various experimenters can thus be reconclied. In any particular case, the equilibrium may be such as to be insensitive to changes in the dissociation constants as compared with the increased diffusion whereas another solution may be in such equilibrium that an alteration in one of the dissociation constants may completely alter the properties of the solution, irrespective of the increased mobility of the ions.

The changes outlined above account for the results of conductivity measurements obtained with solution B. The rise in conductivity expected from the increase in the free cyanide is offset by the other changes.

The picture built up of complex cyanide baths shows that there can be no quick remedy for faults nor can a positive statement of the type "an addition of X will increase the property Y", be made unless it is stated precisely and fully the conditions under which the solution is to have the additions of X. This explains the often

completely contradictory statements made by different workers about similar alterations to plating solutions.

The measurements of the cathode potential were difficult to explain, the potential measurement was definite and accurate. A balance of the galvanometer currents was rapidly made by a simple rheostat movement and the calibration of the potentiometer was steady. There was no doubt that the potential between the jet and the specimen was measured accurately to one millivolt. It was certain, therefore, that variations of potential must have existed across the cathodic film. This potential was established some time after the specimen was introduced into the plating bath. The measurements were made at ten second intervals and a rise in potential was always recorded for the first forty or fifty seconds and occasionally for longer periods, but, eventually, in all cases, a steady value was reached. Since this value was maintained until the specimen was removed from the plating solution, the potential could not have been greatly affected by rapid local changes in the concentration around the cathode, for such variations would be continuous.

It was almost impossible to correlate the potential variations with the structure of the electrodeposit, though since this correlation might depend on the fine

structure of the deposit which was not studied, this conclusion is not final. However, the variation in potential between orientated and non-orientated deposits was not significant.

Two alternative theories to account for this variation remain. Gas was always evolved at the cathode and this might well have been the controlling factor in the cathode potential measurements. The rate of gas evolution, unfortunately, could not be measured with the apparatus available. A second possibility was that a different state of equilibrium was reached at the cathode depending upon more fortuitous conditions. It has already been shown that the equilibrium was very sensitive to small changes in the concentration of even one ion, and a similar slight change of concentration in the neighbourhood of the cathode might well have led to a different chain reaction developing which would be sustained once started and so would lead to a different potential being set up.

B. None of the electron diffraction patterns obtained from the electrodeposited alloy specimens revealed any traces of the crystal structures of phases of alloys other than that corresponding to the phase in the cast metal of the same composition. A clear distinction was seen between specimens plated with brass of composition corresponding to the α-phase and similar specimens plated with brass corresponding to the β-phase (Figures 13 and 15).

There is no a priori reason why the simultaneous electrodeposition of two metals should result in the formation of an alloy of the two metals. Since however an alloy is formed, the metal ions must move across the surface of the deposit to the appropriate lattice positions before discharge, and this is indicated by the increased polarization that is observed with alloy deposition. If the current density is high, the movement of the ions is restricted and insufficient time will be allowed for the ions to move to positions in the lowest energy lattice. This will result in lattices being formed only approximating to the lowest energy one. Also the lattice of an electrodeposited alloy is built up layer by layer and not as in the case of solidification from

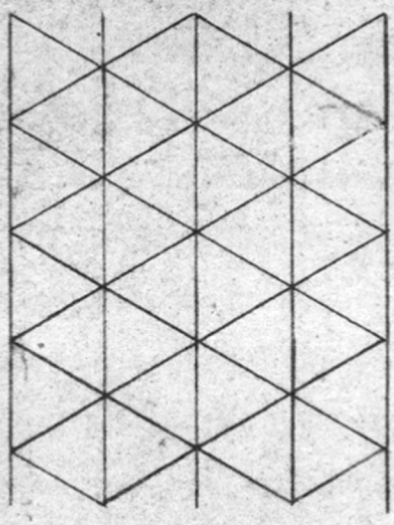
the melt by a three dimensional adjustment to the lowest energy lattice.

In the copper-zinc and silver-cadmium alloy systems within the α range of alloys, the lowest energy structure formed [53] is the face centred cubic structure. This lattice can be supposed to be formed by the closest packing of equal spheres, the centres of the spheres being the normal position of the atoms.

Menzer [54] has shown that there are several ways in which the closest packing of equal spheres can occur. In considering a single sheet there is only one way in which closest packing can be achieved, namely with the centres of the spheres at the corners and centre of a hexagonal grid (Fig. 26a).

