

AN ELECTRON DIFFRACTION STUDY OF THE
STRUCTURE, GROWTH AND ORIENTATION OF
ELECTRODEPOSITS IN RELATION TO THICKNESS,
CURRENT DENSITY, TEMPERATURE, SUBSTRATE
NATURE AND DEGREE OF STIRRING.

By

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CONTENTS.

	Page
ABSTRACT.	
SECTION I. INTRODUCTION.	
1.1. General Introduction.	1
1.2. The Nature and Mechanism of Electrodeposition.	7
1.3. The Structure and Growth of Electrodeposits.	15
1.3.1. The Nucleation Stage of Growth of an Electrodeposit.	15
1.3.2. The Structure and Growth of Electrodeposits on Polycrystalline or Amorphous Substrates.	26
1.3.2.1. Electron Diffraction Studies of the Structure and Growth of Electrodeposits.	26
1.3.2.1(a) Lateral and Outward Types of Growth of Electrodeposits.	27
1.3.2.1(b) The Effect of Co-deposited Hydrogen on the Crystal Growth in Electrodeposits.	32
1.3.2.1(c) The Effect of Rotating the Cathode, About an Axis Normal to its Surface, During Electrodeposition.	34
1.3.2.1(d) The Effect of Stirring the Electrolyte Vigorously During Electrodeposition.	38
1.3.2.2. Studies of Electrodeposits by Optical Microscopy.	41
1.3.2.3. Studies of Electrodeposits by X-ray Diffraction.	42
1.3.2.4. Studies of Electrodeposits by Electron Microscopy.	43

	Page
1.3.3. The Structure and Growth of Electrodeposits on Single-Crystal Substrates.	46
1.3.3(a) Epitaxial Crystal Growth.	48
1.3.3(b) Directed Disorientation in Epitaxial Crystal Growth.	69
1.3.3(c) Systematic Studies of Structure and Growth of Electrodeposits on Single Crystals as a Function of Current Density and Deposit Thickness.	73
SECTION 2. EXPERIMENTAL DETAILS.	
2.1. Preparation of Polished Polycrystalline Copper Substrates.	83
2.2. Preparation and Surfacing of OFHC (Oxygen-Free High Conductivity) Copper Single-Crystal.	84
2.3. The Electropolishing of the Copper Single-Crystal Faces.	88
2.4. Electrodeposition of Nickel from the Standard Nickel Sulphamate Solution :	
$\text{Ni}(\text{SO}_3 \cdot \text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$ - 350 g/l.	
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ - 5 g/l.	
$\text{B}(\text{OH})_3$ - 35 g/l.	92
2.5. Special Precautions Necessary for Preparing Substrates and Electrodeposits for Electron Diffraction Examination.	97
2.6. Electron Diffraction Technique.	99
2.7. Methods of Interpretation of Electron Diffraction Patterns.	102
2.7.1. The Method of Interpreting a Ring Pattern.	104
2.7.2. Method of Interpreting a Spot Pattern.	106

SECTION 3.	RESULTS.	Page
3.1.	Current Efficiency Measurements.	114
3.1(a)	Current Efficiency with the Nickel Sulphamate Bath at Room Temperature ($\approx 20^{\circ}\text{C}$) and Unstirred.	119
3.1(b)	Current Efficiency with the Nickel Sulphamate Bath at 50°C and Unstirred.	119
3.1(c)	Current Efficiency with the Nickel Sulphamate Bath at 50°C and Stirred.	120
3.1(d)	Current Efficiency with the Nickel Sulphamate Bath at 60°C and Stirred.	121
3.2.	Electrodeposition of Nickel on a Rotating Cathode.	121
3.3.	The Degree of Uniformity of Current Density Over the Cathode Surface.	125
3.4.	The Structure, Growth and Orientation of Nickel Electrodeposits on Smooth Mechanically Polished Polycrystalline Copper Substrates, from the Standard Nickel Sulphamate Solution at 50°C .	132
3.4.1.	Nickel Electrodeposits on Polycrystalline Copper, Using the Sulphamate Bath at 50°C , and Unstirred.	132
3.4.2.	Nickel Electrodeposits on Polycrystalline Copper, Using the Sulphamate Bath at 50°C , and Stirred Vigorously.	152
3.5.	The Structure, Growth and Orientation of Nickel Electrodeposit on an Atomically Smooth Electro-polished (100) Face of a Copper Single Crystal Substrate from the Standard Nickel Sulphamate Solution at 50°C .	163

		Page
3.5.1.	Nickel Electrodeposits on the Copper (100) Face, from the Sulphamate Bath at 50°C, when the Bath is Unstirred.	163
3.5.2.	Nickel Electrodeposits on the Copper (100) Face, from the Sulphamate Bath at 50°C, when the Bath is Stirred Vigorously.	168
3.6.	The Structure, Growth and Orientation of Nickel Electrodeposits on an Atomically Smooth Electropolished (110) Face of a Copper Single Crystal Substrate, from the Standard Nickel Sulphamate Solution at 50°C.	178
3.6.1.	Nickel Electrodeposits on the Copper (110) Face, from the Sulphamate Bath at 50°C, when the Bath is Unstirred.	179
3.6.2.	Nickel Electrodeposits on the Copper (110) Face, from the Sulphamate Bath at 50°C, when the Bath is Stirred Vigorously.	185
3.7.	The Structure, Growth and Orientation of Nickel Electrodeposits on an Atomically Smooth Electropolished (111) Face of a Copper Single Crystal Substrate from the Standard Nickel Sulphamate Solution at 50°C.	196
3.7.1.	Nickel Electrodeposits on the Copper (111) Face from the Sulphamate Bath at 50°C, when the Bath was Unstirred.	197
3.7.2.	Nickel Electrodeposits on the Copper (111) Face from the Sulphamate Bath at 50°C, when the Bath was Stirred Vigorously.	211
3.8.	The Structure, Growth and Orientation of Nickel Electrodeposits on Smooth Mechanically Polished Polycrystalline Copper Substrates from the Standard Nickel Sulphamate Solution at Room Temperature ($\approx 20^{\circ}\text{C}$).	216
3.8.1.	Nickel Electrodeposits from the Sulphamate Bath at Room Temperature ($\approx 20^{\circ}\text{C}$), when the Bath is Unstirred.	216

