

THE GROWTH AND STRUCTURE OF METALLIC ELECTRODEPOSITS/
WITH SPECIAL REFERENCE TO THE EFFECTS OF ION-ASSOCIATION,
COMPLEX IONS AND INCLUSION OF NON-METALLIC MATERIAL.

By

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ABSTRACT OF THESIS.

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A study is made of the crystal structure, orientation and size of copper deposited from cyanide baths and of silver deposited from cyanide and thiosulphate baths at various current densities and bath temperatures. The effects of reducing the cation concentration, though still retaining the same total concentration of metal, by increasing the ion-association was also investigated using silver nitrate solutions. Deposition was mostly on to polished metal substrates, but copper was also deposited on copper single-crystal faces.

Recent work has established that the growth of the crystals in an electrodeposit is affected mainly by the bath conditions and the substrate surface effect. "Lateral growth" with the most densely populated atom planes parallel to the substrate surface, occurs when the bath conditions are such as to maintain a high cation concentration at the cathode and a high mobility of the ions over the cathode. "Outward growth", with the most closely packed atom rows perpendicular to the substrate surface, occurs when the cation concentration at the

the cathode is low. The crystal orientation and size in deposits grown on crystalline substrates under lateral growth conditions are largely determined by those of the substrate crystals. Under bath conditions which favour outward growth, the deposit crystals grow uninfluenced by the substrate, except in the first few layers.

It was observed in the present experiments that orientations not characteristic of either lateral or outward growth occurred under some conditions. Both copper and silver were found in some cases to have crystallised with the close-packed hexagonal structure instead of the normal face-centred cubic structure. The crystal size in the silver deposits was generally decreased by increasing the ion-association. A small crystal size was usually found in deposits from the complex electrolytes, but in some cases large crystals were formed.

Three main explanations have formerly been suggested for the small crystal size usually found in metals electro-deposited from solutions of their complex salts: (i) the metal is deposited by the discharge of its simple ions produced by the dissociation of the complex ions, and the very low concentration of cations favours the production of a large number of crystal nuclei; (ii) the metal is deposited by the discharge of the complex ions and the formation of many nuclei

is promoted by the high energy with which the simple cation is held in the complex ion; and (iii) the complex ion solutions lead to a much greater inclusion of non-metallic material in the deposits than do solutions of simple salts, and the crystal size is limited by this inclusion.

The results of the present experiments are discussed in relation to the general problem of cathodic crystal growth, and it is concluded that in the absence of any specific substrate influence the crystal size in electrodeposited metals is chiefly dependent on the adsorption of non-metallic material on the growing crystal faces. The adsorption of such material may also affect the crystal orientation and even the crystal structure.

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INTRODUCTION.

Crystal structure and growth have been much studied in many kinds of deposit on both amorphous and crystalline substrates. Knowledge of the mechanisms involved in such crystal growth should lead to an insight to the nature of the interatomic forces in the deposit, and between the deposit and the substrate, and, more generally, to a clearer understanding of the properties of these deposits.

There are four main physical processes for producing crystalline deposits: (i) growth by condensation from the vapour phase, or by cathodic sputtering, (ii) growth from the molten state, (iii) growth from supersaturated solution, and (iv) growth by electrodeposition. In (i), the atoms, after condensation, have their mobility determined by the temperature of the substrate. The mobility of the atoms being incorporated in the crystal lattice in case (ii) will, in general, be much greater than in case (i). In (iii), the conditions are similar to (i), but the observations lead to the conclusion that the mobility of the atoms is increased by impacts with the solvent molecules, and atoms deposited in metastable positions can dissolve and be deposited again elsewhere. Moreover, there may be specific interaction of the atoms with the solvent, or adsorption of other constituents of the solution, which would affect the crystal growth.

Growth by electrodeposition is, in many ways, the most complex of the four methods. The process is similar to (iii) but the rate of crystal growth is readily controlled by varying the current density at the cathode. Furthermore, a metal may be electrodeposited from various solutions of its salts, and the crystal structures of the metal produced from these solutions may differ in a number of respects, either as a result of a difference of the mechanism of ion discharge in different solutions, or because of the inclusion of foreign matter in the cathodic deposit. The purpose of the present work is to consider and study in some detail the influence of various factors which may affect the growth and structure of metallic electrodeposits.

(a) Cathodic crystal growth.

From the results of a systematic study over many years by Finch and his collaborators [1-13], the main influences under which the crystals of a metallic electrodeposit grow have been determined. These influences fall into two main classes - (i) those due to the bath (i.e. general conditions of electrodeposition); and (ii) those due to the substrate. When the bath conditions favour the maintenance of a high metal ion concentration at the cathode,

and a high ion-mobility over the cathode, the deposit crystals tend to be oriented with a densely (usually most densely) packed atom plane parallel to the substrate surface. This mode of growth is termed "lateral growth", and it is promoted by high concentration of electrolyte, high bath temperature, low or moderate current density and stirring. If, on the other hand, the bath conditions are such that regions of ion impoverishment are set up next to the cathode during electrodeposition, then the deposit crystals tend to grow with the most closely packed atom rows perpendicular to the cathode. This mode of growth is termed "outward growth".

A crystalline substrate may affect the orientation of the crystal nuclei formed in the early stages of electrodeposition, but unless the bath conditions favour lateral growth, the effect of the substrate is lost, and a one-degree orientation characteristic of the bath conditions rapidly develops. Even under lateral growth conditions a one-degree orientation may develop in thick deposits if the substrate is polycrystalline with a small crystal size, or if there is considerable co-deposition of hydrogen or other non-metallic material.

The excessive adsorption of hydrogen on the cathode may result in the crystals of a deposit being

without any preferred orientation, or, in the case of antimony and other metals with weak cohesive forces, it may even cause the deposit to be without any recognisable crystal structure at all. When the mode of growth of the crystals in an electrodeposit is changed by an appropriate change in the bath conditions, there is normally an intermediate stage in which the crystals are randomly disposed.

Although this simple general picture [4,5,6] of the growth of crystals in metallic electrodeposits is supported by a wealth of experimental evidence, a number of cases have been reported in which the crystal orientation was not characteristic of either outward or lateral growth, or in which the crystal lattice had been modified in some way by the conditions of deposition. These cases are summarized in Table 1. Thus, Kersten [22] found that cobalt when electrodeposited from baths with low pH values had a mixed structure of close-packed hexagonal and face-centred cubic lattices, but from high pH baths it has only the hexagonal structure. Bradley and Ollard [23] in 1927 noted in some electrodeposits a close-packed hexagonal modification of chromium, which normally has a body-centred cubic structure, and their findings were subsequently confirmed by a number of other workers [24-28]. In 1935, Wright, Hirst and

Table 1.

Anomalous Orientation in Electrodeposited Metals.

Metal	Lattice Type.	Orientations	References.
Ag	f.c.c.	$(10\bar{1}0) + (112)$, (100)	7, 14.
Au	f.c.c.	(100)	2.
Ni	f.c.c.	(100), (112), $(10\bar{1}0) + (112)$ (120)	3, 4, 9, 14, 15, 19.
Pb	f.c.c.	(112)	16.
Cr	b.c.c.	(100), (112), (0001).	1, 14, 20, 27.
Fe	b.c.c.	(112), (113), $(112) + (113)$	13, 14.
Cd	h.c.p.	$(11\bar{2}2)$	11, 18.
Zn	h.c.p.	$(11\bar{2}2)^*$	11.
Bi	rhomb.	(100)** , (211)**	11, 17.
Sb	rhomb.	(100)**	4, 11.
Sn	b.c.t.	(111)	21.

f.c.c. = face-centred-cubic.

b.c.c. = body-centred-cubic.

h.c.p. = close-packed-hexagonal.

rhomb. = rhombohedral.

b.c.t. = body-centred tetragonal.

* Occurs simultaneously with (1120) orientation characteristic of outward growth.

** Plane indices referred to pseudo face-centred cubic axes.

Riley [28] showed that this hexagonal modification only occurred in deposits from chromic acid baths if there was sufficient trivalent chromium present to ensure an average of at least 18% chromium in the cation. The hexagonal chromium was entirely converted to the cubic form, and large quantities of hydrogen were evolved, if the deposit was heated in vacuum at 800°C. for $1\frac{1}{2}$ hours.

Quarrell [29] observed hexagonal modifications in thin electrodeposited films of the face-centred cubic metals silver, nickel, gold and platinum prepared for transmission examination by the method described by Finch and Sun [2]. The metals showed (0001) hexagonal orientation, but the orientation subsequently became (110) cubic as the deposit thickness increased. Quarrell postulated that this transition might be caused by a rucking of the (0001) planes in the thin deposit which lifted some of the atoms out of the plane and caused the crystals in the subsequent layers of the deposit to have a face-centred cubic structure with (110) planes parallel to the original (0001) planes. He suggested that such a mechanism as this would result in a gradual transition from the hexagonal to the cubic structure which would in turn account for diffuse bands extending from the 200 cubic ring to a sharp limit inside the 111 cubic ring which occurred in electron diffraction patterns from

such transmission specimens. Such bands have been observed before [1], and had previously been explained as being caused by a gradual expansion of the crystal lattice by the interstitial solution of gas in the electrodeposited metal since the bands (and some "extra" rings also sometimes occurring) often disappeared on heating the specimen in vacuum. Fordham [30], however, obtained diffraction patterns from thin electrodeposited films of silver in which the band was resolved into a number of streaks equally inclined to the ring radii, and Finch and Wilman [31] pointed out that the existence of the bands might be explained as being due to diffraction streaks similar to those observed in patterns from metal films evaporated on to rocksalt. These streaks might be associated with refraction at crystal boundary faces or due to poor resolution caused by small crystal dimensions in certain directions, or they might be the result of repeated lamellar {111} twinning.

The occurrence of the hexagonal modification of nickel observed by Finch, Wilman and Yang [4] has recently been investigated in more detail by Yang [32]. He found that a mixture of face-centred cubic and close-packed hexagonal structures was always present in deposits from baths containing a relatively large proportion of nickel chloride at high current densities and low bath temperatures.

The deposits with this mixed structure were found to contain more occluded hydrogen than those having only a ~~simple~~ face-centred cubic structure. Yang also reported the occurrence of hexagonal modifications of silver and copper in electrodeposits from cyanide baths.

The occurrence of (112) and (113) orientations in iron electrodeposits was found by Glocker and Kaupp [14] and by Layton [13] to be associated with ferrous chloride baths with an excess of chloride ions. It was suggested by Layton that these orientations are probably modifications of outward growth caused by the co-deposition of hydrogen or, perhaps, oxides.

The dependence of the physical properties of electrodeposits on the crystal structure has been briefly discussed by Finch and Layton [6], who made it clear, however, that there are a great many related problems still ^{to} be investigated. In commercial plating practice, simple baths are comparatively rare. Nearly all the solutions used contain additions - sometimes inorganic, but more usually organic - which help the production of desirable features, such as small grain size or a bright surface in the electrodeposits. The function of many additions to practical plating baths is very imperfectly understood, and there is no doubt that a clearer insight into their mode of action would be of

great practical benefit as well as being of theoretical interest.

The ways in which various additions may affect the character and properties of an electrodeposit are numerous and diverse. Buffering agents are frequently used since the pH of a solution determines the possibility of the co-deposition of hydrogen with the metal, or the precipitation of oxides, hydroxides or basic salts. The inclusion of such non-metallic material in the deposit is probably one of the most common causes of small crystal size.

It was for a long time thought that small crystal size in electrodeposits was always associated with cathode polarization. Thus Aten and Boerlage [33], for example, observed that in the electrodeposition of silver from solutions of silver nitrate, the number of crystal nuclei was increased by any alteration in the bath conditions which increased the polarization. The two main objections to this view are (i) the fact that fine-grained deposits of silver are obtained from argentocyanide^{solutions} with little or no polarization and (ii) metals of the iron group which show an inherent deposition over-voltage at room temperatures still form fine-grained deposits near 100°C. although at high temperatures the deposition occurs very close to the reversible potential. As pointed out by Blum and Rawdon [34], it is necessary, on thermodynamic grounds, that the potential at which small crystals are deposited

should be more negative than that at which large crystals of the same metal are deposited. This was formerly thought to support the theory that crystal size was dependent on cathode polarization, though Blum and Rawdon themselves made it clear that the differences of potential to be expected would generally not be more than a few millivolts. The possible relations between the form of electrodeposited crystals and cathode polarization have been discussed in some detail by Glasstone [35].

A number of alternative explanations have been advanced for the smallness of silver crystals usually obtained from cyanide baths. Kohlschütter [36] considered that such baths always contained colloidal matter, probably a silver sub-cyanide, which was adsorbed on the growing crystal faces and thus inhibited the growth of large crystals. Vahramian [37], however, observed that passivation of silver cathodes during interrupted electrolysis did not occur in cyanide baths as it did in simple nitrate ones, and he attributed this to such a strong adsorption of cyanide on the cathode that the latter was kept free from colloidal contamination. A number of workers have supported the theory that adsorption of silver cyanide may inhibit large crystal growth, and a possible way in which it might be formed at the cathode is by the discharge of complex cations

e.g. Ag_2CN^+ , forming silver and silver cyanide in close contact [38]. Glaz^unov and Schlotter [39] supported this complex cation theory and considered that the inclusion of non-metallic material distorted the crystal lattice of the electrodeposited metal. Raub and Wullhorst [40], however, found that the cyanide content of the deposited metal decreased with increase in current density and free cyanide content of the bath, and increased with agitation. These facts, and Raub's earlier observation [41] that the inclusions congregate along crystal boundaries breaking the grains up into small crystallites rather than distorting the lattice of larger crystals, led Raub and Wullhorst to conclude that silver was deposited by the discharge of the simple Ag^+ ion dissociated from the complex anion $\text{Ag}(\text{CN})_2^-$. Raub had previously studied the structure of silver in relation to the conditions of deposition [42] and found that the hardness of the deposit increased with increase in the free cyanide content of the bath and decrease in bath temperature. Even when there were no detectable amounts of included material the lattice distortion was similar to that of cold-worked silver. The work has since been extended, and other metals included [43], but Raub's experimental methods were indirect and did not reveal detailed information about the crystal orientation or habit.

Glasstone and Sanigar [44,45] investigated the effect on the cathode polarization, and the appearance and hardness of the deposits, of a number of different salts added to an argentocyanide solution. They found that the addition of carbonate produced softer deposits than without any addition, and the addition of nitrate, formate, acetate, hydroxide, phosphate or sulphate increased the hardness in varying degrees. Borate or chloride additions resulted in very hard deposits. Contrary to Raub's observation [42], they found that an excess of cyanide in the bath yielded soft deposits. They suggested that the CO_3^{2-} , CN^- and NO_3^- ions which contain incomplete octets of electrons may be adsorbed on the growing silver faces, but the other ions, which give harder deposits, possess complete electron shells and are, therefore, possibly, not so readily adsorbed.