A second sheet can be built up on the first only by placing the spheres between alternate spheres of the first sheet (Fig.26b). In respect to the first sheet, however, those in the third sheet can only take up two positions (i) between the spheres of the second sheet and directly over the spheres in the first sheet, or (ii) between the spheres of the second sheet and not over those of the first sheet. These two arrangements are shown in figures 26c and 26d respectively. In the latter case it is not until the fourth sheet that the structure

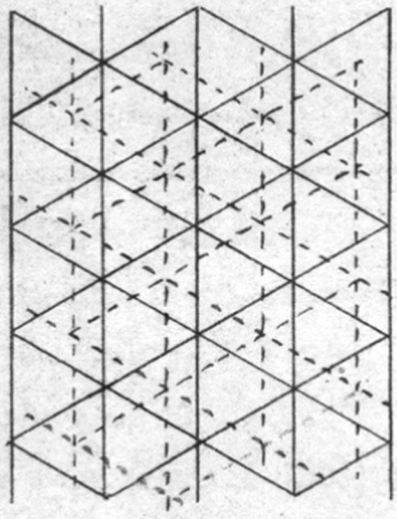
a



SINGLE SHEET OF ATOMS

f.c.c. (111) plane
c.p.h. (001) plane

b

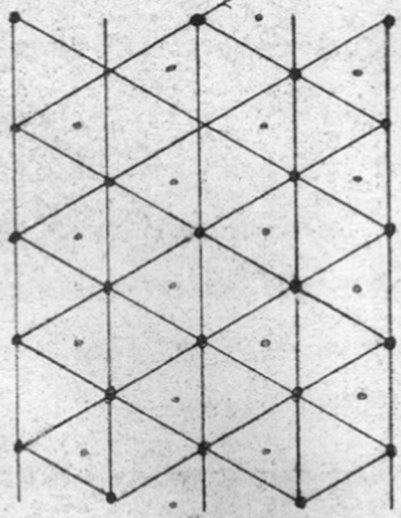


TWO SHEETS OF ATOMS

(CLOSE PACKED)

lines join atomic centres

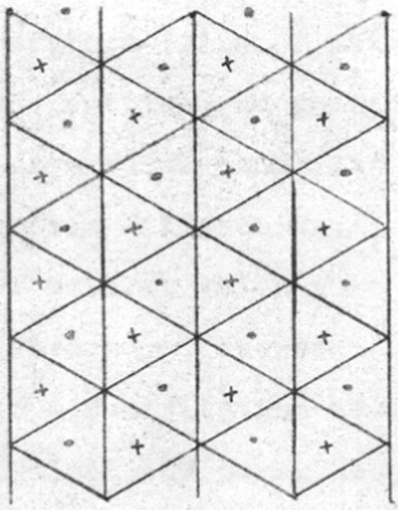
c



THREE SHEETS OF ATOMS

(001) planes c.p.h.

d



THREE SHEETS OF ATOMS.

(111) planes f.c.c.

Figure 26.

will be repeated. Even more complex arrangements are possible [55].

Referring back to crystal lattices, the sheets of atoms so considered are the (111) planes in the face centred cubic lattice. However, such an arrangement is also characteristic of the close-packed hexagonal structure wherein such sheets form the (100) planes. The difference between the two lattices is precisely that outlined above; the face centred cubic being the structure not repeated until the fourth sheet (26d) and the close packed hexagonal being repeated every other sheet (26c).

Kersten [45] had previously shown that cobalt, when electrodeposited, could exist in two forms; the cubic and hexagonal, and in a certain pH range, these could be deposited simultaneously. Quarrell [56] had already investigated the growth of thin films of metals produced by evaporation, electrodeposition and chemical displacement and had found that such films exhibited abnormal structures. Using electron diffraction, Quarrell found that thin films of metals, which in bulk form were of face centred cubic structure, showed anomalies, which he attributed to a modification of the structure to close packed hexagonal to the normal face-

centred cubic form.

Lipson, Edwards and Wilson [57] have recently shown that the imperfections in the structure of cobalt causes transitions from the close packed hexagonal to the face centred cubic structure. They put forward the theory that the structure possessed a lattice in which all the unit cells were approximately the same size and shape but that the distribution of atoms within the cell might differ, e.g. in the way shown in figure 26. Neighbouring cells tend to be alike but there was a possibility of a fault. This gave rise to a broadening of the lines in the diffraction pattern and to a mixed structure.