	Page
3.8.2.	Nickel Electrodeposits from the Sulphamate Bath at Room Temperature ($\approx 20^{\circ}\text{C}$), when the Bath is Stirred Vigorously. 219
3.9.	The Structure, Growth and Orientation of Nickel Electrodeposits on an Atomically Smooth Electropolished (100) Face of Copper Single Crystal Substrate, from the Standard Nickel Sulphamate Solution at Room Temperature ($\approx 20^{\circ}\text{C}$), with the Bath Unstirred. 230
3.10.	The Structure, Growth and Orientation of Nickel Electrodeposits on an Atomically Smooth Electropolished (110) Face of a Copper Single Crystal Substrate, from the Standard Nickel Sulphamate Solution at Room Temperature ($\approx 20^{\circ}\text{C}$) with the Bath Unstirred. 232
3.11.	The Structure, Growth and Orientation of Nickel Electrodeposits on an Atomically Smooth Electropolished (111) Face of a Copper Single Crystal Substrate, from the Standard Nickel Sulphamate Solution at Room Temperature ($\approx 20^{\circ}\text{C}$), with the Bath Unstirred. 239
SECTION 4.	DISCUSSION.
4.1.	The Epitaxial Orientation of the Initial Thin Deposits ($< 1,000 \text{ \AA}$). 243
4.2.	The Effect of Current Density and Deposit Thickness on the Degree of Twinning in the Nickel Deposits. 252
4.3.	The Effect of Current Density and Deposit Thickness on the Development of the Preferred One-degree Orientations of "Lateral" and "Outward" Growth Types. 261
4.3.1.	Nickel Deposits on Polished Polycrystalline Copper. 261
4.3.1(a)	Development of One-degree (100) Orientation in Nickel on Polycrystalline Copper. 262

		Page
4.3.1(b)	Development of One-degree (110) and (210) Orientations in Nickel on Polycrystalline Copper.	265
4.3.2.	Development of Preferred One-degree Orientations in Nickel Deposits on the Cu (100) Face.	267
4.3.3.	Development of One-degree Orientations in Nickel Deposits on the Cu (110) Face.	268
4.3.4.	Development of One-degree Oriented Nickel in Deposits on the Cu(111) Face.	268
4.4.	The Co-deposition of Nickel Hydroxide at the Higher Current Densities and its Relation to Current Efficiency.	270
4.5.	The Effect of Bath Temperature.	273
4.6.	The Effect of Vigorous Stirring of the Bath or of Rotation of the Cathode.	278
4.7.	The Dependence of the Nickel Electrodeposit Structure on the Crystallographic Form of the Substrate.	286
SECTION 5.	GENERAL CONCLUSIONS.	289
	ACKNOWLEDGEMENTS.	293
	REFERENCES.	294

ABSTRACT.

The structure and growth of nickel electrodeposits from a sulphamate bath on polished polycrystalline and single-crystal copper substrates (Cu (100), (110) and (111) faces) is investigated using electron diffraction. This constitutes the first detailed and systematic electron diffraction study of nickel electrodeposits from the sulphamate bath, or indeed from any bath, up to the very high current density of 600 mA/cm^2 . Deposits up to thickness

102,000 Å were investigated. Besides studying in detail the effect of the bath temperature and vigorous stirring of the bath on the nickel deposit surface structure, the effect of rotation of the cathode during electrodeposition has also been examined.

On the polycrystalline copper substrates, the nickel deposits show well-defined regions of c.d. and deposit thickness where "lateral-growth" occurs, leading to one-degree (100) orientation, and of "outward-growth" leading to $\{110\}$ or $\{210\}$ orientation or a mixture of the two at high c.d.

On the copper single-crystal faces, the nickel grows in epitaxial orientation. On Cu (100), there is purely epitaxial single-crystal growth of nickel up to 105 mA/cm^2 at 20°C and up to 250 mA/cm^2 at 50°C in the unstirred bath, and up to 530 mA/cm^2 at 50°C in the stirred bath. On Cu (110) at 50°C in the unstirred bath, the parallel single-crystal growth of the nickel deposits (accompanied by some

twinning and a little random polycrystalline nickel at c.d.

340 mA/cm² (cf. 500 mA/cm² in the stirred bath) occurs up to 60,000 A or more. At 200 mA/cm², there is a little trace of random nickel which gives place in part to one-degree (100) orientation. On Cu (111), the parallel single-crystal growth of nickel shows twinning and presence of some random polycrystalline nickel even in very thin deposits. Above about 25,000 A, the single-crystal structure does not occur, but only one-degree (100) orientation is present under lateral growth conditions, and (110) with (210) under outward growth.

In the region where co-deposition of hydroxide occurs at very high c.d., the thick deposits acquire completely random Ni disposition.

The general effects of stirring the bath or of the rotation of the cathode during electrodeposition are similar to that of increasing the bath temperature, in increasing the number of Ni cations per cm² of cathode^{per second} (i.e. the c.d.) which can be attained without co-deposition of hydrogen.

The dependence of the deposit structure on the current efficiency is also investigated. It is found that the "lateral" type of crystal growth and orientation is followed over the range of c.d. which corresponds to 100% current efficiency.

1. INTRODUCTION.

1.1. General Introduction and Aim of the Present Investigations.

Electrodeposits play an important role in science and industry today. Modern industry depends largely on the use of metals. The final metal product must be suitably finished and the surface should be protected from corrosion.

Electrodeposition is one of the most important techniques employed for metal finishing. Its importance has led to extensive studies on the theory and practice of electrodeposition. Investigations of the crystalline structure of electrodeposited metals have been carried out since 1905. The two main aims of these studies are, firstly to understand the underlying mechanisms of the process of crystal growth in electrodeposits and the related phenomena, and secondly to find the conditions of deposition which give suitable electrodeposits.

For various practical purposes the crystal size, habit and orientation in the deposited metal must be carefully controlled, in order to control the physical and the chemical properties of the deposits. For corrosion protection by electrodeposit layers it is desired to deposit adherent smooth-surfaced/^{metal}layers free from pores and crevices, and these correspond to the lower range of current density being used for the deposition. On the other hand, deposits

at very high current densities are dendritic and metal powders can be prepared under such conditions suitable for use in powder metallurgy.

The present experimental study was made on nickel electrodeposits from a particular concentrated electrolyte consisting mainly of nickel sulphamate. This commercially available electrolyte is recommended for deposition of smooth and bright layers of nickel at very high rates of deposition, the solution being used at 50-60°C.

For the industrial application concerned in the present instance, the substrates were of copper (smooth surfaces of drawn wires), and coherent nickel layers were desired with the aim of minimising the thermal oxidation of the copper in oxidising atmospheres.