Fischer [46,47] has developed a theory of cathodic crystal growth to account for the layered structure of some electrodeposited crystals and the action of growth inhibitors in plating baths. In its later form [48,49,50], the theory is merely an extension of a much earlier theory of Blum and Rawdon [34]. The theory is entirely based on the structural appearance of deposits by optical methods and lacks the necessary foundation of evidence concerning crystal orientation and habit which is yielded by electron diffraction and (to a much smaller extent) X-ray diffraction examinations.

An early theory due to Aten and Boerlage [33], and subsequently developed by Hughes [51], was that after the ions were discharged they remained in an intermediate stage as atoms before being incorporated in the growing crystal lattice. They attempted to relate the crystal growth and structure to the concentration of metal atoms in this hypothetical intermediate layer, and regarded cathodic crystal growth as analogous to growth from the melt. The conditions of crystal growth in electrolytic solutions and molten metals are so different, however, that this analogy and the suggested mechanism of growth from a layer of discharged atoms seem improbable. Blum and Rawdon [34] regarded the discharge of the ions and the incorporation of the atoms in the lattice as a single process, the ions migrating over the cathode and being discharged at those points at which the lowest discharge potential was required. It has been suggested [52] that atoms in metastable positions will become ionized and go into solution to be deposited again in more stable positions, but the extent to which this process could occur on a cathode appreciably more negative than its reversible potential in the solution (as it would be if metal were being deposited) would be almost infinitesimally small. Hunt [53], after a general consideration of the rather scanty information available up to 1932 suggested that the crystalline structure of an electrodeposited metal is governed by the

relation of the metal ion concentration in the cathode film to the concentration of the other constituents of the film.

Generally, it seems that a small crystal size is most easily obtained by deposition from a bath in which the metal is held in a stable complex ion, but it is not true, as is frequently assumed, that such baths cannot yield large crystals. Hammond [54] obtained large crystals of silver from the usual type of cyanide bath used in practice, and during the present work coarse deposits of both copper and silver were obtained from baths containing a variety of complex ions. The mechanism by which metals may be deposited from solutions of their stable complexes has occupied the minds of electrochemists for many years, and several theories, of varying plausibility, have been produced. Some of these are considered in detail below, but it may be remarked here that the deposition of "simple" ions can never really occur since all ions in solution are solvated, i.e. surrounded by a sheath of solvent molecules, and, furthermore, except in dilute solutions of strong electrolytes, all salts are associated to some extent, i.e. a proportion of the ions are bound to oppositely charged ions. Independent evidence of this is given by refractometric data [55] which shows the existence, in aqueous solutions of strong electrolytes, of combinations of oppositely charged ions without water molecules between them.

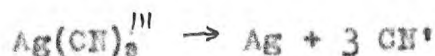
(b) Electrodeposition from complex ion solutions.

In 1903, Le Blanc and Schick [56] suggested that the complex ions in a solution of potassium argentocyanide dissociate very rapidly. They postulated this in order to explain their observation that the rate at which a silver electrode dissolved in a potassium cyanide solution when passing alternating current fell off quite rapidly with increasing frequency. It was supposed that if the complex ions dissociated rapidly, the silver dissolved during the anodic pulses would be redeposited during the cathodic pulses. Their results could, however, have been explained by supposing that there is a slow stage in the passage of a metal atom into the stable complex ion, and a similar, but even slower, stage in the reverse (cathodic) process.

Haber [57] pointed out that with stable complex ions, the recombination rate is very much greater than the dissociation rate, and he calculated that under certain circumstances this would appear to necessitate electron velocities greater than that of light, which, of course, is impossible. As an alternative to the theory that silver was deposited from complex ion solutions by the discharge of the simple Ag^+ ions, Bodländer [58] suggested that the complex anions $\text{Ag}(\text{CN})_2^-$ were discharged at the cathode

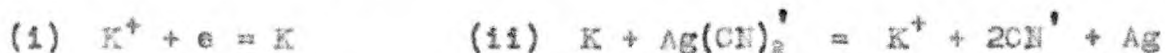


This new complex was supposed to very unstable and to decompose rapidly



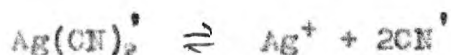
He considered that this indirect production of silver at the cathode was the cause of small crystal size in the deposits.

The earliest theory of the deposition of silver from a cyanide bath is due to Hittorf [59], who supposed that the alkali metal ion is first discharged at the cathode and that it reacts with the complex anion to precipitate silver:

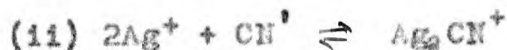


Since the silver would thus be the result of a secondary process, the growth of large crystals would probably not be favoured. This theory is untenable because the measured cathode potentials during electrolysis of argentocyanide solutions are much more positive than the deposition potentials of the alkali metals.

Glasstone [38], in 1929, measured cathode potentials and current efficiencies in the electrolysis of argentocyanide solutions, and found that, within the limits of the experimental errors and the approximate calculations, the limiting current density for a cathode current efficiency of 100% was determined by the rate of diffusion of the anions $\text{Ag}(\text{CN})_2'$ to the cathode. He concluded from this that the dissociation of this complex ion



was probably rapid, tacitly implying that the deposition was not by the discharge of the anion. He finally suggested that in the bulk of the solution there were two equilibrium reactions,

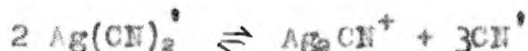


and that silver was deposited by the discharge reaction



An obvious objection to this theory is that since the equilibrium of (i) is so far to the left, it is unlikely that the concentration of simple Ag^+ ions will ever be high enough for (ii) to occur to any appreciable extent.

Glazánov and Schlötter [39] later also postulated the existence of complex cations Ag_2CN^+ formed directly by the reaction



This complex ion is then discharged at the cathode to give an unstable cyanide which decomposes:



Such a process would yield silver and silver cyanide in close contact at the cathode, and thus account for the frequent inclusion of silver cyanide in electrodeposited silver.

Though there is some evidence for the existence of

such cations, it is really based on analogy with complex cations such as Ag_2I^+ and Ag_2I^{++} which were inferred by Hellwig [60] from the results of transport experiments to be present in solutions of the double salt $2\text{AgNO}_3, \text{AgI}$. Since the solubility of AgCN in AgNO_3 is similar to that of AgI in AgNO_3 and since the double salt $2\text{AgNO}_3, \text{AgCN}$ is known, it was thought likely that the complex cations Ag_2CN^+ and $\text{Ag}_2\text{CN}^{++}$ may exist in argentocyanide solutions. Schlötter, Korpium and Burmeister [61] found silver iodide included in silver electro-deposited from iodide baths, and suggested that it was caused by the discharge of complex cations Ag_2I^+ .

According to the well-known Nernst equation, the potential of a metal immersed in a solution of its ions is given by

$$E = E^\circ + \frac{RT}{nF} \ln a_+$$

where R is the gas constant, T is the absolute temperature, n is the valency of the ion, F is Faraday's constant, a_+ is the activity (i.e. effective concentration) of the cations, and E° is a constant equal to the potential at some specified temperature when $a_+ = 1$. The low potential of a silver electrode in an argentocyanide solution as compared with its potential in, for example, a silver nitrate one is thus considered to be due to the very low concentration of simple Ag^+ in the cyanide solution.

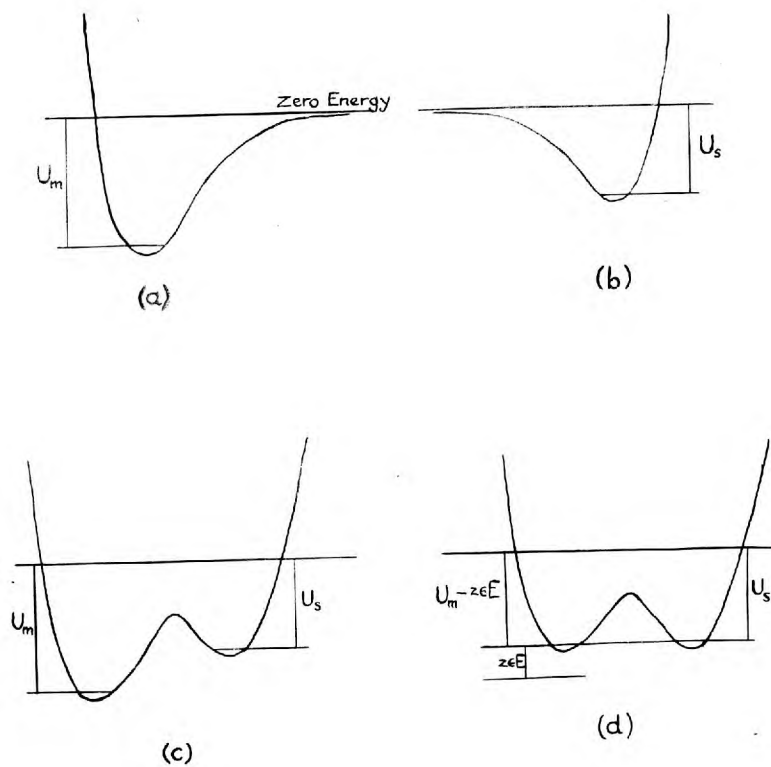


Fig.1. Variation of energy of a metal ion with distance from metal surface and solvent molecules.

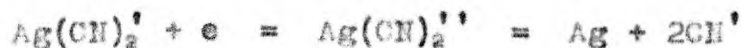
Butler [62], however, interpreted the electrode potentials in different solutions in terms of differences of binding energy of the simple metal ion in the solutions. This theory is similar to that developed by Gurney and Fowler [63] using quantum mechanics and described below. In Fig. /, the horizontal line represents the energy of a metal ion in vacuo, and curve (a) the variation of its energy with distance from the metal surface. Curve (b) represents ~~the~~^{the} variation in the energy of the ion in solution with distance from the solvent molecules, the two energies U_m and U_s being the energies of the ground levels of the ion in the metallic and solvated states respectively. The variation in energy of the ion in transition from the metal lattice into solution, or vice versa, is represented by the combination of these two curves into (c). (The intersection between the two curves is rounded off on quantum considerations). If U_m is lower than U_s , ions will tend to be deposited from the solution on to the metal which will, if insulated, acquire a net positive charge giving rise to a potential difference E between the metal and solution. The energy of all the ions in the metal will then be raised by an amount $z\bar{E}$ where $z\bar{E}$ is the charge on each ion. When $U_m - z\bar{E} = U_s$, equilibrium is attained, and E is the reversible potential of the metal in the solution. This condition is represented by curve (d). If the ion, instead of

being surrounded by solvent molecules, is bound in a stable complex with greater energy so that U_s is lower than U_m , ions will tend to go into solution from the metal, which will then acquire a negative charge. The difference in potential of the metal in two different solutions is then given (ignoring entropy changes) by

$$\Delta E = \Delta W / ze$$

where ΔW is the difference in the energies of the metal ion in the states in which it exists in the two solutions. These energy differences can be found in some cases from the available thermochemical data, and electrode potentials calculated with their aid agree with the measured potentials.

According to this theory, silver, for example, would be deposited by the direct discharge of the complex anion at the cathode, as Bodländer [58] suggested in 1904. Butler [64] considered this process to be analogous to the discharge of the simple hydrated cation, $Ag(H_2O)_x^+$, although the two types of ion involved carry charges of opposite sign. Because of thermal and convectional movements, the complex anions will frequently come into contact with the cathode, in spite of the electrostatic repulsion, and it is postulated that the anion gains an additional charge which causes decomposition of the complex, and deposition of the metal. In the case of the silver cyanide complex, the overall reaction would be



This theory also offers a possible explanation of the ease with which small crystals are obtained from complex ion baths. If the energy "hump" over which the ions have to cross in order to be discharged is low, then large crystals are likely to be formed since ions discharged in unstable or metastable positions will be able to go back into solution. If, on the other hand, the "hump" is high, re-entry of discharged atoms into the solution will be more difficult, and the formation of fresh crystal nuclei will be favoured rather than the development of large crystals.

The theory certainly has the merit of simplicity, though the discharge of anions at the cathode may seem difficult to accept. It was largely this difficulty which led Glasstone and Glaznov and Schlötter, to suggest the existence of complex cations.

Both these theories, i.e. the direct discharge of the complex anion and the discharge of a postulated complex cation, were advanced partly to explain the inclusion of cyanides in the deposits, but chiefly to overcome the difficulty involved in the earlier idea of the discharge of simple cations produced by the dissociation of the complex anions, viz. Haber's calculations concerning the rates of recombination. The complex cation theory, however, seems to create as many problems as it solves. The very existence of such cations

is hypothetical, and nothing is known of their equilibrium constants so that it is impossible to estimate their probable life, i.e. the time during which they are available for discharge at the cathode. The probability that the time required for the discharge of a simple Ag^+ ion was considerably greater than the time during which such an ion was not associated with CN^- ions was one of the main objections to the simple ion discharge theory, and the complex cation theory can hardly be said to have overcome this difficulty.

Butler's interpretation of Haber's calculation as showing that the dissociation of the complex $\text{Ag}(\text{CN})_2^-$ ions could not be regarded as a necessary preliminary stage in the electrodeposition of silver is open to objection since Haber, in fact, considered^{ed} the rates at unit concentration of the reacting species i.e. the specific rates of the dissociation and association reactions. Since the equilibrium constant of the complex ion is the ratio of these specific rates, and since the equilibrium constant of $\text{Ag}(\text{CN})_2^-$, for example, is of the order of 10^{18} , the specific rate of association is 10^{18} times as great as the specific rate of dissociation. The actual rates under any given conditions depend^{also} on the concentrations (or more strictly the activities) of the various ions involved. Under the conditions prevailing near a cathode at which silver is being electrodeposited at all rapidly, the concentration of simple silver ions will be extremely low, and the actual rate

of formation of complex ions from the simple ones will therefore be lower than at equilibrium. In any case, Haber's main object in the paper under consideration was to point out that the very low ionic concentrations and short reaction times for solutions of complex ions obtained by calculation from electrochemical measurements are only of mathematical, and not physical, significance. This fact was reiterated by Ellingham [65], and it is clearly not justifiable to apply statistical results to the consideration of individual ions.

(c) Present work.

It is clear from the above review that the processes of ion-association and complex formation are important in the growth of metal crystals by electrodeposition, though the mechanisms by which these processes exert their influence is not understood.

In order to study some of the effects of ion-association and complex formation on the crystal growth of electrodeposits, the crystal structure of copper and silver, electrodeposited from a number of different baths under various conditions of current density and temperature, was examined by electron diffraction and optical microscopy. Electron diffraction is a particularly powerful tool for the study of the growth and structure of electrodeposits since the precise information it yields concerning the crystal structure

orientation, habit and size is confined to that relating to the surface layers of the deposit. This is due to the low penetrating power of even high energy electrons. It is thus possible to follow the changes in the crystal structure of electrodeposits stage by stage.