There is thus ample evidence furnished both by electron and X-ray diffraction for the existence of metallic structures of other than lowest energy. The complex mechanism of the formation of alloy electrodeposits has already been shown and it is not improbable that this method of building the lattice will result in anomolous structures.

Certain of the electrodeposited specimens when examined by electron diffraction gave patterns similar to that shown in figure 12a. As can be seen, the Debye-Scherrer rings are broken into arcs. This pattern is

analysed in figure 12b.

It was impossible to ascribe all the arcs to any one orientation of either face centred cubic or close packed hexagonal; neither would the pattern fit any combination of orientations of face centred cubic or close packed hexagonal separately. It was finally decided, from the evaluation by the equations given on page 12, to ascribe certain arcs as due to a face centred cubic lattice orientated with the (111) planes parallel to the surface of the deposit (perpendicular to the beam) and other arcs to a close packed hexagonal lattice orientated with the (100) planes parallel to the surface. This is in agreement with the above mentioned theory of mixed structure since the (111) and (100) planes are equivalent and as shown in figure 26 are the "key" planes of the structure.

The compounds formed on the surface of the electrodeposits by oxidation and other reactions were those to be expected and normally found on cast brass surfaces and confirms the nature of the electrodeposit to be a true alloy.

Robins [31] has made a detailed study of the oxides found on copper and brass surfaces under various conditions and his results are summarised in Table XVII

This table also includes the results obtained in this research and indicates the confirmation of the results.

The diffraction results for silver-cadmium alloys were not in complete agreement with the conclusions of previous workers who had used X-rays. No trace of other phases were found to be present, unlike the alloys deposited and examined by Stout and Stillwell [44]. Had even small amounts been present it is difficult to see how their crystal spacings were not recorded. The experiments with graphite dust (page 35, figure 14) showed how small an amount was required to affect the pattern obtained. Even the slightest trace of graphite was revealed. No effort was made to limit the composition of the alloy that was deposited and the analyses of the silver-cadmium plate showed a variation over most of the α -range alloys. Alloys with as much as 95% silver together with those with as much as 25% cadmium were examined without any appreciable difference in the type of pattern being observed. As can be seen from Figure 24 the rings tended to be broader than with the brass deposits. This indicated that a smaller crystal size was present. This would arise if the disturbing factors were greater so that each nucleus was prevented from growing large or from a multitude of nuclei so that deposition proceeded rapidly.

The current density and hence the rate of formation of the deposit were not high so that the first explanation seems most likely.

Conclusions.

A. Some properties of mixed cyanide brass plating solutions have been examined, in particular, changes in pH and conductivity with composition have been studied. It has been shown that slight alterations in the concentration of even one ion can profoundly affect the solution and that for that reason pH and electrical conductivity measurements by themselves are insufficient to maintain a working solution. It was found that the presence of carbonates effectively buffered the solution and that the conductivity of the solution was insensitive to changes in the cyanide ion concentration. Measurements of the cathode potential were inconclusive but it was established that variations could exist without major changes occurring in the solution. Two explanations of this were offered. Some of the contradictory results appearing in the literature were shown to be due to insufficient attention being paid to the minor ion concentrations. It was shown that these affected the equilibrium of the plating solutions. A new type of solution employing zincate ions was investigated and was

shown to deposit α-brass within certain temperature and pH ranges. Silver cadmium alloys were obtained from a mixed cyanide solution in the way described by Faust et al [23].

B. It has been shown that an adequate smoothing system can be provided for the high tension unit of an electron diffraction camera in confirmation of recent results of Rymer and Butler [58].

Brass deposited on mild steel substrates by electrodeposition has been examined by electron diffraction technique and certain anomalies in its structure investigated. It has been shown that the mode of formation of the alloy by deposition will tend to produce structures differing slightly from the most stable form as produced by annealed solidification from the melt. Such structures have been identified. In contradiction to the previous results of Stout and Stillwell [44], using X-rays, no evidence of mixed phases occurring on electrodeposition of alloys has been found. Both α and β phases have been produced and examined by electron diffraction and no trace of different phases has been observed. Experiments on calibrating photographic plates of diffraction patterns, by using graphite dust, have

shown that only extremely minute amounts of a material need be present on the surface in order to give rise to its characteristic structure pattern. The percentage of any such phases must therefore be extremely small.