Electron diffraction was the main technique used, and allowed very sensitive determination of the crystalline structure in the surface region of the substrates and electrodeposits of various thicknesses. Electrons accelerated through a potential of 50-60 KV were used at a grazing incidence of the order of $0.5 - 1^\circ$ on the specimen surfaces. The electron diffraction patterns were recorded on photographic plates at about 48 cm from the specimen. Even with such fast electrons moving at about one third the speed of light, the electrons only penetrate about 5000 Å without loss of energy in the direction of the incident beam

in very light elements such as carbon, silicon, aluminium; and much smaller distance, only some hundreds of angstroms, in heavier elements such as copper and nickel. At about one degree grazing incidence the electron beam only penetrates to a few atoms depth into atomically smooth surfaces, and only 100-200 Å depth below the outer tips of rough surfaces. The structure of the electrodeposits can thus be studied almost atom by atom layer as a function of deposit thickness. The electron diffraction photographs show the crystal size, lattice type and orientation, presence or absence of twinning, and surface smoothness and in some cases the nature of the crystal faces developed at the surface of the deposits.

By comparison, X-ray diffraction is much less intense and can only reveal information about deposits thicker than a thousand angstroms in general, so that rapid changes in structure with increasing thickness cannot be detected and identified.

Optical microscopy was used to study the surface topography of many of the electrodeposits on a coarser scale to the dimension of the order of the wavelength of light. The nickel deposits showed increasing roughness with increase in thickness, as is usually observed. Electron microscopy was used in a few cases to show the fine-scale nature of the surface roughness.

Systematic series of experimental results were obtained to show the effect of the following variable factors: (1) crystallographic form of the substrate, (2) current density, (3) deposit thickness, (4) bath temperature, (5) presence or absence of stirring, and (6) rotation of cathode.

Series of electrodeposits were investigated covering a range of 0 - 100,000 Å thickness and current densities 0 - 600 mA/cm² at 50°C and with the electrolyte unstirred. Similar series were made also with vigorous stirring of the electrolyte. In each case the results were obtained on copper substrates of the following types:-

- (a) mechanically polished polycrystalline copper;
- (b) an electropolished copper single-crystal cube face, (100);
- (c) an electropolished copper single-crystal (110) face;
- (d) an electropolished copper single-crystal (111) face.

For comparison, a series of experiments were made using the same sulphamate bath at room temperature ($\approx 20^{\circ}\text{C}$) and again with the bath unstirred and stirred respectively. Some experiments were also made with a rotating cathode.

The electron diffraction results obtained define primarily the nickel crystal orientation in the deposit, and the crystal surface form, and their systematic dependence on the current density and the deposit thickness.

The dependence of the degree of preferred orientation on the deposit thickness at various c.d. and on polycrystalline copper substrates is shown quantitatively. The correlation of the type of orientation developed with the form of the crystallographic faces on the growing crystals at the deposit surface is also established clearly in the region of "lateral growth" conditions, i.e. at c.d. up to about 270 mA/cm^2 at 50°C . Results of this type do not appear to have been obtained previously in this degree of quantitative detail.

The results also make clear quantitatively the effect of stirring, and allow this to be defined by the factor by which the rate of supply of ions to the immediate region of the cathode is increased by the stirring. No such quantitative definition of the effect of stirring seems to have been established previously.

The results for the nickel deposits on the atomically smooth copper single crystal faces show in all cases the nucleation of the nickel crystals epitaxially on the copper crystal lattice, in the parallel lattice orientation. The slightly different size of the copper and nickel f.c. cubic atomic lattices causes, however, an appreciable misfit and stress at the interface, which evidently is responsible for a considerable degree of octahedral twinning even in nickel deposits of a few hundred angstroms thick.

On all the substrates, above a certain current density, the deposits more and more rapidly show co-deposition and of green or dark-coloured hydroxide, /the deposits have a very rough surface. The current density at which such rough deposition developed is correlated closely with the c.d. at which the current efficiency falls below one hundred per cent and evolution of gas occurs. At current densities higher than this, the degree of roughness and hydroxide development on the deposit is very sensitive to the degree of stirring used.

The effect of temperature is well shown by the results at room temperature (ca. 20°C) and 50°C. The current density above which rough deposits and (at slightly higher c.d.) codeposition of hydroxide occur, shows a close correlation with c.d. at which the current efficiency falls below one hundred per cent, at both temperatures.

1.2. The Nature and Mechanism of Electrodeposition.

The electrodeposition process depends on the chemical changes brought about by a passage of current through a solution of an electrolyte. The nature of the process of conversion of dissociated metal ions to a solid crystalline deposit is not yet fully known (Bockris and Razumney, 1967), though many investigators have attempted to explain the process in terms of different theories (Hunt, 1932, 1934 and 1947; Blum and Hogaboom, 1933 and 1949; Kortüm and Gustav, 1951; Schuldiner, 1952; Bockris, 1952, 1959 and 1964; Hamer, 1952; Fischer, 1954; Potter, 1956; Gerischer and Tischer, 1957; Gerischer, 1958; Lorenz, 1958 and 1959; Yeager, 1959; Mantell, 1960; Fleischmann and Thirsk, 1960 and 1963; Vermilyea, 1963; Bockris and Damjanovic, 1964; Fleischmann and Harrison, 1966).

Bockris and Razumney (1967) have summarised the present state of knowledge of the nature of electrodeposition in respect of the experimental observations and theoretical conclusions.

It has long been rather difficult to picture the process involved in actual deposition of metal at the cathode. However, on the basis of the accepted simple theory, it is expected that in the electrolytic bath the dissociation of the metallic salt solution gives rise to ions carrying charges. On application of a potential between the

electrodes, positively charged cations migrate towards the cathode and negatively charged ions to the anode. As the cathode is negatively charged, it has a high concentration of the electrons near the cathode surface. When these combine with positively charged ions at the cathode surface, neutral atoms are formed and they are deposited on the cathode surface. With the discharge of cations, the electrodeposits grow in thickness and develop a form and crystal orientation characteristic of the conditions of deposition.

The rate of deposition is determined by the current strength. The uniformity in thickness of the deposit depends on the shape and disposition of the electrodes, the concentration of the bath, the temperature, the degree of agitation, the rate of diffusion of the metal ions from the bulk of the electrolyte to the vicinity of the cathode, etc. The passage of the electrically charged ions makes the conditions of deposition in this process different from that in other processes where there is no such transfer of electrical charge - such as crystallisation from solution or from condensation of a vapour, though the actual growth of the crystals does not seem to differ much in nature.

The process of electrodeposition is also influenced by factors like overvoltage and concentration polarisation. During the evolution of hydrogen and oxygen at the cathode

and anode respectively, the potential required is almost always greater than that corresponding to the equilibrium potential of a hydrogen or oxygen electrode in that solution. This difference in the potential, known as the overvoltage, varies with the composition and the structure of the electrode surface and it increases with current density. The phenomenon of concentration polarisation occurs when there is a depletion of the metal ions near the cathode, and if replenishment of the metal ions from the bulk of the solution to the cathode region is slow.