Copper was deposited from three solutions each consisting simply of cuprous cyanide and potassium cyanide in various proportions. It is known that about 1.5 equivalents of alkali metal cyanide are needed to dissolve CuCN , and Glasstone [66] interpreted this as indicating that $\text{Cu}(\text{CN})_2^-$ and $\text{Cu}(\text{CN})_3^{--}$ ions are formed in such a solution in approximately equal quantities. Silver was electrodeposited from cyanide baths containing silver cyanide and various quantities of "free" potassium cyanide (i.e. cyanide in excess of the 1 equivalent required to dissolve the silver cyanide) and also, in some cases, containing additions of potassium carbonate or potassium chloride. These two additions were found by Glasstone and Saniger to give very soft and very hard deposits respectively. Silver was also satisfactorily deposited from a complex thio-sulphate bath and from nitrate baths in which the ion-association had been increased.

Close-packed hexagonal modifications of both copper and silver were found to be deposited under some circumstances. The crystal size in electrodeposits from silver nitrate baths

was found to be decreased by increasing the ion-association, and it was also found that large crystals could sometimes be obtained from complex cyanide baths. Further examples of crystal orientations which were not characteristic of either simple outward or lateral growth were also found.

These results, together with those of previous work [13] on the deposition of silver from nitrate baths and of iron from sulphate and chloride baths, are discussed in relation to the general problem of crystal growth by electrodeposition.

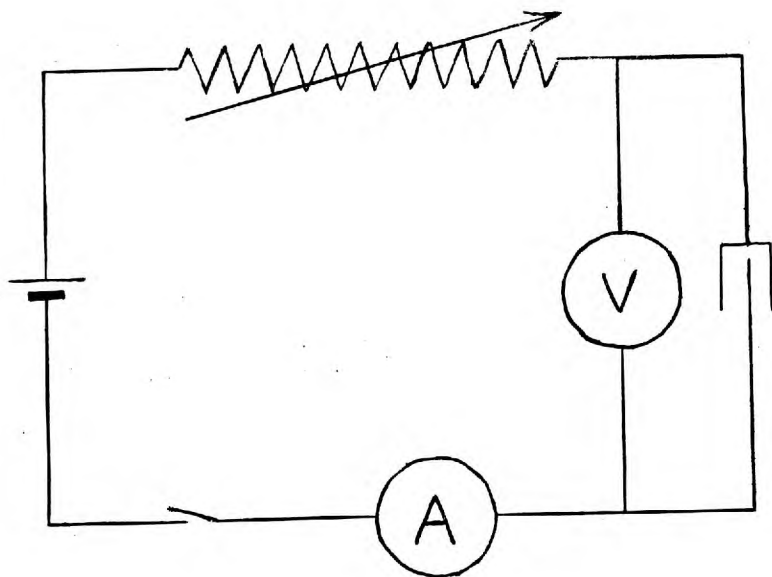


Fig.2. Circuit diagram.

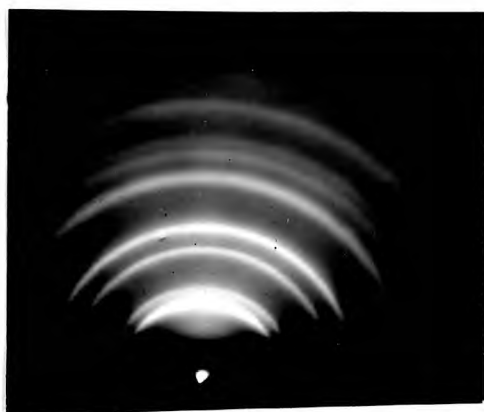


Fig.3. Silver deposited from dilute cyanide bath at 2 mA/cm^2 and 20°C . for 20 sec.

EXPERIMENTAL DETAILS.

Electrodeposition was carried out using about 200 cc. of the appropriate solution in a 250 cc. beaker which was surrounded by a thermostatically controlled water jacket. By this means the temperature of the electrolytic bath was maintained constant within $\pm \frac{1}{2}^{\circ}\text{C}$. The electrical circuit is shown in Figure 2. The cathode was suspended in the middle of the bath with an anode each side of it in order to achieve as uniform a distribution of current as possible.

For general investigations of the effects of bath conditions, brass discs 1 inch in diameter were used as cathodes. These discs were polished with "Bluebell" commercial metal polish on chamois leather, and degreased in a jet of grease-free crystallizable benzene. When silver was to be electrodeposited on them, the discs were given a 20 second "flash" deposit at 2 mA/cm^2 from a bath containing 3.5 g./l. AgCN and 60 g./l. KCN in order to avoid the formation of a silver deposit by chemical displacement. Electron diffraction examination showed this deposit to consist of small randomly disposed crystals (Fig.3). Copper was also electrodeposited on to copper single crystals, and these were prepared by carefully smoothing the desired faces on 3/0 emery paper lubricated with benzene, and then electropolishing in a 50% phosphoric acid solution [67].

After electrodeposition, the specimens were washed immediately in distilled water, dried in acetone and transferred to the electron diffraction camera. The surfaces of the specimens were subsequently examined by vertical illumination microscopy. The weight of metal deposited was determined by weighing the discs before starting deposition and after examination by electron diffraction, and from this weight, the current used and the time of deposition, the cathodic current efficiency was calculated.

The detailed compositions of the copper and silver cyanide baths are given in Tables 2 and 3 with the experimental results. The three copper cyanide baths may be represented as $N/5[CuCN, 4KCN]$, $N/5[CuCN, 2.5KCN]$ and $N[CuCN, 2KCN]$, respectively. In all the silver baths used, except some of the aqueous nitrate and chloride ones, the solutions were $N/4$ with respect to silver. Complex silver baths, other than the cyanide ones, used were obtained by dissolving silver chloride in almost saturated solutions of calcium chloride or magnesium chloride, or in solutions containing sodium thiosulphate $Na_2S_2O_3 \cdot 5H_2O$. Although $AgCl$ is ^{more} ~~most~~ soluble in solutions of calcium chloride or magnesium chloride than in solutions of any other chloride, the maximum solubility only corresponds to a silver ion concentration of about 0.05 normal [68].

The association of a dissolved electrolyte can, in general, be increased either by increasing the concentration of the electrolyte or by decreasing the dielectric constant of the solvent. Fuoss and Kraus [69] derived an expression for the fraction of association, θ , of an electrolyte

$$\theta = \frac{4\pi N c}{1000} \cdot \left(\frac{\epsilon^2}{DkT} \right)^3 \cdot Q(b) \quad Q(b) \equiv \int_2^b e^y y^{-4} dy$$

$$y \equiv \frac{\epsilon^2}{DrkT} \quad b \equiv \frac{\epsilon^2}{DakT}$$

where N = Avogadro's number,
 c = concentration of electrolyte in moles per litre,
 ϵ = electronic charge,
 D = dielectric constant of the solvent,
 k = Boltzmann's constant,
 T = Absolute temperature,
 r = distance apart of the ions in the solution,
 a = smallest distance of approach of the ions.

Values of $Q(b)$ for various values of b have been tabulated [69, 70]. It will be apparent from the expression above that the value of θ is much more affected by changes in the dielectric constant of the solvent than by changes in the concentration of the electrolyte.

Deposition of silver was therefore attempted from $N/4$ solutions of $AgNO_3$ in mixtures of water and dioxan. Mixtures containing 6% water and 10% water were used, and these had dielectric constants of about 4.5 and 6 respectively [69]. Gemant [71] has estimated values of the dissociation constant of $AgNO_3$ dissolved in water-dioxan mixtures from measurements

of the potential differences in concentration cells, and by extrapolation it seems likely that in the solutions used in the present work, the dissociation constant would have a value of the order of 10^{-9} .

The experimental technique of electron diffraction and the interpretation of patterns have been described by Finch and Wilman [31]. The interpretation of one-degree orientation patterns has recently been discussed in detail by Wilman [72], but a brief note on the derivation of the patterns to be expected for certain orientations is given in an appendix to this thesis.

RESULTS.

Electrodeposition of Copper.(a) Amorphous substrates.

The experimental results are summarized in Table 2.

It is well known that copper dissolves in cyanide solutions with the evolution of hydrogen, and this, and the very low current efficiencies found at 20°C. in the first bath, are due to the potential of a copper electrode in solutions containing an excess of cyanide being below the reversible hydrogen potential in such solutions. Although the hydrogen overvoltage at copper is about 0.2 volt [73], the excess of cyanide in the first bath is sufficient to cause preferential deposition of hydrogen rather than copper. The preference of crystal orientation in these deposits produced at such low current efficiencies was very weak and indeterminate (Fig.4). The general appearance of the deposits was rather dark, as if they had been oxidised, and there was no appreciable variation in the crystal size, which was small (about 200 Å. diameter), with current density. Müller and Bradley [74] obtained very dark deposits of copper from copper sulphate solutions, and X-ray examination of these deposits showed the inclusion of up to 25% of a copper hydride, CuH. They had previously examined this hydride, prepared chemically, and assigned to it a

Table 2.

Orientations in Copper Electrodeposited from Cyanide
Baths on to Polished Brass.

Bath Composition g./l.	Bath Temperature °C.	Current Density mA/cm ²	Current Efficiency %	Orientation
1 CuCN 18 KCN 50	20	1	3.2	VW(110)
		5	2.3	?
		10	2.4	?
	60	1	100	S(110)
		5	-	-
		10	65	S(110)
2 CuCN 18 KCN 34	20	1	62.5	?
		5	59	(110)
		10	38	R
	60	1	70	?
		5	81	(110)
		10	82.5	(10 $\bar{1}$ 0)
3 CuCN 90 KCN 130	20	1	95	?
		5	95	(100)
		10	90	(110)
	60	1	85	(110)
		5	95	VW (110)
		10	90	(111)+(100) at centre (110) at edge

S - strong orientation; VW - very weak orientation;
R - crystals randomly disposed; ? indeterminate orientation

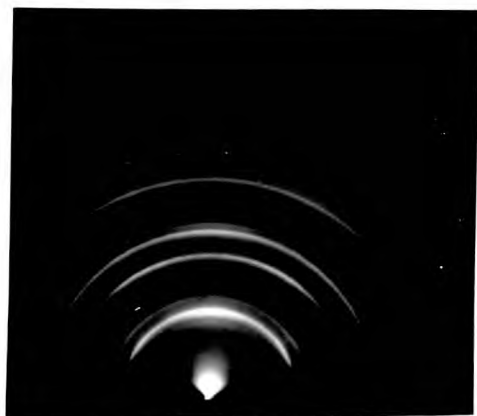


Fig.4. Copper deposited from Bath 1 at 5 mA/cm² and 20°C.



Fig.5. Copper deposited from Bath 1 at 10 mA/cm² and 60°C. (110) orientation.

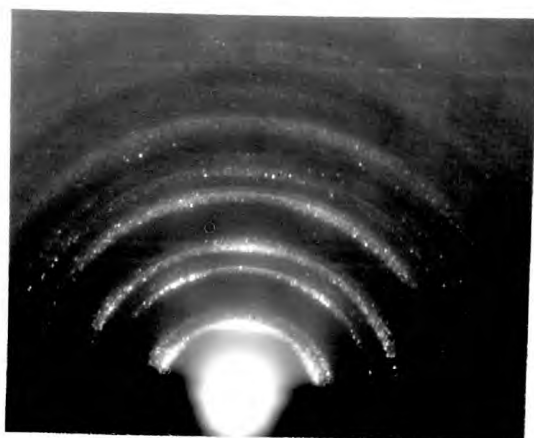


Fig.6. Copper deposited from Bath 2 at 10 mA/cm² and 60°C. (1010) orientation.

hexagonal structure with $a = 2.89 \text{ \AA}$. and $c/a = 1.595$.

Hütting and Brodkorb [75], also from X-ray examination, assigned to CuH a cubic structure like that of metallic copper, but expanded, with $a = 4.33 \text{ \AA}$.

Electron diffraction examination of the deposits obtained in the present work, however, did not suggest the presence in the deposits of CuH with either of these structures, but revealed the inclusion of Cu_2O in many deposits. At 60°C although the hydrogen overvoltage was decreased by the rise in temperature, the diffusion of other ionic species was increased, and the current efficiency thereby improved. This lower rate of hydrogen deposition relative to copper deposition enabled the crystals of the deposit to grow with a strong orientation (cf. ref.[4]). This orientation (Fig.5) was (110), characteristic of outward growth, because of the small total concentration of copper in the bath. The crystal size at 60°C . was greater than that at 20°C . as shown by the spottiness of the rings in the diffraction pattern, Fig.5.

The second bath, though containing the same total amount of copper, had a smaller quantity of free cyanide. With this bath, it was found that at ~~both~~ 20°C . ~~and~~ 60°C . the current efficiency decreased as the current density was raised, but, as in the first bath, the efficiencies at the higher temperature were greater than those at the lower. The crystal

size in deposits from the bath at 20°C. increased markedly with increasing current density, and, as the relative rate of hydrogen deposition also increased, the crystals deposited at 10 mA/cm² were randomly disposed instead of having (110) orientation like the crystals deposited at 5 mA/cm². The indeterminate orientation at 1 mA/cm² may be due to adsorption of cyanide or other non-metallic material inhibiting any preferred type of crystal growth. At 60°C. the current efficiency increased with increasing current density. The electron diffraction patterns from these specimens indicated that all the deposits contained Cu₂O, at least on the surface, and they also showed that the crystal size in the deposits was greater at higher current densities, though this was not so obvious from microscopic examination. At 10 mA/cm², the crystal structure was hexagonal in (10 $\bar{1}$ 0) orientation with, perhaps, some cubic crystals in (112) orientation also (cf. Figs. 21 and 22). It is clear from the spottiness of the rings of the diffraction pattern, Fig. 6, that the crystal size was large (greater than about 500 Å. diameter).

In the deposits from the third bath, which had five times the total copper concentration of the first two baths but a copper to alkali cyanide ratio comparable to that of the second bath, the crystal size decreased as the current density was increased. The current efficiency did not vary much with

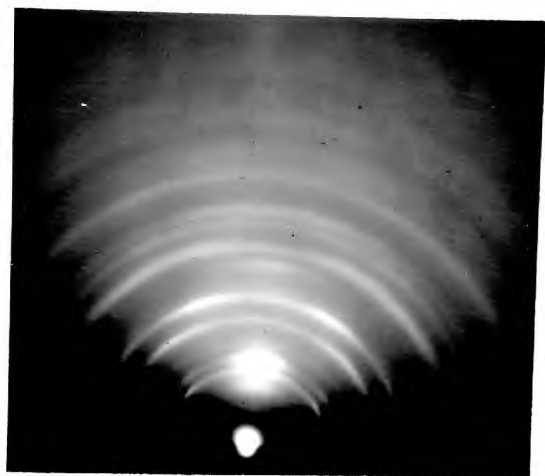


Fig.7. Copper deposited from Bath 3 at 10 mA/cm^2 and 60°C . (111) and (100) orientations at centre of specimen. Thickness $\sim 39,000 \text{ \AA}$.