It has been shown that electrodeposited alloys are similar to the cast metal in chemical behaviour; oxides and sulphides formed on the surface of electrodeposits are similar to those occurring on the cast metal. It has been shown that silver-cadmium alloys can be formed and have similar structures to those of brass. A finer grain size has been observed with these alloys indicating that a less stable chain reaction was occurring.

APPENDIX.

THE APPLICATION OF ELECTRON DIFFRACTION TO A PROBLEM OF SURFACE FINISH.

Introduction.

After the working surfaces of an internal combustion engine have been machined and assembled and before the engine is ready for use, a period of "running-in" is resorted to in order to remove high spots on the surfaces, thus reducing friction between the moving parts, and also to provide a tough skin more resistant to wear. It has been observed [59] that without a preliminary "running-in", surface structures are formed on bearing surfaces that have high rates of wear and are difficult to correct later.

In order to obtain this low wear surface, the running intime is prolonged and since, during this time, the engine cannot develop full power the total production time is increased. It was necessary to reduce this time to a minimum in order to increase the supply of certain aircraft engines and it was thought that by using special methods of finishing the bearing surfaces so as to produce a very smooth finish, the running in time might be reduced.

The methods employed consisted of honing and lapping the surfaces with several different abrasive powders

carried in different materials. Test engines with such "superfinishes" as they were called were then run in for a number of hours, at the end of which time they were stripped and the wear on the working surfaces examined.

It was found that whilst some methods gave good results in that the engine was run in with low wear; certain methods which produced smoother (higher) finishes resulted in very high rates of wear which continued throughout the period of the test.

That this was a problem in surface reactions was evident since the same nitrided steel was used in the construction of all the test engines and the same machining was carried out on them all. It was only in the surface finish that the engines differed.

Electron diffraction especially assisted by micrography had been used previously to investigate wear and lubrication problems. Finch and others [60] had examined the nature of polished surfaces and the effects on metal bearing surfaces of additions to lubricants [61]. It was therefore decided to investigate these phenomena by the same means.

Experimental.

In order to ascertain where differences in sturcture occurred the whole manufacturing process was examined from the point where the methods differed (the initial grinding to size) through to the stripped-down run-in engine. Specimens were cut from engine parts at all stages of the process and examined by electron diffraction methods.

So as to ensure that comparable results were obtained, attention was concentrated on one particular engine part and for that reason all the experiments were carried out on sleeve valves. The wearing surface of these executed a combined rotating and sliding motion so that the rate of wear was high and running-in tests correspondingly shortened. The sleeve valves had cylindrical concave surfaces and specimens about one inch long in the direction of the axis and about one half to three quarters of an inch across were trepanned from the sleeves, care being taken not to overheat the specimens. The edges of these were chamfered so that the surface to be examined was raised above the bulk and thus the electron beam could be sent at grazing incidence, in the direction of the axis.