The mechanism of electrodeposition has been interpreted by different workers in different ways. Blum and Rawdon (1923) in their discussion on the form of electrodeposited metals, concluded that the discharge of positively charged metal ions at the cathode and their subsequent atomic fitting on to the lattice is one and the same process, i.e. metal ions are discharged singly, but not haphazardly. According to their views, the metal ions reaching the cathode by electrostatic force and thermal diffusion were considered to be discharged at those places where the lowest discharge potential is required, with the least expenditure of energy.

The theory put forward by Volmer (1928) suggests that the metal deposition takes place in such a way that layer after layer of atoms is built up. Until one layer is completed, the arriving ions remain in an intermediate state,

that is, between the states they had in the original solution and that they would eventually take up when positioned in a crystal lattice. The observed polarisation was attributed to this cause.

The nucleation-based theory of crystal growth suggested by Kossel (1927) and developed by Stranski (1928) dominated the concept of crystal growth during the 1930's and 1940's. The basic idea of this theory is of two-dimensional nucleation, after which layer growth occurs. The recently deposited atom travelling over the surface is considered to move until it reaches the edge of the advancing layer. It then travels along the edge until it finds the characteristic position of co-ordination known as "kink site". The following atoms also repeat the same process until a layer is built up. After building up one layer, nucleation must again occur and a further layer is thus commenced. This layer covers the atoms which were incorporated in the previous layer and hence these become part of the metal.

Erdey-Gruz and Volmer (1931) suggested that a metal ion did not undergo charge transfer at the point at which it arrived in the double layer (of + and - charge) which is believed to occur just outside the cathode, but first diffused in solution until it was opposite a point where growth is favoured, presumably on edge or even a 'kink'.

Brandes (1929) stressed the Kossel-Stranski model for electrolytic deposition, i.e. charge transfer from the metal to the ion at the point of arrival, and diffusion along the surface to growth sites, in contrast with Volmer's views that the transfer of charge was directly at a growth site after lateral diffusion in the double layer. Brandes also developed the idea of Volmer, and suggested that the ions on entering the Helmholtz electrical double layer lose their water envelope and finally take up positions in the crystal lattice. The double layer is regarded as constituting a condenser. The potential difference in the double layer would be proportional to the amount of electricity brought into the layer by the ions. If the ions find a place of low potential energy easily on the substrate and are neutralised, there would be less polarisation than if they tend to remain adsorbed. Both the theories suggested by Volmer and Brandes agree that the electrolytic deposition is almost an instantaneous process, although Brandes assumes a delay between the arrival of the cation and its discharge.

Kohlschütter (1927) established much of our early knowledge of non-morphological phenomena. Kohlschütter and Torricelli (1932) measured the rate of spreading of layers (many atoms thick) on silver deposited from AgNO_3 solution. They also suggested that material did indeed reach growth points by means of diffusion along the surface,

that is, charge transfer occurs at sites on the plane surfaces of the growth layers. They also noticed that layers growing over the metal crystal would remain unchanged and continue where they had left off on switching off, and then again on, the depositing current, respectively; but if the time interval was too great (3.5 secs) the fresh surface became inactive. They also suggested that there would be high current density at edges and corners where a layer begins.

Gardam (1947) suggested that metal ions become discharged where they reach the cathode and then migrate to a position of minimum potential energy unless prevented from doing so by low temperature or by the presence of adsorbed material. This mechanism raises some controversial points because the mobility of the atoms on the surface of a solid at temperatures used in electrodeposition is very small. The ions therefore must get discharged at a stable place of minimum potential energy.

Ibl and Trümpler (1952 and 1953) and Ibl (1954) investigated the nature of electrodeposition, and found that deposition occurs only at parts of the cathode where unchecked growth is possible. The actual current density at these depositing regions is thus much larger than the normally quoted mean c.d. When the deposit surface becomes rough as the growth proceeds, the effective c.d. is further increased as compared with the mean c.d.

Many investigators have worked on the kinetics of electrodeposition (Sheludko and Bliznakov, 1951; Sheludko and Todorova, 1952; Lorenz, 1954; Kaishev and Mutaftschiev 1954 and 1955; Fleischmann and Liler, 1958; Vermilyea, 1956 and 1957; Mohl and Bockris, 1959; Despic and Bockris, 1960; Piontelli, Poli and Serravalle, 1961; Fleischmann, Thirsk and Torressillas, 1962; Fleischmann, Harrison and Thirsk, 1965. Vetter (1967) has discussed the theoretical aspects of kinetics of electrodeposition.

In the light of their views, in electrodeposition the growth centres are nucleated at a rate which can be specified in terms of a rate constant, during deposition of a new phase. The growth centres once nucleated, will grow along the cathode either in one dimension (as an atom row) or as bundles of rows (cylinders), or as more compact groups of atoms (e.g. approximately hemispheres) in three dimensions. These reactions are in a non-steady state. At longer times, the nuclei have grown until they meet neighbouring nuclei or crystals and will interact and the growing surfaces may have some overlap. A steady state is reached when the substrate is completely covered.

In the earlier theories of crystal growth suggested by Volmer (1921 and 1939) and Stranski and Kaischew (1935), the formation of new lattice planes has been assumed to be

governed by two-dimensional nucleation. It has been thought that this would require appreciable overpotentials. However, electrodeposition can proceed at very low potentials and so it has more recently been assumed that edges are sometimes present, generated by screw dislocations (Burton, Cabrera and Frank (1951)).

The combined effect of diffusion along the surface and through the solution have been taken into account by Fleischmann et al. (1965).

1.3. The Structure and Growth of Electrodeposits.

Many studies have been published about the structure and growth of electrodeposits and the literature is conveniently outlined in a recent review by Lawless(1967). Bockris and Razumney (1967) have also summarised the present views on the nature of the growth of a crystal during the process of electrodeposition, in so far as concerns the layerwise growth and the development of dendritic forms.

Although the techniques of optical microscopy and X-ray diffraction have made some useful contributions, the main detail and systematic understanding of the structure and growth of electrodeposits has been developed from the more sensitive technique of electron diffraction and to some extent electron microscopy.

The following are the main aspects which it is convenient to distinguish, mainly based on the by now extensive electron diffraction results which are available.