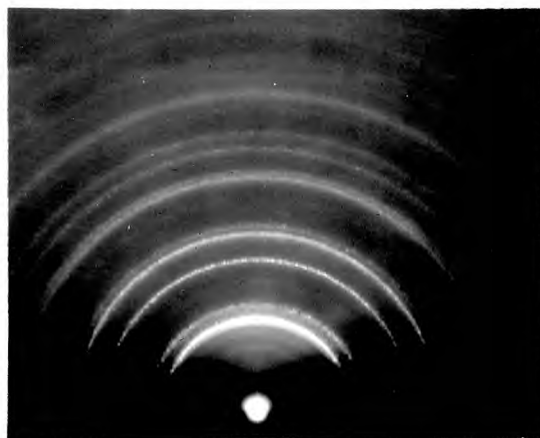


Fig.8. As Fig.7, but thickness $\sim 5,000 \text{ \AA}$.

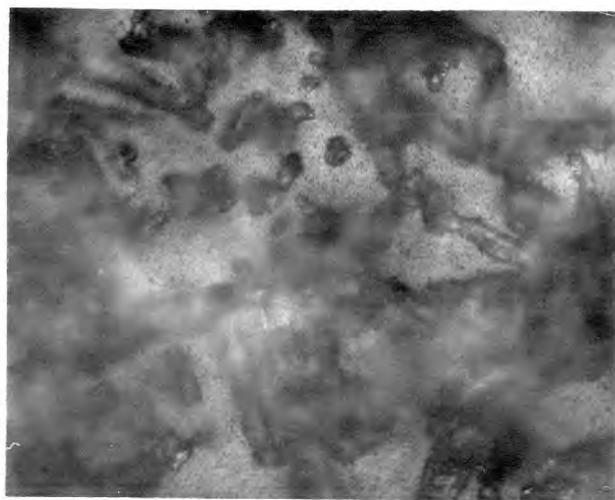


Fig.9. Micrograph of copper deposited from Bath 3 at 1 mA/cm^2 and 60°C . $\times 600$.

either current density or temperature. At 20°C., the change in crystal orientation with increasing current density was from an indeterminate orientation to (100) and then to (110). A thinner deposit, 5,000 Å. thick, also prepared at 5 mA/cm², showed (100) orientation at the edges, but the crystals at the centre were randomly disposed. At 60°C., the orientation, which was (110) in all the deposits, was not very strong. The crystal structure of the deposit at 10 mA/cm² was more complex since the crystals in the centre of the specimen were partly in (111) and partly in (100) orientation, Fig.7, and the deposit was rougher, with larger crystals, at the edge rather than in the centre. In this case, also, a thinner deposit was prepared and examined, and it was found to consist of fairly large crystals randomly disposed (Fig.8). Fig.9 shows that some of the crystals in the specimen deposited at 1 mA/cm² were very large indeed.

(b) Single-crystal substrates.

In order to find whether there was any difference in the rate of loss of substrate influence on different crystal faces, a copper single crystal with (100), (110) and (111) faces on it was used as a substrate. Copper was deposited on it from bath 2 at 60°C. and 5 mA/cm², (conditions for outward growth) to an average thickness of 10,000 Å, and from bath 3 at 20°C. and 5 mA/cm² to an average thickness of 2,000 Å. Diffraction

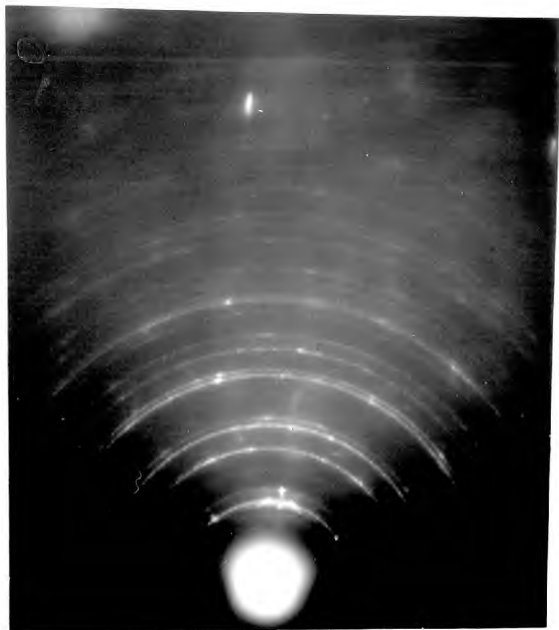


Fig.10. Copper deposited from Bath 2 at 5 mA/cm^2 and 60°C . on copper (100) face.

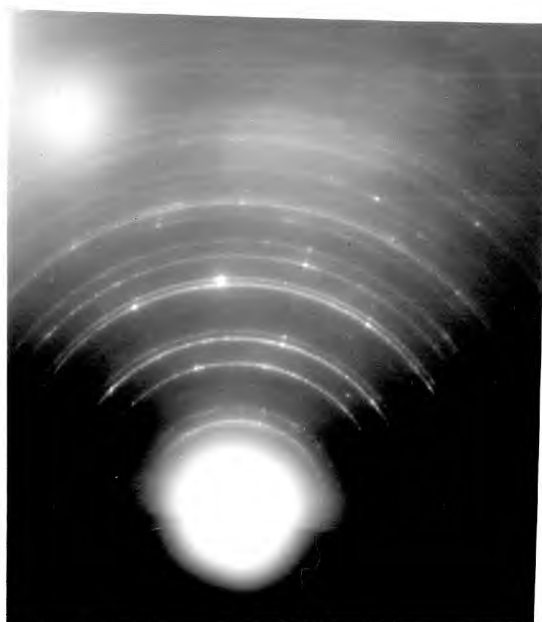


Fig.11. Copper deposited from Bath 2 at 5 mA/cm^2 and 60°C . on copper (110) face.

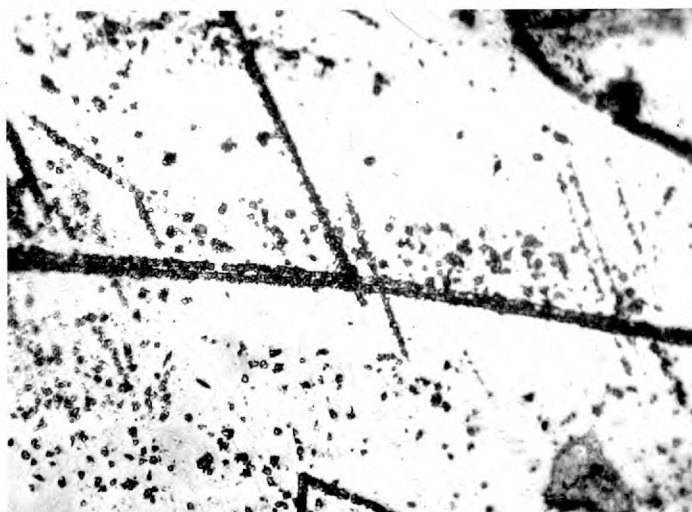


Fig.12. Micrograph of copper deposit of Fig.10.
x 600

patterns from the deposits on the (100) and (110) faces under the above outward growth conditions (Figs. 10 and 11) show that on both faces much of the deposit was growing independently of the substrate, the deposit crystals being randomly disposed. Fig.10 indicates, however, that in the deposit on the (100) face, considerable parallel growth with {111} twinning has occurred. There is also strong evidence of part of the deposit having grown in a close-packed-hexagonal lattice in $(10\bar{1}0)$ orientation with $[001]$ hexagonal parallel to $[001]$ cubic. The pattern further indicates the presence of Cu_2O in the deposit.

Fig.11 with the beam parallel to the cube edge of the substrate crystal (110) face shows, in addition to the ring pattern due to randomly disposed deposit crystals, diffraction patterns due to copper (i) in a close-packed hexagonal lattice with $(10\bar{1}0)$ parallel to the substrate and $[001]$ parallel to the beam, (ii) in a face-centred cubic lattice in (111) orientation and $[112]$ azimuth, and (iii) in a face-centred cubic lattice in (100) orientation and $[001]$ azimuth.

In both these deposits, the electron diffraction evidence shows that the hexagonal lattice has been developed with the $[100]$ hexagonal rows parallel to the $[110]$ cubic row of the substrate crystal. The atom spacing along both these rows is identical (since they are both the closest packed rows)

In the second case the most densely packed planes in the close-packed hexagonal deposit crystals and in the substrate crystal - (0001) and (111) in the hexagonal and cubic lattices respectively - are perpendicular to the substrate surface, though equivalent rows in these planes are at right angles.

Microscopic examination (Fig.12) showed that there was a strong tendency for the crystal nuclei to form along traces of scratches on the substrate surfaces not completely removed by electropolishing.

Under bath conditions leading to (100) orientation in polycrystalline deposits, the crystals on the (111) face grew parallel to the substrate crystal in the two equivalent arrangements, i.e. with $[1\bar{1}0]$ and $[\bar{1}10]$ parallel to the $[1\bar{1}0]$ of the substrate. From the pattern, Fig.13, it is also clear that some Cu_2O crystals had been formed on the crystal with the oxide lattice parallel to the substrate lattice. The elongation of the diffraction spots perpendicular to the shadow edge shows that the surface was relatively smooth, at least over considerable areas. The strong spot pattern was due to the copper deposit, and the fainter, but nevertheless clear, pattern was due to the copper oxide. The complexity of the copper oxide pattern is the result of double scattering, strong beams diffracted by the copper lattice having acted as primary beams and been diffracted by the cuprous oxide lattice.

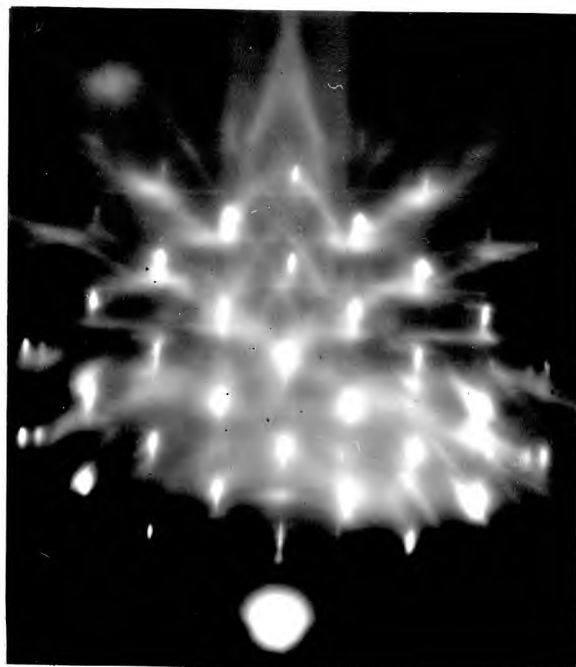
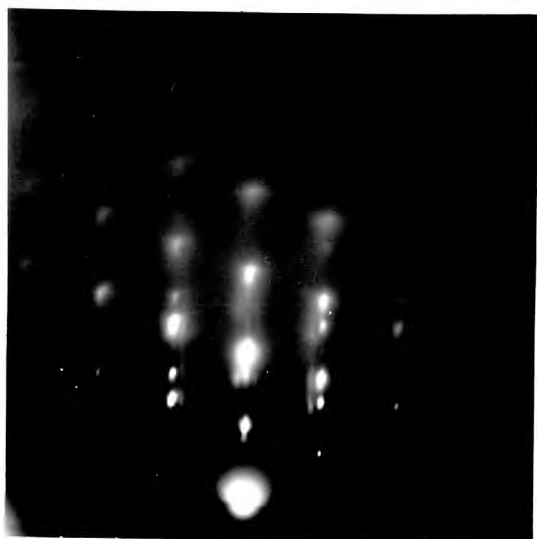


Fig.13. Copper deposited from Bath 3 at 5 mA/cm^2 and 20°C . on copper (111) face $[110]$ azimuth.

Fig.14. Copper deposited from Bath 3 at 5 mA/cm^2 and 20°C . on copper (001) face $[110]$ azimuth.

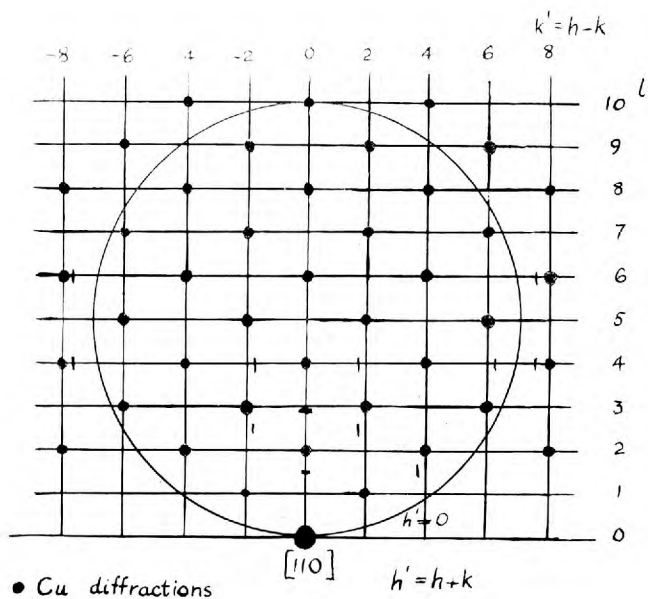


Fig.15. Indexing of Fig.14.

The diffraction patterns, Figs. 14, 16 and 17, due to the deposits on the (110) and (100) faces are more complex. The main strong spot patterns and clear Kikuchi line patterns indicate that the deposit has continued the crystal structure of the substrate and maintained a high degree of lattice perfection. Together with these patterns due to copper growing parallel to the substrate, there are fainter patterns of sharp spots clearly visible. It has not been possible to work out fully the interpretation of these additional spot patterns and determine the substances giving rise to them. In the pattern (fig.14 and indexed in Fig.15) from the deposit on the (001) face with the beam parallel to $[110]$, the additional spot pattern near the undeflected beam position corresponds to a crystal lattice having an interplanar spacing of 2.37 Å. in the direction perpendicular to the substrate surface and a spacing of 1.47 Å. in the direction perpendicular to the beam and parallel to the substrate surface. These spacings do not correspond to Cu_2O , CuCN or either of the reported structures for CuH . It does not seem possible, either, to account for the extra spots by twinning of the copper lattice.

The pattern, Fig.17, from the deposit on the (110) face with the beam parallel to $[001]$ is indexed in Fig.18. Twinning does not seem to offer an explanation of the

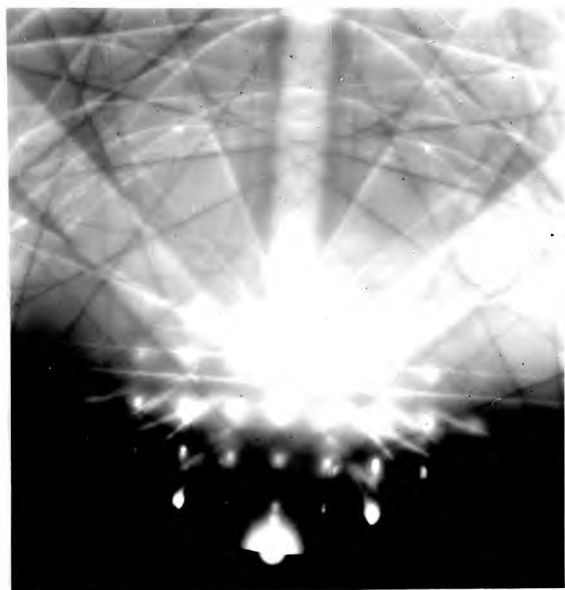


Fig.16. As Fig.14, but [100] azimuth.