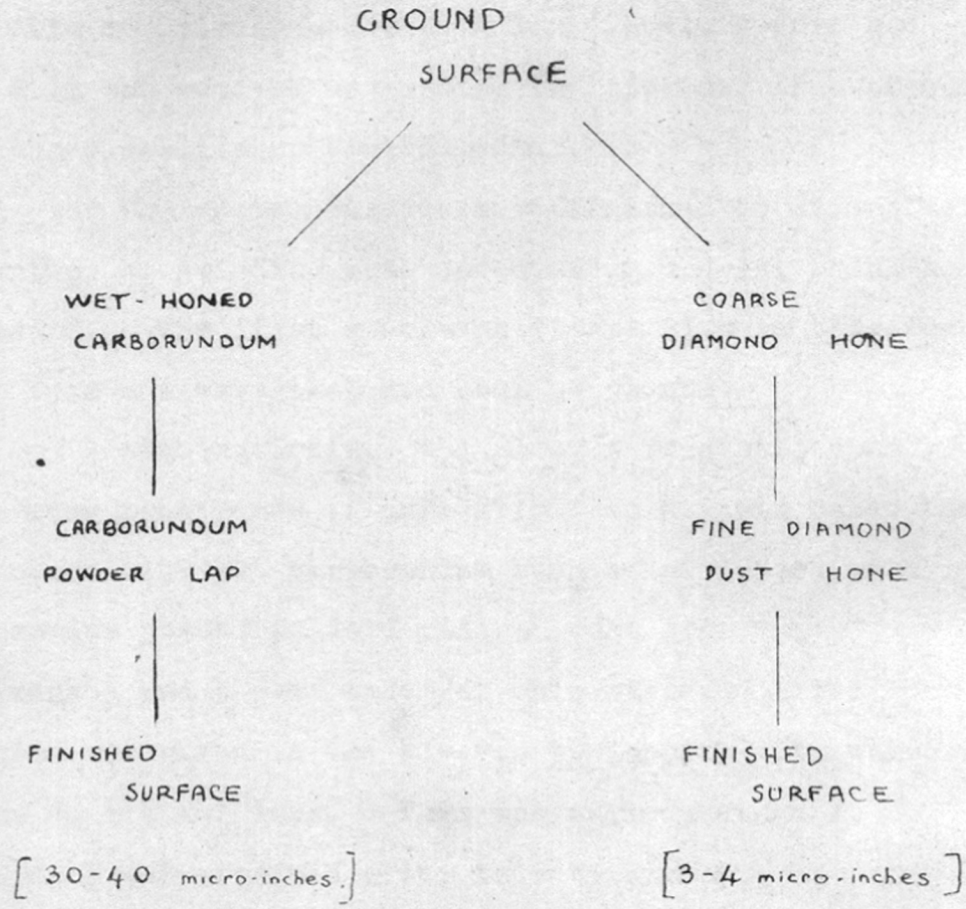

GROUND
SURFACE
WET - HONED
CARBORUNDUM
CARBORUNDUM
POWDER LAP
FINISHED
SURFACE
[30-40 micro-inches]
COARSE
DIAMOND HONE
FINE DIAMOND
DUST HONE
FINISHED
SURFACE
[3-4 micro-inches]

figure 27.

All the specimens were obtained and prepared at the factory and were sent to the laboratory protected by a film of petroleum jelly. Immediately before use this film was removed by washing the specimen in a stream of hot redistilling petroleum ether.

The engine sleeves were finished to size after machining, by grinding with carborundum wheels, using a lubricant. The first specimens (1 and 2) were therefore taken from a sleeve that had been so ground.

Aftermgrinding, the sleeves were subjected to differeing treatments (figure 27). In certain cases they were honed with wet carborundum stones and lapped with carborundum powder in lard oil, on cast iron laps. Specimens 3 and 4 were taken at this stage. After this, a finish was given to the sleeves by lapping with carborundum powder on leather laps. This was called Method A. Specimen 5 was obtained after this treatment.

Instead of this honing and lapping with carborundum powder, the ground sleeves were subjected to a different process. Coarse diamond dust, retained on 150 mesh, set in bakelite hones, was used to hone the surface. Specimen 6 was cut from a sleeve thus treated. A finish was set to these sleeves by honing with similar hones set with a finer diamond dust, retained on 400 mesh. Specimen 7 was taken

at this stage. This was called Method B.

A measure of the 'flatness' of the surfaces was obtained by direct measurement of the contours with an instrument called the "Talysurf". This instrument amplified the irregularities on a surface so that projections and crevices of the order of microinches could be detected. A quantitative measure of surface roughness was given by the deviation from a mean level and was expressed in microinches. A dead smooth surface would register zero deviation. The method A produced surfaces which when measured on this instrument gave results of twenty to thirty microseconds. Method B, however, gave a finish as high as two to three microinches, which should have represented a great saving in running-in time.

Engine sleeves finished by these two methods were run in on single cylinder test units for varying times between fifty and one hundred hours. The units were afterwards stripped down, the radial wear on the sleeves measured, and specimens cut from the places of maximum wear. Specimen 8 was taken from a sleeve prepared by method A and run in for 100 hours; specimen 9 was taken from a sleeve prepared by Method B and run in for 110 hours; specimen 10 was cut from a sleeve prepared by method B and run in for 65 hours.

The radial wear on the sleeve from which specimen 8 was obtained was less than 0.0002 inches; that on specimen 9 was the same, whilst on specimen 10, which had the smoother finish, the wear was 0.0022 inches.

On visual examination, it was seen that the smoothness of the surface became greater as the finishing processes were applied. Specimens 1 and 2 had a matt appearance; specimens 3 and 4 had a smoother surface, but were still matt and only diffusely reflected light. Specimen 5, finished by carborundum had a satin-like matt finish and in fact was referred to as the "satin" finish. Specimen 7, that with the highest finish as measured by the 'Talysurf', gave almost specular reflection and was called the "mirror" finish.

Electron Diffraction Examination.