1.3.1. The Nucleation Stage of Growth of an Electrodeposit.

Two-dimensional surface nucleation, i.e. formation of incipient rows of atoms or sheets of atoms on a plane surface by aggregation of adions, is a kinetic process (Fischer, 1954, Kortum, 1957). It forms an important basis of earlier theories of metal deposition but it is now regarded as less necessary, since it has been realised in

more recent years that on a real metal crystal surface there are steps having edges, and there may be "edge"- or "screw"-dislocation . (which present a perpetuating edge). Such stepped edges present growth sites to which adions can diffuse and where they can be retained preferentially and be discharged, the metal atoms then building up a crystal lattice.

Nuclei, once formed, provide new sites on which further growth can occur by deposition of the adsorbed species. While at low growth rates near the reversible potential, the intrinsic defects in the substrate cathode surface can provide sufficient growth sites, nucleation is more probable at higher current densities. At high rate of growth, at high c.d., the surface concentration of adions can increase if surface diffusion is slow.

A detailed treatment of nucleation is given by Fleischmann and Thirsk (1963), Bockris and Damjanovic (1964) and Vetter (1967). They have also outlined the previous literature on nucleation, particularly in the case of electrodeposition.

According to Damjanovic and Bockris (1963) adion clusters, or embryos, can be regarded as being in equilibrium with adions. An embryo may either disintegrate, after momentary formation or it may grow. When it reaches a critical size, it becomes a stable nucleus.

If the radius of the embryo (for simplicity usually assumed to be circular) exceeds a certain value, the free energy of the formation of an embryo from adions becomes negative, that is the nucleus continues to grow.

An embryo having the critical radius may become a stable nucleus after the lapse of time necessary for a further adion to join it. The rate of nucleation is strongly dependent on overpotential and, for a given potential, on the dislocation density (Fleischmann and Thirsk, 1960).

The probability of nucleation on a stepped surface is much less than that on an atomically flat surface, because the adion concentration, even at the mid-point of the steps, is less than that at a step-free surface under the same conditions. Analysis shows that on a surface with a high density of dislocations ($\sim 10^{10} \text{ cm}^{-2}$) no nucleation is possible unless cathodic overpotentials are over 150 mV.

After application of a constant overpotential to an ideally flat surface, net ion flow across the double layer takes place, but only until the adion concentration has reached a certain value.

Theoretical calculations show that significant nucleation may be expected in the case of silver, for instance, if the overpotential is of the order of 80-100 mV.

Vermilyea (1957) found that copper whiskers which

were supposed to be bounded by ideally flat surfaces, with no steps and growth sites on them, there was no deposition current unless overpotentials of the order of 100 mV were reached. The c.d. which would be observed just after the commencement of nucleation is governed by surface diffusion and can now reach significant values as the nucleation has provided necessary growth steps to which ions can diffuse to be retained.

Finch, Wilman and Yang (1947), in studies of cathodic crystal growth, found that a Cu electrodeposit of 200 Å thickness, from an acid sulphate bath at 20°C and 0.5 mA/cm², gave parallel growth with less smooth surface than the substrate. This indicates that the new surface was covered with crystal outgrowths. At 500 Å thickness, the diffraction pattern indicated still rougher surface and that was almost entirely due to the transmission of the electron beam through these projections. The increase in roughness of the surface is due to preferential deposition or nucleation on the projecting parts of the cathode surface.

Dickson et al. (1965) studied by electron microscopy the nucleation and growth of gold electrodeposits on (111) surfaces of silver films. The gold was found to be initially in the form of thin isolated plate-like islands. The surface coverage by these islands was only about 22% for an average deposit thickness of 20 Å. The nuclei had a

population of $\approx 4 \times 10^{10}/\text{cm}^2$. Further deposition led to the gradual coalescence of these islands until an almost continuous film was formed at about 80 to 100 Å. It was concluded that the mode of nucleation and growth was largely independent of the mode of deposition and depended mainly upon surface migration of gold over the silver substrate and the gold nuclei.

E.R.Thomson (1966) studied by electron microscopy the early stages of the deposition of gold and nickel onto thin single-crystal films of copper of (110) and (111) orientations. The results for gold deposits were similar to those of Dickson et al (1965) in that isolated nuclei were observed for small amounts of deposits (< 50 Å), and the film became continuous at about 100 Å. It was also found that nuclei of gold were present at the early stages of deposition onto thin films of nickel. Nickel on copper, however, showed a somewhat different behaviour: the deposits were continuous for the thinnest films observable (< 20 Å). Isolated nickel nuclei were observed in only one deposit and for a thickness of 50 Å.

Jesser (1966) using transmission electron microscopy observed the formation of many small isolated Pt nuclei onto (111) gold films. There was no obvious relationship between the nuclei formed and the dislocations present in the substrate. The average thickness of the

deposit was less than 50 Å.

With increasing thickness of the platinum deposits, the films were essentially continuous and showed well-defined, although somewhat irregular moiré fringes. These films nearly always showed small somewhat circular areas which did not show moiré fringes and, therefore, apparently had no platinum on them. It is likely that these areas were regions in which impurities were trapped at the surface of the substrate and for relatively thin deposits prevented the complete coverage of the surface with platinum. Similar areas were observed by Lawless (1965) in nickel deposits. If these gold substrates with a Pt deposit were annealed to about 700°C, it was found that the Pt improved its orientation and became isolated on the gold surface in the form of triangular nuclei. It was found that contamination at the interface, as observed by Atkinson (1958), was removed in the annealing process.

Lawless et al (1962,1963,1965) made a fairly extensive electron microscope study of copper deposits on single crystal films of nickel which had previously been prepared by electrodeposition onto bulk copper single crystals. An acid sulphate bath was used and the deposits of copper were made at room temperature at a c.d. of 1 mA/cm²... The substrate films were characterised by the presence of numerous deformation twins and a density of

dislocations somewhat less than the normal for evaporated films.

The copper deposits, as shown by the moiré fringes, were essentially continuous over the nickel substrate, even for deposits of thickness ≤ 20 Å. The fringes were not clearly broken up into small clusters such as might be expected if the film were formed by individual, well developed nuclei growing together as has been observed in evaporated deposits. Since the nickel substrate surfaces were finely faceted, many kink sites and edges were available so that nuclei of copper could have been initiated simultaneously at many different points on the surface. The coalescence of this high density of nuclei on kink sites present on small facets could then lead to the very thin continuous film observed with the irregularities in the moiré pattern.

Toshev and Mutaftschiew (1964) studied the activity of Pt single crystal electrodes during the process of eletrolytic nucleation of Hg deposits. The Pt electrode was treated periodically with HNO_3 prior to the nucleation process. The results lead to the concept that the nuclei were formed only at preferential sites on the electrode surface. Those sites most probably were breaks in the oxide layer, normally covering the Pt electrode under the experimental conditions.