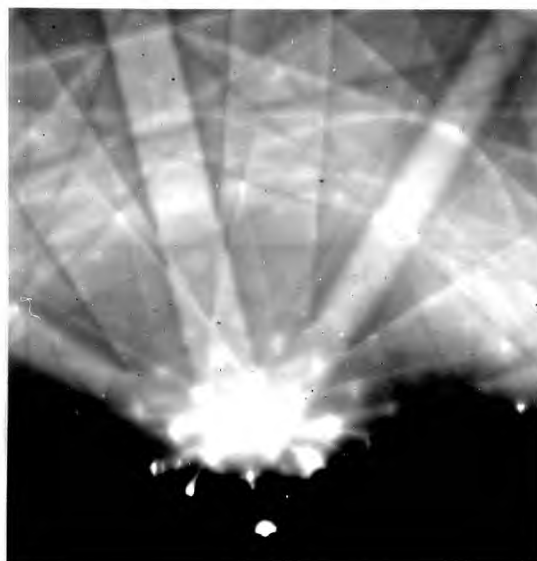


Fig.17. Copper from Bath 3 at 5 mA/cm² and 20°C. on copper (110) face, [001] azimuth.

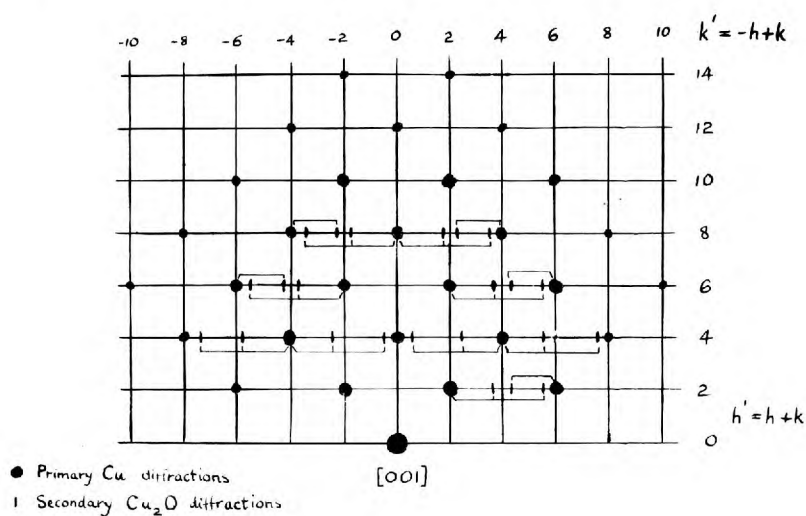


Fig.18. Indexing of Fig. 17.

appearance of the spots on the same horizontal layer lines as the copper spots. Double scattering seems the most likely explanation because of the symmetry of the additional spot pattern with respect to the strong copper diffractions lying on the zero order Laue zone. The origin of the spots would then be as indicated in Fig.18, and the spacing of the spots corresponds to an interplanar spacing in the direction perpendicular to the beam and parallel to the surface of 3.01 Å. This is very close to 3.04 Å., the (110) spacing in Cu_2O . There is also a pattern of diffuse spots near the undeflected beam position which indicates the formation ^{of} Cu_2O on the surface in parallel orientation.

Electrodeposition of Silver.

(a) Cyanide baths.

The experimental results for the electrodeposition of silver from cyanide baths are summarized in Table 3.

Attempts were made to deposit silver from a bath containing 35.5 g/l AgCN and 18 g/l KCN (1.75 g/l free KCN), but it was found that even at current densities as low as 1 mA/cm² the voltage across the bath rose rapidly to about 5 volts, and the anode became covered with a white film. Though deposits were formed on the cathode under these conditions, none of them gave diffraction patterns clear enough

Table 3.

Orientations in Silver Electrodeposited from Cyanide Baths on to
Polished Brass.

Bath Composition	AgCN KCN 33.5 23		AgCN KCN 33.5 35		AgCN KCN 33.5 35 K ₂ CO ₃ 34.5		AgCN KCN 33.5 35 KCl 37.25	
	Current Density mA/cm ²	Temp °C	20	60	20	60	20	60
1			VW(111)	?			?	
5			?	?	?	(111)T+ W(112)+ V(1010)	(111)T +W(1010)	
10				(111)T+ W(1010)		(111)T+ (112)+ (1010)	(111)T+ (112)+ (1010)	?
15				(111)T+ (112)+ (1010)		(111)T+ (112)+ (1010)		
20				?	VW(1010)	?	VW(1010)	?

(111)T Deposit crystals in (111) one-degree orientation twinned on {111} planes
W Weak orientation
VW Very weak orientation
? Indeterminate orientation.

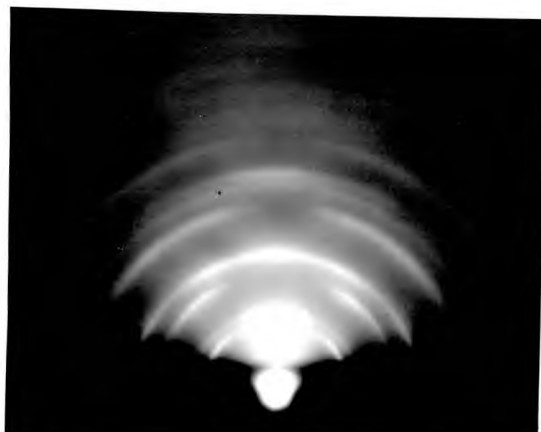


Fig.19. Silver deposited from cyanide bath with carbonate addition at 5 mA/cm^2 and 20°C . (111) orientation with {111} twinning.

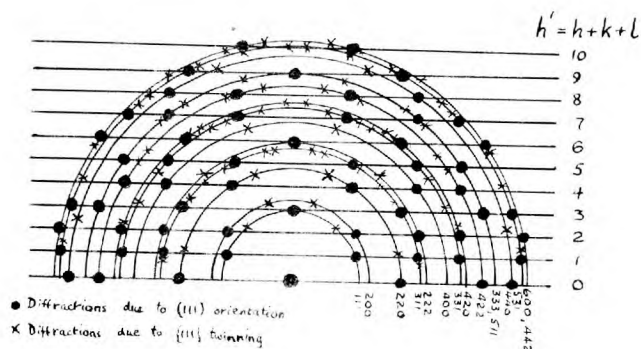


Fig.20. Theoretical diffraction pattern due to face-centred cubic lattice in one degree (111)-orientation with {111} twinning.

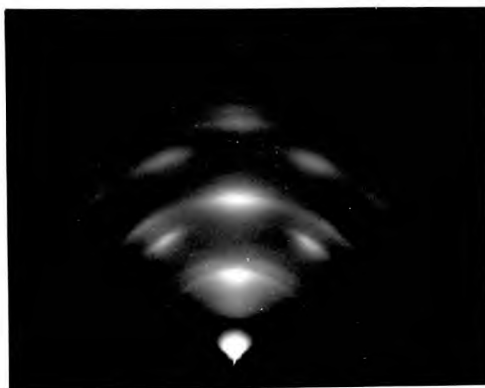


Fig.21. Silver deposited from cyanide bath with carbonate addition at 10 mA/cm² and 20°C. (10 $\bar{1}$ 0) orientation.

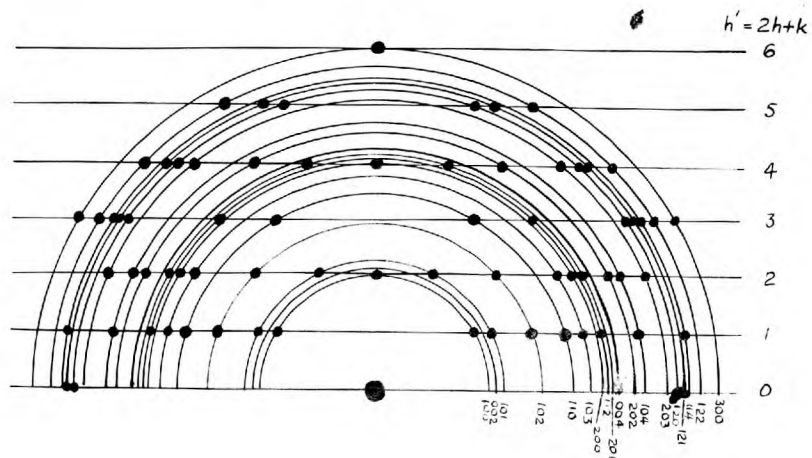


Fig.22. Theoretical diffraction pattern due to close-packed hexagonal lattice in one-degree (10 $\bar{1}$ 0) orientation.

to be of any use. Even with 23 g/l KCN, deposition could ^{not} ~~only~~ be satisfactorily carried out at cathode current densities greater than about 5 mA/cm² because the voltage rose rapidly. This polarisation was partly caused by the anode current density being too great since increasing the anode area alleviated the effect largely. It was still found, however, that the voltage across the bath tended to be somewhat high, and the cathode current efficiency rather low at higher current densities. With 35 g/l KCN the anode dissolution was satisfactory and deposition could be carried out at cathode current densities of as much as 20 mA/cm² without difficulty.

Deposits from all the three main silver baths (i.e. with 35 g/l KCN, and the same with added K₂CO₃ or KCl) showed the same general characteristics. At low current densities the deposit crystals were only weakly oriented, the orientation, which was not clearly identifiable, probably being (111). From deposits at slightly higher current densities, clearer diffraction patterns were obtained which showed that the crystals initially in (111) orientation had twinned on {111} planes (see Figs. 19 and 20). As the current density was further increased, deposits were obtained in which there were, besides the crystals in (111) orientation twinned on {111}, some crystals which had grown in a close-packed hexagonal lattice in (10 $\bar{1}$ 0) orientation (Figs. 21 and 22). At current

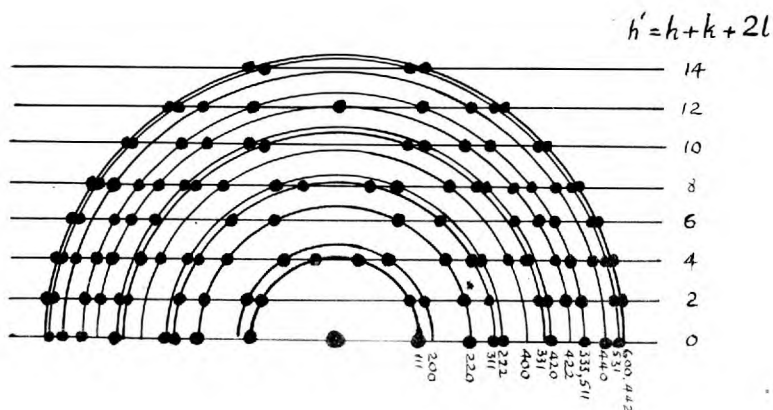


Fig.23. Theoretical diffraction pattern due to face-centred cubic lattice in one-degree (112) orientation.

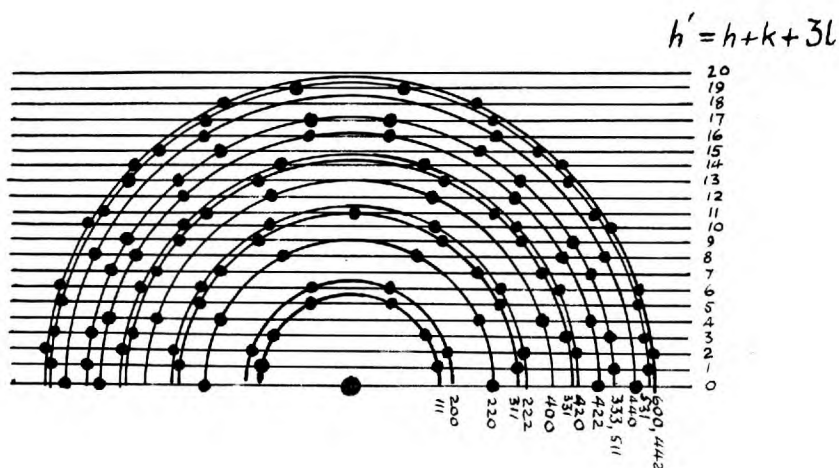


Fig.24. Theoretical diffraction pattern due to face-centred cubic lattice in one-degree (113) orientation.

densities higher still, the deposit crystals became only weakly oriented again.

The frequent occurrence of the hexagonal modification instead of the usual face-centred-cubic silver is of particular interest. In the corresponding diffraction patterns (Fig. 21) the spacing of the layer lines parallel to the shadow edge corresponds to hexagonal crystals oriented with the $\langle 210 \rangle$ atom rows, or cubic crystals oriented with the $\langle 112 \rangle$ atom rows, perpendicular to the specimen surface. (The planes to which these rows are normal are $\{10\bar{1}0\}$ and $\{112\}$ respectively). The atomic spacings in these two rows are identical in the two lattices. The corresponding theoretical one-degree orientation patterns are shown in Figs. 22 and 23. The strong arc nearest the central spot in the plane of incidence lies just inside the 111 cubic ring, and this, the spacing of the layer lines, and the fact that the second order arc in the plane of incidence appears to lie on, or just inside, the 311 cubic ring, prove that the main orientation is not (111) cubic. The disposition of the strong arcs in the plane of incidence show that the orientation is primarily $(10\bar{1}0)$ hexagonal rather than (112) cubic.

The appearance of a weak arc on the 111 cubic ring and the position of the arcs on the 200 cubic ring above the second horizontal layer line indicates that there is cubic

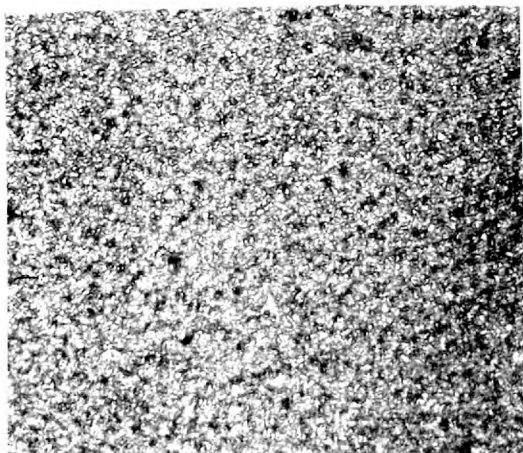


Fig.25. Silver deposited from cyanide bath with AgCN 33.5 g/l. and KCN 23 g/l at 1 mA/cm^2 and 20°C. x 600.

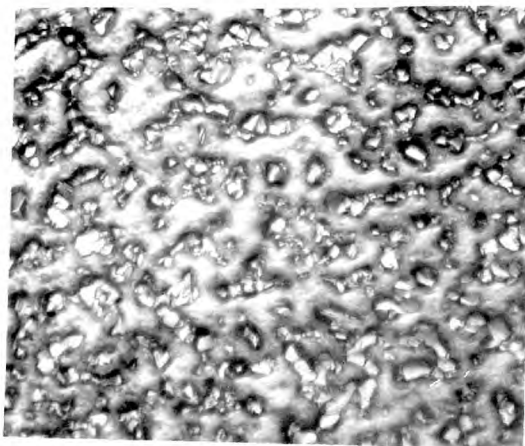


Fig.26. As Fig.25, but 60°C. x 600.