Most of the specimens examined by electron diffraction did not give any clear ring pattern, but all gave a sharp shadow edge with considerable general scattering of the electron beam (Figure 28).

The ground surface, specimen 2, gave rise to a diffraction pattern as shown in Figure 29; the ring radii and the calculated spacings being given in Table XVIII. The similar specimen (Specimen 1) merely gave rise to considerable general scatter with a sharp shadow edge.

FIGURE 28

FIGURE 29

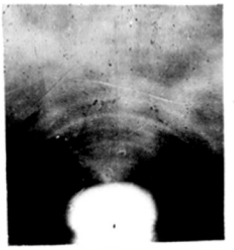


FIGURE 30

FIGURE 31

The "satin finished" surface, Specimen 5, gave rise to a pattern, shown in Figure 30, whose measurements are given in Table XVIV. Specimens 6 and 7 resulted in faint patterns whose measurements and calculated spacings are given in Table XX.

The specimen 8, run in for one hundred hours did not give a clear ring pattern; specimen 9 gave a pattern whose measurement and spacings are given in Table XXI. The run in specimen with high wear, specimen 10, did not give any clear pattern on the first examination.

After this preliminary search, the specimens were abraded with fine emery paper (Durex 400 A) in order to remove any surface contamination, and then were re-examined in the diffraction camera. Specimen 10 after this treatment gave a pattern as shown in Figure 31. This was identified by comparison with calibrated plates as due to α-iron of small crystal size.

TABLE XVIII.

ELECTRON DIFFRACTION MEASUREMENTS OF

GROUND SURFACE OF CYLINDER SLEEVE VALVE.

Plate No. A.5524.

R mm.	d_{hkl} A	I
12.79	1.98	MS
13.77	1.83	S
15.22	1.66	MS
17.05	1.48	VS

TABLE XVIV.

ELECTRON DIFFRACTION MEASUREMENTS OF

'SATIN FINISHED' SLEEVE VALVE.

Plate No. K.738.

R mm.	d_{hkl} A	I
11.00	2.39	VVW
12.80	2.05	VVW
13.73	1.92	S
15.07	1.74	MW
16.45	1.595	MS
18.37	1.435	VVS
21.42	1.225	MS

TABLE XX.

ELECTRON DIFFRACTION MEASUREMENTS OF CYLINDER SLEEVE VALVES DIAMOND HONED.

Plate No. K.640.

R mm.	d_{hkl} A
6.05	4.21
7.85	3.24
13.90	1.83
16.55	1.53
18.40	1.375

TABLE XXI.

ELECTRON DIFFRACTION MEASUREMENTS OF

SATIN FINISHED SLEEVE RUN IN FOR 100 HOURS.

Plate No. K.698.

R mm.	d_{hkl} A	I
7.48	3.37	VW
8.14	3.10	W
11.50	2.20	VVS
15.51	1.62	VS
18.86	1.335	S
19.78	1.275	S
25.90	0.976	VS

Discussion of Results.

Figure 28 shows the general type of pattern produced by these specimens. The pattern has a sharp shadow edge but there are no clear rings visible. There was apparently a considerable general scattering of the electron beam, which is indicated by the even fogging of the photographic plate above the shadow edge.

The specimens were examined by the so-called "reflection" method, wherein the electron beam strikes the specimen at grazing incidence. The pattern produced is, in general, the same as that produced by transmission through a thin film except that in the former case the shadow of the bulk of the specimen will cut off slightly more than half the circumference of the rings.

If a transmission specimen is too thick, the electrons will lose an appreciable proportion of their energy by their passage through the atomic electric fields and hence diffuse scatter will be caused. With "reflection" specimens a similar diffuse scatter can be caused by the projecting crystallites being too thick or of the wrong shape.

Nelson [35] investigated the surface oxidation of iron by electron diffraction. He obtained patterns from

reflection specimens of iron that had been rubbed on a succession of emery papers of finer and finer grades taking care not to rub too heavily and ensuring that the specimen was not rubbed over the same emery twice. This produced a surface which he called an "abraded" surface. He then took similar specimens and rubbed them in the same way on different grades of emery, but using more pressure and allowing the specimen to retrace its path on the abrasive. This surface he called "burnished". Using a profile meter the abraded surfaces were seen to possess much sharper, thinner ridges than the burnished specimens which only exhibited flattened thick ridges. The difference between the diffraction patterns was equally striking. The abraded surface yielded a definite ring pattern due to polycrystalline material whereas the burnished specimen yielded only a heavy general fogging of the photographic plates above the shadow edge. By suitably modifying the treatment the specimen received, mixtures of the two patterns and also of the profiles were obtained. It was concluded that the burnishing had caused the metal to flow thus flattening the ridges and hence causing considerable general scatter.