The distribution of Hg nuclei formed in the case of electrodeposition of Hg on a spherical Pt single crystal in the course of a single rectangular pulse was shown in a micrograph. The nuclei were deposited mainly around the octahedral poles where the regions around the $\{100\}$ and $\{110\}$ poles remained practically unoccupied.

After treatment, the activity of the electrode surface increased strongly with regard to the process of electrolytic nucleation, and nuclei were formed everywhere except on the $\{110\}$ surface which apparently was not reduced under the given conditions. Toshev and Markov (1967) studied the electrolytic nucleation of Cd.

The plot of the frequency of formation of one nucleus on the cathode was plotted against the pulse duration at different voltages, giving 'S' shaped curves. This shows that the transition from non-occurrence to 100% probability of the event is not abrupt, but more or less continuous. The size of the critical nucleus was, however, found to be small, as found by many other workers [Kaischew, 1965; Kaischew et al, 1950; Fleischmann and Thirsk, 1955, Kaischew and Gutzow, 1964, and Kaischew and Mutaftschiew, 1965] in the case of three dimensional nucleation.

As communicated by Kaischew et al (1964) and (1965), and Toshev and Mutaftschiew (1964) the nucleation of Hg and some other metal deposits around the crystallographic poles

of unpretreated Pt electrodes was found to be in the succession $\{111\}$, $\{100\}$, $\{110\}$.

These results were treated in terms of the concept of an oxide layer covering the electrode surface.

In the case of Cd, the poles are occupied in the order $\{311\}$, $\{111\}$, $\{100\}$, $\{110\}$.

The electrolytic nucleation of Hg, Ag, Pb and other metals on Pt has been successfully investigated with a pulse technique by Scheludko and Todorova (1952), Kaischew and Mutaftschiew (1954, 1955), Mutaftschiew and Kaischew (1960), Mutaftschiew and Toshev (1960), Kaischew, Scheludko and Bliznakov (1950), Scheludko and Bliznakov (1951), Mutaftschiew and Kaischew (1955), and Kaischew and Gutzow (1962).

The electrodeposition of a metal on an inert electrode begins with the formation of separate nuclei which by further growth coalesce into a continuous deposit. The initial stage of the deposition is thus controlled by the process of heterogeneous nucleation. Various techniques have been used to study the electrolytic nucleation of a number of metals on Pt. These methods and the main results obtained are reviewed by Kaischew (1965).

The rate of three-dimensional nucleation is given by:

$$J = K_1 \exp \left[- \frac{A}{KT} \right] = K_1 \exp \left[- \frac{K_2}{n^2} \right]$$

where A is the activation energy for the nucleus formation, n is the overvoltage, and K_1 and K_2 are constants. This equation denoting the kinetics of the nucleation process has been successfully tested by Kaischew et al (1950) and Budewski et al (1966) for the case of three- and two-dimensional nucleation respectively.

Maybourn (1968) observed nucleation in the electrodeposits of zinc from an aqueous solution of KOH saturated with ZnO. The electrodeposits were prepared on (0001), (11 $\bar{2}$ 0), (10 $\bar{1}$ 0), (21 $\bar{3}$ 1) faces of Zn single crystal, and were examined by scanning- and transmission electron microscopy.

On the Zn (0001) plane and at 100 mA/cm², the early stages of deposition were characterised by growths about 1 μ m diameter, which did not have clearly-defined crystallographic form. After the passage of 6 C/cm² (a theoretical deposit of 2.8 μ m) the density of these small growths was 10⁶/cm² as shown by the electron micrograph. The density remained unchanged up to 12 C/cm² when some of the nuclei had started to grow into dendrites.

On the Zn (10 $\bar{1}$ 0) plane and at 6 C/cm² and 100 mA/cm² the number of growth centres or nuclei was about 2 x 10⁸/cm². Later some of the nuclei grew into tree-like dendrites.

On the Zn (11 $\bar{2}$ 0) plane, nuclei formed at a c.d. of 100 mA/cm² with a density of 10⁸/cm². Of these small growths 1 in 100 grew into a tree-like dendrite of 25 μ m in length at 3 C/cm².

On the Zn (21 $\bar{3}$ 1) plane, at a c.d. of 100 mA/cm², nuclei formed with a density of 5 x10⁷/cm² at 6 C/cm².

The results showed that the major effect of the substrate orientation was the lower density of the small growths on the basal plane as compared with the other planes.

Vaughan and Pick (1960) concluded that nucleation sites in Cu were probably impurity sites and that physical defects act as nucleation sites primarily because such defects are preferred sites for impurity segregation.

There is good evidence that for Cu (Danjanovic, Setty and Bockris, 1966) the most close packed atomic plane, (111), has a lower exchange c.d. than other planes. In zinc, the atomic packing in the basal plane is much closer than that on any other plane, and one would expect the basal plane to be less active and therefore produce fewer nuclei than any other plane.

1.3.2. The Structure and Growth of Electrodeposits on Polycrystalline or Amorphous Substrates.

The detailed structure of electrodeposits has been studied by various techniques, such as optical microscopy, X-ray diffraction, electron diffraction and electron microscopy. Of these techniques, electron diffraction is the most sensitive in showing the nature of the crystal orientation in the deposit, especially when using an electron beam at grazing incidence. Mainly from the extensive electron diffraction results now available, the relation of the deposit structure to the deposition conditions is now more clearly understood in a systematic way. The electron diffraction results will therefore be considered first.

1.3.2.1. Electron Diffraction Studies of the Structure and Growth of Electrodeposits.

The extensive electron diffraction results can best be considered under several main headings as follows.

1.3.2.1(a). 'Lateral' and 'Outward' Types of Growth of Electrodeposits.

With the development of the electron diffraction technique, it has been possible to derive very detailed information regarding the nature, growth and orientation of the electrodeposited crystals. This is a technique best suited for this purpose, since it is only the surface region of the crystal which contributes effectively to the coherent diffraction pattern.

Systematic investigation of the structure of the deposited metals on epitaxially inert polycrystalline or amorphous substrates were made by Finch and his collaborators (1936-1953). The fundamental principles which govern the development of preferred crystal orientations of the deposits have been established by them. The crystal size, habit and orientation are mainly influenced by (a) the substrate surface structure and (b) the bath conditions. These two factors are sometimes found to have opposing influences.

Two main types of crystal growth, (i) "Lateral growth" and (ii) "Outward Growth", were first recognised by Finch and his co-workers [Finch and Sun (1936); Finch, Wilman and Yang (1947); Finch and Layton (1951)]. In 'lateral' type of growth, the crystals grow more or less laterally in compact block-like crystals with the most closely-packed atomic plane parallel to the substrate.