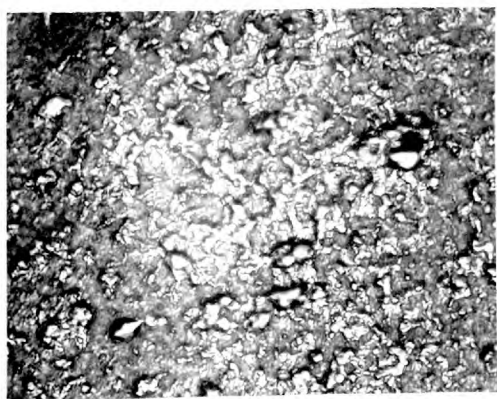


Fig.27. Silver deposited from cyanide bath with added carbonate at 1 mA/cm^2 and 60°C. x 600.

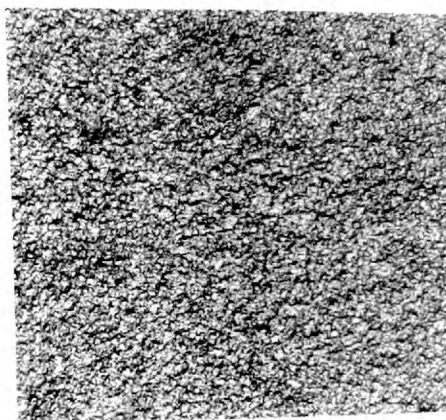


Fig.28. As Fig.27, but 20°C. x 600

silver in $\{111\}$ orientation twinned on $\{111\}$, since if all the cubic silver crystals were in $\{112\}$ orientation, all the arcs due to both the cubic and hexagonal modifications would lie on the same layer lines. The second arc in the plane of incidence is very close to the 311 cubic ring, but comparison of the pattern with Fig.24 makes it clear that $\{113\}$ cubic orientation does not occur among the deposit crystals. Not all the diffractions to be expected from $(10\bar{1}0)$ and (112) one-degree orientations appear in the patterns - the arcs on the even-order layer lines on the 101 hexagonal ring are absent, for example - and this can be explained as due to the crystals being well developed parallel to the most closely populated planes ($\{0001\}$ hexagonal and $\{111\}$ cubic).

In the first bath, the mean crystal size increased with increasing current density and with increasing temperature (Figs. 25 and 26). With a higher cyanide concentration, however, the increase of crystal size and surface roughness with increasing current density and temperature was only slight. The deposits from the baths with added carbonate or chloride showed very little variation in crystal size with current density, but the surfaces were rougher, and the crystals slightly larger, in deposits at 60°C . than in those at 20°C . (compare Figs. 27 and 28). The general appearance of the deposits from the simple potassium silver cyanide bath was a

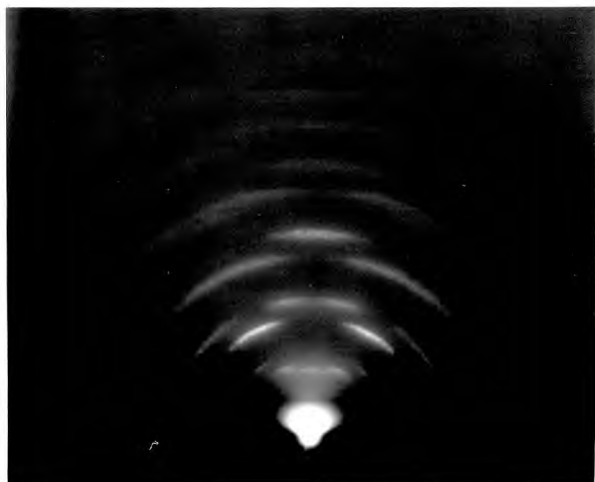


Fig.29. Silver deposited from thiosulphate bath at 3 mA/cm^2 and 20°C . (112) cubic and (10 $\bar{1}$ 0) hexagonal orientations.

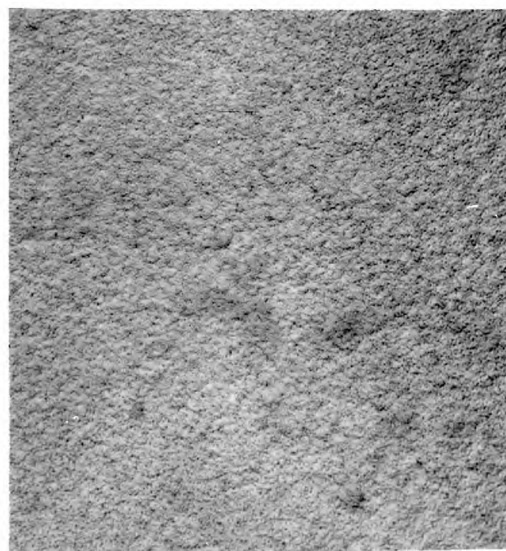


Fig.30. Silver deposited from thiosulphate bath at 5 mA/cm^2 and 20°C . x 600.



Fig.31. Silver deposited from K/4 silver nitrate solution in 10% water-dioxan mixture at 1 mA/cm^2 and 20°C . Weak (112) orientation.

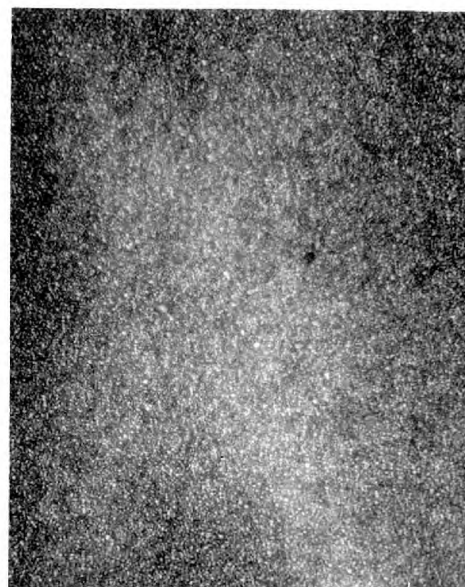


Fig.32. Micrograph of deposit of Fig. 31. x 600

smooth and glassy whiteness resembling glazed porcelain, whereas deposits from the baths containing added carbonate or chloride were semi-bright or had a satin sheen.

(b) Other complex baths.

The conductivity of the complex chloride baths was poor, and in spite of repeated attempts, good adherent deposits could not be obtained from them.

Good deposits were readily obtained from the complex thiosulphate baths. The solutions, however, were not very stable and sulphur was slowly, but continuously, precipitated from them. Sulphur may, perhaps, have been included in some of the deposits, since some of them appeared to have a yellow tinge when viewed at certain angles. With 36 g/l AgCl and 120 g/l $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, strong (110) orientation was found in deposits at 5 mA/cm². With the sodium thiosulphate concentration increased to 150 g/l, strong (10 $\bar{1}$ 0) hexagonal and (112) cubic orientations were observed in deposits at lower current densities of 1 and 3 mA/cm² (Fig.29). At 8 mA/cm² in this latter bath, the deposit consisted of randomly disposed crystals. The appearance of the surfaces of these deposits under the microscope, Fig.30, was very similar to that of smooth deposits from the cyanide baths (cf. Fig.28, for example).

(c) Nitrate baths.

Earlier work [13] with N/2 and N/10 silver nitrate solutions had shown that the ionic concentration immediately next to the cathode had an important effect on the growth of the crystals in the deposit. In the present case, similar solutions with small additions of nitric acid, or with the addition of almost enough sodium nitrate or potassium nitrate to saturate the solution were used. Although deposits having a small crystal size were readily obtained at moderate current densities from the baths with a large addition of nitrate, the deposits were rather loose and usually mostly dislodged from the cathode during washing.

The conductivity of the solutions in water-dioxan mixtures was not very high (the potential difference across the bath was about 4 volts at a current density of 4 mA/cm^2). Fairly smooth deposits, matt in appearance, were readily obtained from these baths on silver sheet, or silver-plated brass discs. At current densities of 1 and 2 mA/cm^2 the deposit crystals were in weak (112) orientation (Fig.31). The deposits consisted of small discrete crystals clearly visible under the microscope (Fig.32).

It was found that after about 24 hours a very fine dark precipitate was being slowly formed in the water-dioxan baths. The solution was filtered, and the precipitate examined by

electron diffraction. This showed (Fig.33 and Table 4) that the precipitate was silver. It is interesting to note that Skarulis and Ricci [76] obtained by crystallisation from solutions of silver nitrate in water-dioxan mixtures a solid dioxenate to which they gave the tentative formula $(\text{AgNO}_3)_8 \cdot \text{C}_4\text{H}_8\text{O}_2$.

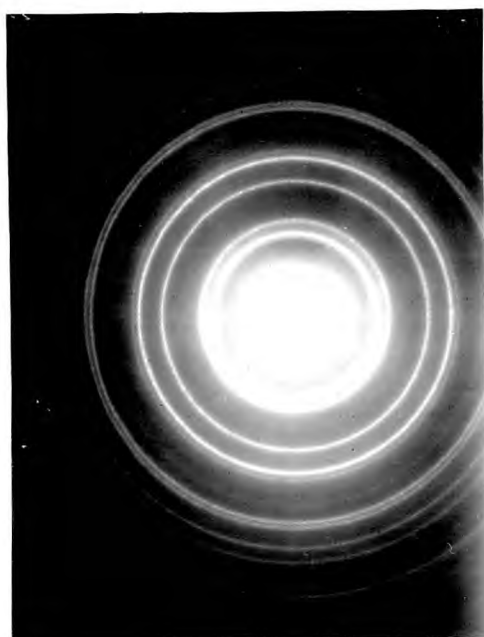


Fig.33. Diffraction pattern due to precipitate from solution of silver nitrate in water-dioxan mixture, normal transmission.

Table 4.

Identification of substance giving rise to diffraction pattern of Figure 33.

Voltage = 50 KV.

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

$L = 47.5 \text{ cm.}$

Observed		ASTM. Data. for silver		
d(Å)	Intensity	d	I/I ₁	hkl
2.36	VS	2.37	100	111
2.04	M	2.05	80	200
1.44	M	1.44	80	220
1.23	S	1.23	90	311
1.18	MF	1.18	50	222
1.02	F	1.02	20	400
0.93	M	0.94	60	331
0.905	M	0.91	60	420
0.827	MF	0.83	40	422
0.778	MF	0.79	40	333, 511
0.714	VF	0.72	10	440

S = strong; M = medium; F = faint; V = very.

DISCUSSION.

The results are most conveniently considered and their bearing on the problem of cathodic crystal growth discussed under separate headings, and the conclusions summarized at the end.

(a). Effect of current density and its distribution.

The effect of current density on crystal orientation has been previously discussed [6], and in many cases an increase in the current density leads to a change in the mode of growth of the deposit crystals from the lateral mode to the outward mode. The change from (100) orientation to (110) orientation in copper deposits from bath 3 at 20°C. and 5mA/cm² and 10mA/cm² respectively is an example of such a transition.

The complexity of the copper deposit from bath 3 at 60°C. and 10 mA/cm² is possibly due to inequality of the current density distribution. From a theoretical analysis, Wagner [77] has shown that greater uniformity of current at different parts of the cathode is to be expected at low current densities. As the mean current density is increased, a larger proportion of the current is carried by the edges and corners of the cathode. The occurrence of (111) and (100) orientations in the deposit under consideration suggests that on this particular specimen the actual current density at the middle of the surface was

lower than the current densities in the middle of the surfaces of the deposits formed at lower average current densities under conditions otherwise the same.

(b). Occurrence of hexagonal modifications of copper and silver.

Hexagonal copper was found in some deposits, and hexagonal silver was frequently found in the deposits prepared under the conditions described in the previous part of the thesis.

The reason for some metals growing in close-packed hexagonal lattices rather than face-centred cubic ones is not fully understood. Some hexagonal metals, e.g. cadmium and zinc, have an axial ratio considerably different from 1.63, which corresponds to the hexagonal close-packing of spheres, and the lattices of these metals in fact correspond to the close-packing of spheroids. This has been explained by Hume-Rothery [78] as being due to incomplete ionization of the atoms in the crystal lattices. In the present cases of copper and silver, the axial ratio of the hexagonal cell is 1.63, and the lengths of the axes are such that, within the experimental errors, the atoms in the hexagonal lattice have the same radius as they do in the cubic one. It is, perhaps, significant that three metals, cerium, cobalt and thallium, which normally crystallize in close-packed hexagonal lattices with axial ratios very close to 1.63 are dimorphic and show face-centred cubic modifications.

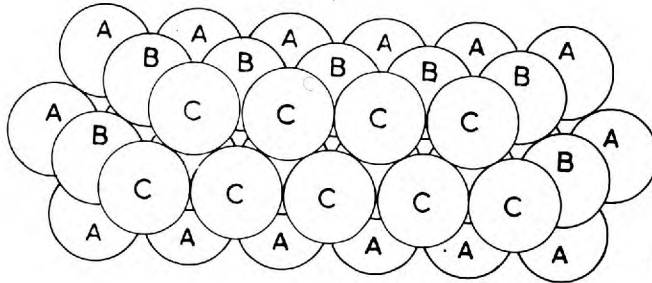


Fig.34. Cubic close packing
of spheres.
Plan on (111) plane.

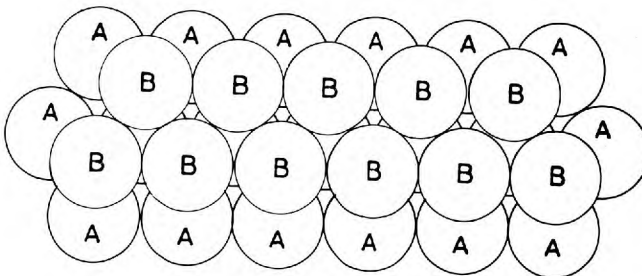


Fig.35. Hexagonal close packing
of spheres.
Plan on (0001) plane.

(c) Relation between cubic and hexagonal close-packed lattices.

Both the face-centred cubic lattice and the close-packed hexagonal lattice represent the closest possible packing of spheres so that each sphere is surrounded by twelve equidistant neighbours. Assuming that the atoms have the same effective radius in both lattices, the relationship between the axes of the lattices is given by

$$a_h = a_c/\sqrt{2} \quad \text{and} \quad c_h = \sqrt{8/3} \cdot a_h = 2a_c/\sqrt{3}$$

where the suffices h and c refer to the hexagonal and cubic lattices respectively.

The interplanar spacing, d_{hkl} , for the (hkl) planes is given by

$$1/d_{hkl}^2 = 1/a_c^2 (h^2 + k^2 + l^2) \text{ for the cubic lattice, and}$$

$$\begin{aligned} 1/d_{hkl}^2 &= 4/3 a_h^2 (h^2 + k^2 + hk) + l^2/c_h^2 \\ &= 1/a_c^2 [8/3(h^2 + k^2 + hk) + 3/4 l^2] \end{aligned}$$

for the hexagonal lattice.