From the amount of general scatter it seems probable that large round crystallites were similarly present on the specimens used in this research. It was considered that the

action of the abrasive was to cut grooves in the metal and to leave the detritus above the surface. In the case of the slower cutting carborundum particles, the grooves would be shallow, the metal would be able to flow and inclusions of detritus would occur in the surface layers. This inclusion had been shown by previous workers to be possible [37]. With the much faster cutting diamond abrasive, the grooves cut would be deeper and much less flow would occur, the detritus would then pile up at the sides of the grooves.

It has been shown by experiments previously carried out [59] that the initial oxide formation occurring during finishing and preliminary running in profoundly affects the subsequent rate of wear of the surface. A low rate of wear has been associated with a surface consisting of smaller crystals of iron intimately mixed with crystals of iron oxide. A surface formed of large crystals with little surface protection and only a thin film of air formed oxide was found to have a high rate of wear. In this respect it has been reported by Greensmith [38] that the superfinishing process removed the surface layers but left the basis metal untouched, hence exposing larger crystal formations.

Other workers have obtained similar results. Young [40] reports that where α-iron surfaces are exposed to abrasion by the stripping of surface films, serious wear occurs. Rosenberg and Jordan [62] by working with apparatus in a

controllable atmosphere showed that the presence of air considerably reduced wear at iron bearing surfaces. They analysed the detritus in the two cases of wear (i) in ordinary air and (ii) when only an inert gas was present. The former case revealed only iron oxides in the detritus whereas under the latter conditions, when high wear occurred, α -iron was found.

CONCLUSIONS.

It has been shown that electron diffraction can be used in investigating problems arising from a consideration of the wear at moving metal surfaces. In particular an investigation of the cause of excessive wear occurring during the running in of certain airplane engines has been described. It was reported that the preparation of the bearing surfaces greatly affected the rate of wear; surfaces given a very smooth finish, contrary to expectations, had a higher rate of wear than less smooth surfaces (only 30 microinches finish compared to 3 to 4 microinches of the smoother surfaces).

It was shown that different electron diffraction patterns were produced from specimens obtained by the two methods of finishing the surfaces. The material present on the surface could not be positively identified, but the nature of the electron diffraction pattern gave very good indication of the size and shape of crystallites present.

From previous work on the wear of ferrous metal surfaces it was concluded that the high rate of wear associated with the smooth finish was due to the rapid and thorough cutting of the surface layers by the diamond dust used in this method. When the surface material was given time to flow during the cutting, which took place with the slower

cutting carborundum particles, a surface layer rich in oxides and of smaller crystal size was formed. This had been previously shown to be a cause of wear.

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BIBLIOGRAPHY.

1. Glasstone, J.C.S., 690 (1929); J.C.S., 702, (1929); and Trans.Farad.Soc., 31, 1211, 1232, (1935).
2. Bancroft, Trans.Amer.Electrochem.Soc., 44, 397, 1923.
3. L.B.Hunt, J.Phys.Chem., 36, 1006, 2269, 1932.
4. O'Sullivan, Trans.Farad.Soc., 26, 89, 1930
5. Huntington, Trans.Farad.Soc., 1, 324, 1905.
6. Blum and Rawdon, Trans.Amer.Electrochem.Soc., 44, 305, 1923.
7. Graham, Trans.Amer.Electrochem.Soc., 44, 427, 1923.
8. Wood, Proc.Phys.Soc., 43, 138, 1931.
9. Hothersall, Trans.Farad.Soc., 31, 1242, 1935.
10. Finch and Sun, Trans.Farad.Soc., 32, 852, 1936.
11. Finch and Williams, Trans.Farad.Soc., 33, 564, 1937.
12. Bragg and Darbyshire, Trans.Farad.Soc., 28, 522, 1932.
    Preston and Bircumshaw, Phil.Mag, 20, 706, 1935.
13. Laue, Jahrb, Radioakt. und Electronik., 11, 308, 1914.
14. Thomson, Proc.Roy.Soc., A 128, 649, 1930.
15. Thomson, Proc.Roy.Soc., A 117, 600, 1928; A 119, 651, 1928.
16. Hull and Davey, Phys.Rev., 17, 549, 1921.
17. Knaggs, Karlik and Elam, "Tables of Cubic Crystal Structure", 1932.
18. R.W.G.Wyckoff, "The Structure of Crystals", 1931 and 1935.
19. Ewald and Hermann, Strukturbericht, 1931 et.seq.
20. Hanawalt, Rin and Frevel, Ind.Eng.Chem., 10, 1938 (Sept).
21. H.P.Coats, Trans.Electrochem.Soc., 80, 445, 1941.