In f.c.cubic crystals this corresponds typically to (111) orientation, and in b.c.cubic, (110). In this case the deposition occurs without setting up regions of strong ion impoverishment locally. The initial crystal nuclei of the deposit are formed on the substrate by two or three adjacent deposited atoms, the crystals then tending to grow at first as a single densely populated atomic sheet parallel to the substrate. In practice, a second atomic sheet begins to grow on the first, when the latter reaches a certain extent, and so on - leading to the growth of the crystals in three dimensions.

The 'lateral growth' takes place only if the rate of supply of ions to the cathode region by diffusion and migration is not less than, or very much less than, the rate of deposition of ions on the cathode. It does not involve undue impoverishment of ionic concentration of the solution in the cathode region, and the ions diffuse freely to the cathode surface. The chief bath conditions favourable to lateral growth are:- (i) high ion concentration; (ii) low current density; (iii) high bath temperature and (iv) stirring of the bath. In the case of deposition on a random polycrystalline or amorphous substrate-surface, the deposit crystals grow with the closest-packed atomic plane parallel to the substrate and then atomic sheets grow sideways rapidly, but the deposit crystals have random

azimuthal orientation.

In 'outward growth' there is preferential deposition on any projecting part of the cathode surface, leading to prominent outgrowth and even dendritic growth. The crystals tend to grow with the most densely-populated atom row as common axis of orientation normal to the substrate. Outward growth results when the formation of the deposit greatly impoverishes the ion concentration in the neighbourhood of the cathode, and the conditions are such that ion replenishment is slow. The further growth of the deposit is preferentially outward towards new ion-rich regions, that is, in a direction normal to the substrate. As the atom rows grow out rapidly into regions of undiminished ion concentration, the crystals will also gain slowly in girth as some ion replenishment occurs in the depleted regions. This leads eventually to the formation of needles or dendrites in which the longer axis is an atom row of close atomic packing, usually the closest possible atomic packing, normal to the substrate. For example, this gives rise to (110) orientation, typically, in f.c.cubic metals, and to (111) orientation in b.c.cubic metals.

This outward growth is favoured by: (i) a low ion concentration in the bath; (ii) high c.d. leading to rapid ion depletion; (iii) a low bath temperature (causing only slow diffusion of the ions); and (iv) lack of stirring. The

optical micrograph [Finch and Layton (1951)] and later the electron micrograph [Matthews, Mutucumarana and Wilman(1961)] are clear visual examples of outward growth.

Wilman (1955) suggested that outward growth one-degree orientation must represent a preferential deposition on the crystals which grow outward most rapidly to less ion-impooverished regions of the solution. The crystals having two or more densely-populated faces normal to the substrate and thus the most densely populated atom row (or a densely populated one) normal to the substrate. In particular the often observed (110) orientation appears to be associated with the preferred growth of crystals having two $\{111\}$ facets simultaneously normal to the substrate in f.c.c. metals.

With respect to one-dimensional orientation finally developed in the upper regions of thick electro-deposits at medium or high c.d., Wilman (1955) pointed out that the increased energy transfer to the growing deposit surface can be expected to result in an even higher degree of mobility of the deposited ions or atoms there, than at the lower c.d., and hence lead to an even more pronounced development of plane crystal faces. It was suggested, therefore, the preferred orientation results from the strong outward growth at such c.d. favouring growth of crystals (out of the early random shape) having simultaneously two

faces normal to the substrate and thus the lattice row along their common intersect is also normal to the substrate. Since the faces developed depend to some extent on the nature of the adsorption (even if this is transient) of compounds present in the bath, this could account for both usual outward growth orientation with the most densely populated row (and two of the most densely populated atomic planes) normal to the cathode and also the occasional observation of the less simple type of orientation.

Matthews, Mutucumarana and Wilman (1961) outlined the previous literature on electrodeposition under outward growth conditions and they used electron diffraction and electron microscopy to study this type of growth in Cu deposits at high c.d. from 0.3 and 0.1 M CuSO_4 and Ag from 0.1 M AgNO_3 . Recently, Naybour (1968) observed dendritic growth in Zn electrodeposits from aqueous KOH solution saturated with ZnO on (0001), ($\bar{1}0\bar{1}0$), ($11\bar{2}0$) and ($\bar{2}3\bar{1}1$) faces of zinc single-crystal. He examined the deposits by scanning and transmission electron microscopy. The deposits were dendritic at 100 mA/cm^2 .

1.3.2.1(b). The Effect of Co-deposited Hydrogen on the Crystal Growth in Electrodeposits.

In electrodeposition, some hydrogen ions are in general adsorbed on the cathode surface in a state of dynamic equilibrium with the hydrogen ions in solution. The adsorption of hydrogen ions brought to the cathode by the applied electric field is stronger than the tendency for these ions to redissolve, when the cathode potential exceeds the reversible deposition potential of hydrogen ions in the corresponding solution. In order that they may evolve as a gas, the cathode must acquire a more negative potential than the sum of the reversible hydrogen deposition potential of the solution and the minimum hydrogen overvoltage of the cathode metal, below which the adsorbed hydrogen, either in the form of ions or atoms, will be accumulated on the cathode surface.

A cathode metal having a higher hydrogen overvoltage leads to a greater difficulty of the transformation of those adsorbed hydrogen ions or atoms into hydrogen gas. If these adsorbed hydrogen ions or atoms are removed as hydrogen gas, it is evident that there would be more free space on the cathode surface for the growth of the deposit metal crystals. On the other hand, the accumulation of adsorbed hydrogen ions or atoms on the cathode in a more static manner causes more hindrance to the normal crystal growth.

Sometimes amorphous deposits are found in the case of metals with weak cohesive forces; such as antimony, bismuth, arsenic, selenium, etc. (Sun, 1935; Finch and Sun, 1936; Finch, Wilman and Yang, 1947). In these metals, the lattice formation is disturbed due to excessive evolution of hydrogen or accumulation of hydrogen ions on the cathode. They are found to be less resistant to the disturbances due to hydrogen evolution on their growth than the deposits of harder metals, such as nickel, gold, iron, etc. The metals with weaker cohesive forces usually show random structure even at a current efficiency of 80 to 90% while under approximately the same current efficiency, the deposit of the harder metals may still be highly oriented.