The difference between the cubic and hexagonal close packing of spheres can be recognized by reference to Figures 34 and 35. The circles marked A represent a closely packed layer of spheres, and those marked B represent a second such layer placed on the first in such a way that each sphere is over a space in the first layer and in contact with three spheres A.

The third layer may now be placed in one of two positions relative to the first two layers: either each sphere may be placed directly over a sphere A, or the spheres C may each be placed over the spaces between the spheres A which were not covered by the spheres B. The former arrangement consists of alternate layers ABAB.... and results in a close-packed hexagonal lattice, and the second arrangement consists of a sequence of layers ABCABC.... and gives a face-centred cubic lattice. These layers clearly correspond to the layers of closest atomic packing which are the basal (0001) planes in the hexagonal lattice and the octahedral (111) planes in the face-centred cubic lattice. The directions of closest atomic spacing in these planes are respectively [100] and [110].

(d) Possible origin of hexagonal modifications.

(i) Twinning. Twinning in face-centred cubic metals is generally on $\{111\}$ planes, and produces a reversal of the stacking sequence of the densely packed layers, e.g. ABCABC*BACBA... (twinning has occurred here on the plane C*). It will be noticed that the twin-plane and the planes each side of it are equivalent to a small region of hexagonal close packing, and therefore, if for any reason the crystals undergo frequent twinning during the course of their growth, the deposit will contain a large proportion of metal in a what is tantamount to a close-packed hexagonal lattice in an

orientation equivalent to that of the cubic lattice. (The orientations are equivalent in the sense that the most densely packed planes of the two lattices are parallel and the most densely packed atom rows in these planes are also parallel).

The simultaneous occurrence of (112) cubic and (10 $\bar{1}$ 0) hexagonal orientations might therefore be due to repeated lamellar twinning (or repeated stacking faults) of deposit crystals originally in (112) orientation. Repeated {111} twinning in thin lamellae or in cyclic groups of five is very common in copper [79]. Many of the diffraction patterns clearly indicate, however, that there is a large proportion of material in the close-packed hexagonal form, and it seems reasonable to suppose that it grew in that way without twinning.

Quarrell's explanation [29] of the bands occurring in some transmission patterns from electrodeposited metals as being due to a gradual transition from a hexagonal lattice in the initial layers of the deposit to a cubic one at greater thicknesses is possible, but it seems more probable that generally the bands are related to the streaks which some patterns exhibit (see above, page 6). These streaks were due to twinning, together with flexural distortion, of the deposit crystals.

Frequent twinning of the crystals on {111} planes to form thin lamellae will result in the reciprocal lattice points

being very much extended along the cube diagonals so that the latter become effectively continuous. Distortion of the deposit crystals, corresponding to a rotation about an appropriate axis, will then result in a series of continuous hyperbolas appearing on the photographic plate [80]. The closest the vertices of these hyperbolas can approach the central spot corresponds to the perpendicular distance between two adjacent parallel cube diagonals in the reciprocal lattice. This distance is $\sqrt{8/3} \cdot a^*$, which corresponds to the 100 diffraction from a close-packed hexagonal lattice built up of atoms with the same radius. If the original crystals of the deposit are randomly disposed, then the streaks due to the various crystals in all possible orientations will merge into a continuous band with a sharp edge at a distance from the central spot corresponding to the 100 hexagonal ring position.

Though this explanation of the origin of the bands observed in some patterns by Sun and Quarrell may be the true one in many cases, the present work proves that hexagonal modifications of copper and silver do actually occur extensively under some circumstances.

Furthermore, although $\{111\}$ twinning of cubic crystals in (111) one-degree orientation was observed in some deposits, and though repeated lamellar $\{111\}$ twinning of cubic crystals in (112) one-degree orientation would account for the

simultaneous occurrence of some layers of hexagonal structure in $(10\bar{1}0)$ orientation, it is not possible to account for the appearance of (112) cubic orientation by $\{111\}$ twinning from an initial orientation which was either (111) or (110) even if allowance is made for the imperfection of the initial orientation as shown by the angular spread of the arcs in the diffraction patterns.

(ii) Inclusion of non-metallic material. In the cases of nickel and chromium it was found by Yang [32] and by Wright, Hirst and Riley [28] respectively that the deposits with a hexagonal structure had considerable quantities of hydrogen included, and the fact that hexagonal cobalt is obtained from baths with a low pH suggests that in this case also the inclusion of hydrogen is associated with the occurrence of the hexagonal modification. No evidence of the occurrence of copper hydride, CuH , in copper deposits was found in the present work, and the existence of a solid silver hydride is very doubtful [81]. It is possible, however, that the inclusion of non-metallic materials other than hydrogen, such as oxides or cyanides, could affect the growth and structure of electro-deposited metals. Evidence of the inclusion of cuprous oxide was found in both polycrystalline and single-crystal copper deposits, and the observed epitaxial growth of Cu_2O on the single crystal faces shows how readily the oxide could be

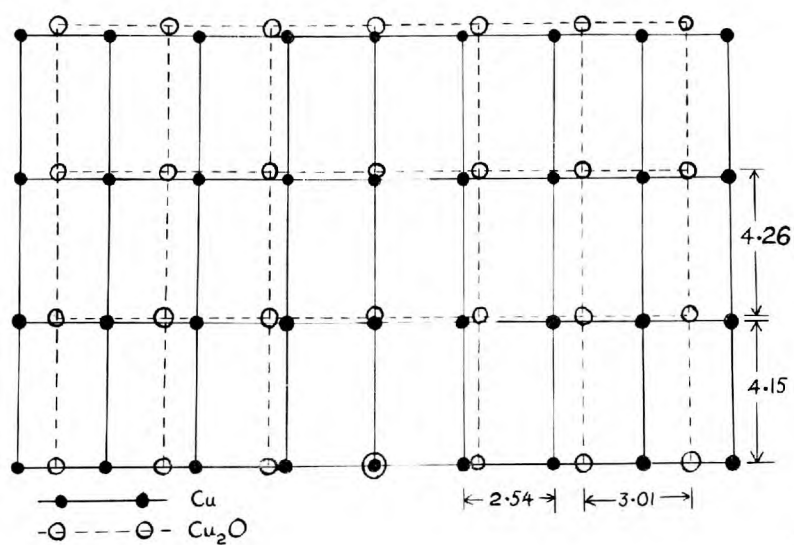


Fig.36. Atomic fitting between Cu₂O (110) plane and Cu (1010) plane.

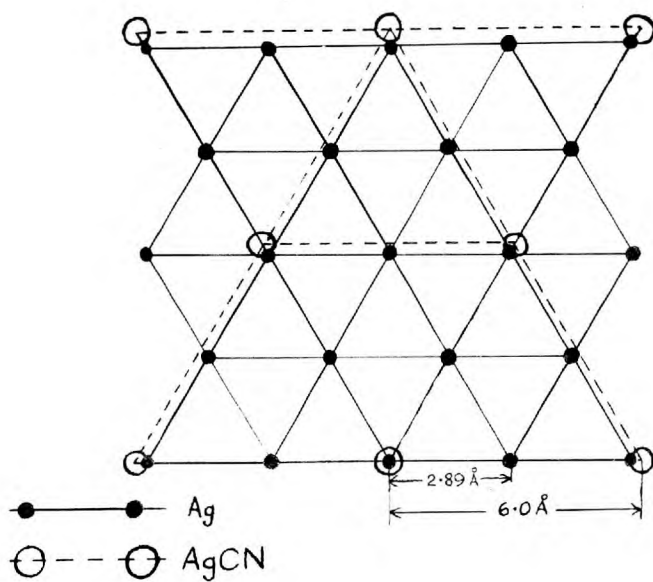


Fig.37. Atomic fitting between AgCN(0001) plane and Ag(111) plane.

formed on the growing crystals and included throughout the deposit.

It has been found by the present author, and by other workers [⁶⁷82,83], that Cu_2O grows on the copper (110) face in parallel orientation. The occurrence of hexagonal copper in $(10\bar{1}0)$ orientation in deposits from bath 2 at 60°C . and 10 mA/cm^2 may therefore be caused by the growth of Cu_2O crystals on the (110) faces of copper which are parallel to the substrate. Copper subsequently deposited on this oxide layer might then tend to grow in the hexagonal form in $(10\bar{1}0)$ orientation because of better atomic fitting rather than in the original cubic form. The atomic fittings across the interfaces under such circumstances are shown in Figure 36. Support for this explanation is afforded by the deposit on the single crystal (110) face under outward growth conditions where copper in $(10\bar{1}0)$ orientation occurred with the [001] hexagonal row parallel to the [001] row of the substrate (cubic) crystal (see page 33).

Ag_2O has the same type of structure as Cu_2O , and the formation of oxide might account for the occurrence of hexagonal silver in $(10\bar{1}0)$ orientation in a similar manner. Some diffractions which might have been due to Ag_2O have been noticed in some of the silver patterns, but the evidence for the inclusion of oxide in silver deposits is not conclusive. The

baths used had a pH of about 10, so the precipitation of Ag_2O from these solutions at the cathode is possible.

It is possible that cubic silver in (112) orientation or hexagonal silver in $(10\bar{1}0)$ orientation could be caused by the adsorption of AgCN on the growing crystal faces. The reported structure of AgCN is hexagonal with $a_0 = 3.88 \text{ \AA}$ and $\alpha = 101^\circ 11'$ [85]. This gives $a_h = 6.0 \text{ \AA}$. and $c = 26.1^{5.2} \text{ \AA}$. The atom spacing along [110] of silver is $2.89 \text{ \AA}$., so the atomic fittings between the (0001) plane of AgCN and the (111) plane of silver, as shown in Figure 37, is quite close. The AgCN crystal is built up of parallel rectilinear chains $-\text{Ag}-\text{C}\equiv\text{N}-\text{Ag}-\text{C}$ etc., the distance between successive silver atoms being $5.26 \text{ \AA}$. [85]. The spacing along the [112] cubic and the [210] hexagonal rows of silver is $5.0 \text{ \AA}$., and these rows lie in the most densely populated planes of the respective lattices. Hence, if AgCN were adsorbed on the ~~growing~~^{silver} crystals/^{growing} in (111) orientation with the (0001) planes of AgCN in contact with the (111) planes of silver, then subsequent deposit crystals might tend to grow with their most densely populated planes perpendicular to the substrate and with the atom row whose spacing most nearly corresponds to the Ag-Ag spacing in the c-direction of AgCN normal to the substrate.

The adsorption of cyanide is not the most probable explanation of the occurrence of (112) cubic and $(10\bar{1}0)$

hexagonal orientations, however, since these orientations were also observed in silver electrodeposited from the complex thiosulphate baths. Furthermore, weak (112) orientation was observed in deposits from silver nitrate solutions in water-dioxan mixtures. Electron diffraction examination did not reveal the presence of any material other than silver in the deposits from the nitrate baths, but minute traces of non-metallic ~~water~~^t might nevertheless have been included.

(e) Effect of ion-association and formation of complex ions.

It is clear from the results of the experiments on the deposition of silver from silver nitrate solutions in water-dioxan mixtures, and from aqueous solutions with large additions of potassium or sodium nitrate, that the crystal size in electrodeposited metals can be decreased by increasing the ion-association of the electrolyte.

Sarkisov [86] has investigated the variation in the crystal size of silver electrodeposited on to a platinum cathode from $N/4$ solutions of $AgNO_3$ in water, or water mixed with methyl alcohol, ethyl alcohol or pyridine. (The last three solvents have a lower dielectric constant than pure water). He found the product of n th number of nuclei formed under constant conditions and the dielectric constant of the solvent to be approximately constant except in the case of the solution

containing pyridine. The variation in the number of nuclei formed was attributed by Sarkisov to the formation of complex anions $\text{Ag}(\text{NO}_3)_2^-$ in the alcoholic solutions. This seems unlikely, however, since, as Koch [87] has pointed out, the formation of complex anions of a binary electrolyte in solution is only to be expected if the solvent molecules specifically interact with the cations. Koch has also shown [88] that molecules containing ammoniacal or nitrile groups are much more strongly attracted to Ag^+ ions than molecules with hydroxyl or ketonic groups, and it therefore seems probable that of the four solutions used by Sarkisov, only that containing pyridine would have had $\text{Ag}(\text{NO}_3)_2^-$ ions formed in it to any appreciable extent. The results of transport experiments carried out by Abegg and Heustadt in 1909 [89] suggested the existence of $\text{Ag}(\text{NO}_3)_2^-$ ions in solutions of AgNO_3 in pyridine.

When cations and anions are associated in solution, they are held together by ionic bonds similar to those which bind them in the solid state. Solvation is the result of interaction or attraction between the ions and the solvent molecules filling the unsatisfied bonds of the ions. When a metal cation exists in solution as part of a stable complex ion, the same complex ion is found to exist as an entity in solid salts. From a general consideration of the interactions

between ions and solvent molecules, Koch [90] concluded that complex formation and solvation were not basically different.

If it is postulated that the deposition of metals from complex solutions is by the discharge of simple cations, then, since the probable life of a simple cation in such a solution is very short, dissociation of the complex must occur very close to the point at which the metal ion is to be discharged. Dissociation of the complex ion and discharge of the simple cation may thus be regarded as successive stages of what would be virtually one process. The alternative theory of deposition of the metal by the discharge of the complex ion also involves the decomposition of the complex ion. The basic difference between the two theories is that the former supposes the complex to dissociate spontaneously to yield a free metal ion to be discharged, and the latter supposes the complex to decompose as a result of the addition to it of a negative charge from the cathode. Although the experimental evidence available at the present time is not completely conclusive as to which of these mechanisms actually occurs, it seems more probable that metals are deposited by the direct discharge of the complex ions.

Smooth deposits with a matt appearance and fairly small crystal size were obtainable from all the solutions containing complex ions, but in some instances very large crystals were deposited. This occurrence of large crystals

shows that the effect of the energy "hump" over which a metal ion has to pass in the discharge process on the crystal size in electrodeposits is, at the most, of only minor importance. Nevertheless, the binding of simple cations by solvent molecules, anions, or in complex ions will probably have some effect on the rate at which the ions can be discharged at the cathode.

(f) Rate of ion-discharge.

(i) Evidence for the existence of a slow stage. Gardam [91] has measured the variation of cathode potential with current density during the electrolysis of argentocyanide, copper sulphate and nickel sulphate solutions. He found that in the first two cases, the cathode potential was directly proportional to the current density at low current densities, but at higher current densities with these solutions, and throughout the current density range with the nickel sulphate solution, the cathode potential was proportional to the logarithm of the current density.