22. S.O.Cowper Coles, Brit.Pat. 13,460, Aug., 1891;
13,910, 1892.

23. Faust, Henry and France, Trans.Electrochem.Soc., 72, 1937.

24. Stout and Thummell, Trans.Electrochem.Soc., 59, 337, 1931.

25. Mathers and Johnson, Trans.Electrochem.Soc., 74, 221, 1938

26. Finch and Wilman, Ergeb.d.exakt.Naturwiss., 16, 353, 1937.

27. Finch, Quarrell and Wilman, Trans.Farad.Soc., 31, 1650, 1935.

28. Houghton and Bingham, Proc.Roy.Soc., A 99, 47, 1921

Genders and Bailey, J.Inst.Metals, 33, 213, 1925.

Gayler, J.Inst.Metals, 34, 235, 1925.

Bauer and Hansen, "Der Aufblau der Kupfer-Zinc Legierungen", 1927.

29. Westgren and Phragmen, Phil.Mag., VI, 50, 311, 1935.

Owen and Preston, Proc.Phys.Soc., 56, 49, 1923.

30. Lamchen, Ph.D.Thesis, London Univ., 1937.

31. W.G.H.Robins, Private communication.

32. Miyake, Sci.Pap.Inst.Phys.Chem.Res.Tokyo, 29, 167, 1932.

33.

34. Durant, J.Inst.Metals, 45, 99, 1931.

Hume Rothery, Mabbot et al, Phil.Trans., A 283, 1, 1931.

35. Nelson, J.Chem.Phys., 5, 257, 1937.

36. Hughes, Trans.Farad.Soc., 17, 442, 1921.

38. Schlesinger, Proc.Inst.Mech.Eng., 151, 169, 1944.

39. Symposium, Trans.Farad.Soc., 31, 1935.

40. Young, Proc.Inst.Auto.Eng., 30, 69, 1935.

41. Kohlschutter and Schact, Z.Electrochem., 19, 172, 1913.

42. Friederich and Knipping, Sitz.der.K.Bayerischen Akademie der Wissenschaften, 303, June, 1912

43. Neuberger, "Roentgengraphie der Eisen und seiner Legierungen der Metalle und ihrer Legeirungen," Enke, 1928-9.

44. Stout and Stillwell, J.A.C.S., July, 1932.

45. Kersten, J.Phys.Chem., 35, 3644, 1931.

46. Bradley, Sykes et al., Proc.Roy.Soc., A (1942 et seq.).

47. Clarke, J.Electrodepos.Tech.Soc., 12, 1, 157, 1937.

48. McNaughton and Hothersall, J.Electrodepos.Tech.Soc., 5, 63, 1935.

49. Moore, Proc.International Assoc.for Testing Materials, 1909.

50. M.R.Thomson, Trans.Electrochem.Soc., 1941.

51. Ernst and Mann, Trans.Electrochem.Soc., 61, 363, 1932.

52. Britton and Dodd, J.C.S., 2332, 1931; ibid., 1940, 1932.

53. Astrand and Westgren, Z.anorg.allgem.Chem., 175, 90, 1928.

54. Menzer, Naturwiss., 26, 385, 1938; Z.Krist., 99, 378, 1938.

56. Quarrell, Proc.Phys.Soc., 49, 279, 1937.

57. Lipson, Edwards and Wilson, Proc.Roy.Soc., A 180, 268, 272, 1942.

58. Rymer and Butler, Phil.~~Trans~~ Mag., 36, 821, 1945.

59. Brummage, Ph.D. Thesis, London Univ., 1942.

60. Finch and Zahoorbux, Inst.Mech.Eng., Disc.Gp.IV., 100, Oct. 1937.

61. Soole, Ph.D.Thesis, London Univ., 1945.

62. Rosenberg and Jordan, Bur.Stand.J.Res., 13, 267, 1934.