This is the type of relationship between cathode potential and current density to be expected if there is a slow stage in the discharge of the ions. According to the theory of rate process [92], for a sheet of metal immersed in a solution of one of its salts and at its reversible potential in the solution, the cathodic current due to ions deposited on the

metal from the solution is given, for univalent ions, by $I_c = F k_1 a_+ e^{\alpha FE/RT}$, and the anodic current due to the dissolution of the metal is similarly given by $I_a = F k_2 e^{-(1-\alpha)FE/RT}$. In these equations, k_1 and k_2 are specific reaction velocities of the cathodic and anodic reactions respectively, a_+ is the activity of the cations in the solution, E is the reversible potential, and α is a factor between zero and unity. Since the metal is under equilibrium conditions, these two currents are equal and can both be designated I_0 . If the metal sheet is made cathodic it will have a new potential $E' = E + w$, and w is defined as the overvoltage. The new cathodic and anodic currents are now given by

$$I_c = F k_1 a_+ e^{\alpha FE'/RT} \quad \text{and} \quad I_a = F k_2 e^{-(1-\alpha)FE'/RT}$$

The net current of deposition is therefore

$$\begin{aligned} I = I_c - I_a &= F [k_1 a_+ e^{\alpha FE/RT} e^{\alpha Fw/RT} - k_2 e^{-(1-\alpha)FE/RT} e^{-(1-\alpha)Fw/RT}] \\ &= I_0 [e^{\alpha Fw/RT} - e^{-(1-\alpha)Fw/RT}] \end{aligned}$$

If w is small, then on expanding the exponentials all the terms except the first of the expansion can be neglected giving

$$I = I_0 \frac{Fw}{RT}$$

$$w = \frac{RT}{F} \frac{I}{I_0}$$

$$\text{i.e. } w = \text{const.} \times I$$

For larger values of w , this simplification is not valid, but since $e^{\alpha Fw/RT}$ increases rapidly with w whereas $e^{-(1-\alpha)Fw/RT}$ decreases, the latter term can be neglected in comparison with the former, giving

$$I = I_0 e^{\alpha Fw/RT}$$

$$w = \frac{RT}{\alpha F} \ln I - \frac{RT}{\alpha F} \ln I_0 \quad \text{i.e. } w = \text{const.} + \frac{RT}{\alpha F} \ln I$$

Gardam's results would therefore seem to indicate that there is a slow stage in metal deposition, at least in the three cases he studied. At high current densities, the rate of diffusion of the metal containing ions to the cathode will always be the limiting factor, and the cathode potential will then be given by an equation of the form

$$E = \frac{RT}{F} \ln \frac{I_d}{I_d - I}$$

for univalent ions, where I_d is the current density when the ions diffusing to the cathode at their maximum rate, are discharged [93]. An equation of this form was found by Levin [94] to be satisfied in the deposition of silver from complex electrolytes containing $[\text{Ag}(\text{NH}_3)_2]_2\text{SO}_4$, $\text{K}_2[\text{Ag}(\text{CN})_4]$ or $\text{K}_3[\text{AgI}_4]$.

(ii) Possible slow stages and their effect on crystal growth.

Possible slow stages in the overall deposition process, i.e. the transition from the metal ion in solution to the atom in the crystal lattice, are (1) removal of the ion from its atmosphere of solvent molecules or associated ions, or from a complex ion,

(2) neutralisation of the ion, and (3) incorporation of the discharged atom into the growing crystal lattice. If (1) is the slow stage, an ion discharged and deposited in a metastable position would have a very small chance of re-entering the solution and being deposited again elsewhere. Provided, however, that the other stages occur rapidly, the growth of large crystals should not be prevented because atoms in metastable positions could migrate to more stable ones.

The neutralisation of ions, stage (2), i.e. the transfer of charge from the cathode to the ions, probably occurs rapidly in most cases. Heyrovsky's polarographic work [95], however, suggests that this stage may be slow in the deposition of the transition elements. It further showed that when the electrolytic solution contained deformable anions, the process appeared to be hastened and to occur reversibly. Even if the neutralisation of the ions does occur slowly, the crystal size will not be affected provided stage (3) occurs rapidly.

If stage (3), the incorporation of deposited atoms, is slow, atoms deposited in metastable positions would have a high probability of becoming ionized again and re-entering the solution except at high current densities when the large overvoltage due to the slow stage would tend to inhibit the passage of ions from the cathode to the solution. Except, possibly, at very low current densities, the growth of large

crystals would be impossible because the rate of deposition of atoms would exceed their rate of incorporation into the existing lattices, and the continual formation of fresh nuclei would therefore be favoured.

Glasstone has suggested [96] that since the valency electrons of the transition elements are known to have a tendency to enter higher energy orbits than their normal stable ones, the inherent deposition overvoltage of iron, nickel and cobalt may be due to the atoms of these elements being initially deposited in an excited state and slowly reverting to normal. If this explanation be correct, it would result in the incorporation of the atoms of these elements into the crystal lattice being slow since they would not immediately be able to form their usual bonds with neighbouring atoms.

The most usual cause of slow incorporation, however, is probably low mobility of the atoms over the crystal faces on the cathode. That the atoms can move over the surface is shown by the work of Schwarz[^] [97] who found that polonium atoms deposited on silver had a measurable mobility even at room temperature. (The ions in solution have, of course, a much higher mobility than the atoms on the cathode surface). The mobility of the atoms over the surface would be greatly reduced by adsorption or co-deposition of non-metallic material on the cathode. The presence of such foreign matter, especially if

adsorbed, will also hinder the incorporation of atoms in the lattice since the materials will generally be most strongly retained in the sites of lowest potential energy which would otherwise be occupied by metal atoms.

(g). Effect of adsorbed non-metallic material on crystal growth

It is to be expected that, if conditions allow, crystals deposited on an inert substrate will grow with a most densely populated atom plane parallel to the substrate since such an arrangement has least potential energy. This mode of growth (lateral growth) may be prevented by an inadequate supply of ions to the cathode [6]. Even when the supply of ions is high enough, lateral growth may be prevented by adsorption or co-deposition of non-metallic material at growing steps of the deposit crystals. As a result, an orientation such that a somewhat less densely populated plane is parallel to the substrate may occur. Outward growth may also be modified by a similar inhibiting process. The occurrence of (113) and (112) orientations in iron electro-deposited from chloride baths is an example of such a modification, and the relative rates of discharge of the ferrous and hydrogen ions are probably important in this case [13].

Further evidence of such modification to a pronounced orientation is the effect of a small quantity of CS_2 added to

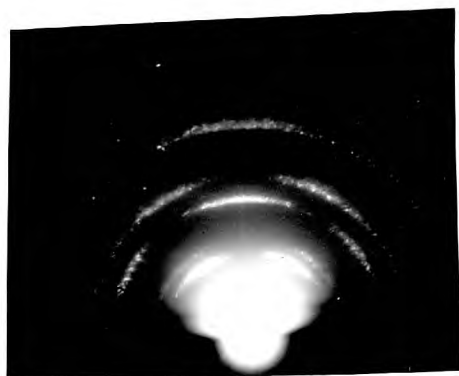


Fig. 38. Silver from cyanide bath with carbonate addition. Pronounced outward growth.



Fig. 40. Silver deposited under same conditions as for Fig. 38, but with CS_2 added to the bath.

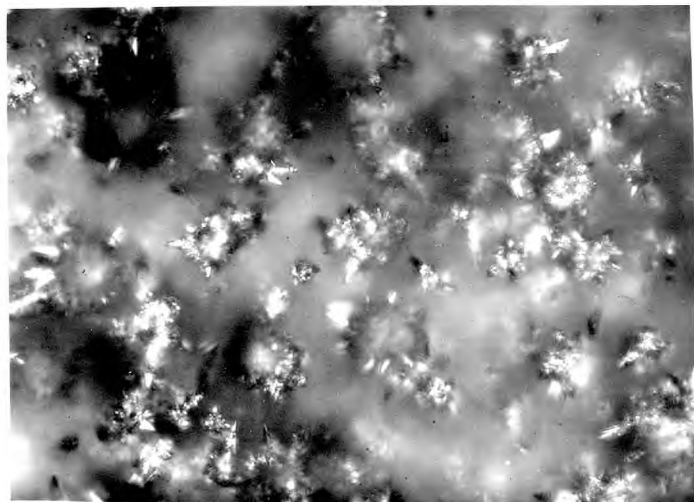


Fig. 39. Micrograph of deposit of Figure 38. x 155

an argentocyanide bath on the crystal growth of deposits. Under conditions very favourable to outward growth, the predominant orientation was (110), Figure 38. The spottiness of the rings of this pattern showed that the crystal size was large, and a micrograph of the surface, Figure 39, revealed the development of many needle-like crystals. With about 0.1% CS_2 added to the bath, however, a deposit produced under otherwise identical conditions presented a semi-bright appearance and consisted of randomly disposed crystals whose size, estimated from the diffraction pattern (Figure 40), was about 50 Å.

Since the crystal size is largely independent of the binding energy of the complex ions or cation-solvent clusters from which the metal is deposited (see above, page 55), and also virtually independent of the rate of the first two stages in the deposition process, it must be concluded that, in the absence of any specific substrate influence, the crystal size is chiefly determined by the rate at which the deposited atoms can be incorporated into the growing crystal lattice. This in turn will largely depend on the adsorption, co-deposition or chemical formation of non-metallic matter on the cathode. The crystal size is, of course, dependent to some extent on the number of nuclei initially formed per unit area, but if the bath conditions are such as to permit the growth of

large crystals, then those nuclei which are most favourably oriented will grow more rapidly than the others. The crystal size at the surface of thick deposits will therefore be determined by the rate of growth of individual crystals, and this in turn will be governed by the bath conditions and the extent of adsorption and inclusion of foreign matter in the deposit.

According to Raub and Wullhorst [40], the inclusion of cyanide in deposits from complex cyanide baths should be decreased by (i) increasing the current density, (ii) increasing the concentration of CN^- ions, and (iii) increasing the temperature. No such general relations between crystal size and these three variables were found in the present work. Since, however, it seems probable that the inclusion of oxides are of chief importance in the present experiments, the conclusions of Raub and Wullhorst concerning the adsorption of cyanides may still be valid.

GENERAL CONCLUSIONS.

Previous studies by Finch and his collaborators of the structure, orientation and size of the crystals in electrodeposits, and the dependence of these factors on the bath conditions, have shown that the crystal orientation is primarily determined by the concentration of the metal-containing ions at the cathode surface. In some cases however, the co-deposition or adsorption of non-metallic material, such as hydrogen for example, was found to modify the orientation and even, sometimes, the structure of the electrodeposited metal.

The present experiments are an extension of the previous work to investigate the effects of the presence of complex ions, and of increased ion-association in the electrolytic solutions, on the electrodeposited metals. It has been found that the crystal size of silver electrodeposited from silver nitrate solutions is decreased by increasing the ion-association in the electrolyte. A small crystal size was usually found in metals electrodeposited from solutions containing complex ions, but in some cases very large crystals were found to occur in both copper and silver deposited from cyanide baths. These facts indicate that the retention of the metal in solution in complex ions does not have a large direct influence on the crystal size of the electrodeposited metal.

The present experiments also revealed that both copper and silver are sometimes electrodeposited with a close-packed hexagonal structure instead of the usual face-centred cubic one. This modification of the structure might be the result of repeated lamellar twinning of the deposit crystals or it might be caused by adsorbed non-metallic material on the growing crystals modifying the crystal orientation and structure. It seems most probable that the modifications are due to the precipitation and inclusion in the deposit of an oxide. No evidence for the existence of a definite hydride of either copper or silver was found in any of the deposits, though hydrogen co-deposited with the metal could affect the growth and possibly even the structure of the metal crystals without forming a compound with the metal.

It has been known for many years that the addition of small quantities of various materials, either organic or inorganic, to electrolytic solutions can profoundly affect the physical appearance of electrodeposited metals. Such addition agents are commonly used in commercial practice in order to obtain bright electrodeposits and thereby eliminate, or at least reduce, the need for subsequent polishing. These addition agents may affect the bulk diffusion of the ions, or they may by adsorption on the ions or the cathode affect the actual process of ion discharge, or they may be adsorbed on the

cathode surface and affect the manner of growth of the crystals. The modes of operation of different types of addition agents are therefore probably quite different.

As has been shown in the present work, the use of solutions of complex ions does not always result in a small crystal size in the electrodeposited metal, but in such solutions the rise in cathode potential with current density is greater than in solutions of simple salts and a more uniform distribution of current density over the cathode surface is therefore obtained. The small crystal size usually associated with deposition from complex solutions is probably due to the co-deposition or inclusion of non-metallic matter in the electrodeposited metal. It is commonly supposed that the adsorption of cyanides occurs in deposits from complex cyanide baths, but since such solutions are always alkaline, the precipitation of oxides is to be expected.

It can be concluded that the orientations sometimes observed which are not characteristic of either simple outward or lateral growth are due to the adsorption or inclusion of non-metallic material having altered the mode of growth of the deposit crystals. In the absence of any specific substrate influence, the crystal size in electrodeposited metals is also chiefly determined by the presence of foreign material.

Further research directed towards a systematic study of the effect of various addition agents in electrolytic solutions on crystal habit, orientation and size of electrodeposited metals should lead to results of great interest and importance.

APPENDIX.

Derivation of theoretical one-degree orientation reflection patterns.

If the crystals of a deposit are so oriented that they have an axis $[UVW]$ perpendicular to the substrate, but with random azimuthal distribution about this axis, the resulting diffraction pattern will consist of spots lying at appropriate intersections of the Debye-Scherrer ring positions with layer lines parallel to the shadow edge. These layer lines are spaced apart by a distance $\lambda L/T_{UVW}$ where λ = wavelength of the electron beam, L = camera length and T_{UVW} = lattice translation along the direction $[UVW]$. The spots on the hkl ring position will appear at the intersections of this ring with the layer line of order h' where

$$h' = Uh + Vk + Wl \quad (1)$$

Account must be taken of all permutations of $\pm h$, $\pm k$ and $\pm l$ which correspond to symmetrically equivalent planes.

If (HKL) is the crystal plane perpendicular to the axis of orientation $[UVW]$, then a diffraction will appear on the HKL ring position in the plane of incidence. Other diffractions may also occur on the HKL ring position at intersections with all layer lines satisfying equation (1).

An alternative method of deriving the corresponding pattern for crystals in one-degree orientation with the (HKL)

planes parallel to the reflection specimen surface is to superimpose all the spot patterns which would be given by a single crystal (HKL) face with the beam parallel, in turn, to all the main zone axes parallel to (HKL). If the diffractions expected in one of these azimuths do not occur in the observed pattern, and they remain absent at all directions of the beam relative to the specimen, then the habit of the one-degree oriented crystals must be such that the crystals are too thick in the direction parallel to that particular azimuth for the electron beam to penetrate them.

By constructing the theoretical pattern corresponding to any particular one-degree orientation thought to be present, the positions of the other diffractions appearing can be checked, and the orientation axis thereby determined. The theoretical patterns corresponding to the one-degree orientations encountered in the present work are shown in Figs. 20, 22, 23 and 24.

In practice, the orientation is not perfect, i.e. the (HKL) planes of the crystals are not accurately parallel to the surface, and the diffractions are therefore drawn out into arcs on the ring positions.

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