Metals of higher cohesive forces, such as zinc, nickel, cobalt, iron, silver and gold, always give crystalline deposits. The deposit crystals are randomly arranged under conditions where there is an excessive evolution of hydrogen gas, that is the current efficiency is low, or there is an accumulation of adsorbed hydrogen ions or atoms on the cathode surface owing to the high hydrogen overvoltage of the deposited metal. In such circumstances, the mobility of the deposited metal atoms over the cathode surface, and the tendency of the outward growth of the deposit crystals from the projections of the cathode surface, are reduced. This leads to a random disposition of the

deposit crystals (Finch, Wilman and Yang, 1947). In some cases, however, by raising the current density and giving the cathode potential a more negative value, the evolution of hydrogen begins to occur and the deposit is oriented.

1.3.2.1(c). The Effect of Rotating the Cathode during Electrodeposition, about an Axis Normal to its Surface.

It is a general experience that during electrodeposition, usually the 'burning' of the deposit, that is the dark appearance due to the inclusion of basic metal hydroxides, and the dendritic crystal growth tendency at higher c.d., is suppressed by the rotation of the cathode. Regarding the effects of the speed of rotation on the crystal orientation of the electrodeposits, the information available is limited.

Burgers and Quanjel (1942) observed by X-ray examination that nickel deposited from nickel acetate bath at 11 mA/cm^2 developed (100) orientation when the cathode was rotated at 100 r.p.m. In the absence of rotation the resulting textures showed uncontrollable variations.

Wyllie (1948) found that nickel electrodeposits from a nickel chloride bath (NiCl_2 205 gms/l., KCl 8 gms/l. and NH_4Cl 17 gms/l.) at room temperature and 50 mA/cm^2 was randomly oriented on a stationary cathode, whereas on a cathode rotated at 25 r.p.m., other conditions remaining the

same, (110) orientation was developed.

Yang (1948), in this laboratory, studied the effect of rotating the cathode during electrodeposition. He observed by electron diffraction that a silver deposit 35,000 Å thick from a cyanide bath (AgCN 35 gms/l., KCN 37 gms/l., K_2CO_3 38 gms/l.) at 20°C and 30 mA/cm^2 on a stationary polished brass cathode had (110) orientation (characteristic of outward growth), while on a cathode rotated at 3,000 r.p.m., other conditions being the same, the deposit consisted of (111) oriented silver (i.e. typical of a lateral form of growth). The current efficiency with and without stirring was found to be 100% and 80% respectively.

He also observed that copper deposited (25,000 Å thick) on a stationary cathode from a cyanide bath ($\text{CuAc}_2 \cdot 2\text{H}_2\text{O}$ 25 gms/l., $\text{Na}_2\text{SO}_3 \cdot \text{H}_2\text{O}$ 50 gms/l., KCN 35 gms/l., Na_2CO_3 10 gms/l.) at 80°C and 7.5 mA/cm^2 had (110) orientation and the current efficiency 75%, but if the cathode was rotated at 3,000 r.p.m. with other conditions unchanged, the current efficiency was increased to 90% and the deposit crystals showed (111) orientation. No change in orientation was observed, however, when copper was deposited (30,000 Å thick) from the same bath at 20°C and 3 mA/cm^2 , whether on a stationary cathode or on a cathode rotated at 3,000 r.p.m. In both cases the deposit crystals had the same (110)

orientation although the current efficiency was found to increase from 55% on a stationary cathode to 92% on the rotated cathode. From these results it was concluded that current efficiency was not the only factor which prevents the copper crystals from being arranged into the most densely packed (or nearly so) orientation, but both high bath temperature and high current efficiency are necessary for achieving the results.

Further, he also observed that nickel electro-deposited (50,000 Å thick) on a stationary brass cathode from a nickel sulphate-boric acid bath ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 240 gms/l., H_3BO_3 30 gms/l.) at 20°C and 12.5 mA/cm^2 had (110) orientation, the current efficiency being 90%, while if the cathode was rotated at 3,000 r.p.m., other conditions remaining unchanged, the current efficiency dropped to only 45%, and the deposit crystals became randomly arranged. At a bath temperature of 52°C , the deposit from the same bath and at the same c.d. showed (100) orientation on a stationary cathode, with a current efficiency of 95%. On a rotated cathode with other conditions unchanged, at 3,000 r.p.m., the current efficiency was only 55% and the deposit crystals were randomly disposed.

The same phenomenon was observed in the case of iron electrodeposits as well. Thus, iron deposited (53,000 Å) from a sulphate bath ($\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ 350 gms/l., H_2SO_4 2.5 gms/l.) at 20°C and 37.5 mA/cm^2 showed (111)

orientation with a current efficiency of 90% on a stationary cathode, while if the cathode was rotated at 3,000 r.p.m. with the other conditions as before, the current efficiency decreased to only 25% and the deposit crystals were randomly disposed.

Yang(1948) concluded that the loss of crystal orientation in these cases was therefore due to the disturbances in the lattice formation of the deposited atoms caused by excessive evolution of hydrogen during the deposition on the rotating cathode.

The changes in the electrodeposit structure caused by rotating the cathode are evidently closely related to the changes in the ion-concentration in the solution close to the cathode surface. This is a complex mathematical problem which can be solved in certain ideal cases. Levich (1962), in his book "Physicochemical Hydrodynamics" has discussed mathematically the flow of liquid over a disc rotating about a normal axis through its centre.

The papers by Alberly (1966), Alberly and Brucke/nstein (1966), and Alberly, Brucke/nstein and Napp (1966) describe a mathematical approach which enables solutions to be derived from the problem of diffusive and convective transfer of solution for the disc to the ring in the case of a rotating ring-disc electrode. The disc used was 0.5 inch diameter and speed about 200 radians/sec. ($\approx$ 1900 r.p.m.).

Albery et al. (1968) using aqueous mixtures of $10^{-2}M$ NaBr and $6 \times 10^{-2} M$ $HClO_4$ at $25^\circ C$, found experimentally that the current distribution in the case of rotating ring-disc electrodes was uniform. They also concluded the uniformity of current distribution in more concentrated solution.

These results are contrary to Newman's theory (1966) which predicts a greater c.d. at the edge of the disc compared to the average c.d.

1.3.2.1(d). The Effect of Stirring the Electrolyte during Electrodeposition.

The effect of stirring on the structure and growth of electrodeposits as shown by electron diffraction has been indicated in a general way in section 1.3.2.1(a). The stirring increases the degree of the maintenance of the supply of ions to the electrolyte close to the cathode surface and thus increases the lateral growth tendency and reduces the outward growth tendency.

Although there appears to have been no systematic studies, the present results in section 3 provide an extensive detailed systematic study of the quantitative effect produced by a particular degree of vigorous stirring (maintained approximately constant) as compared with the observations made in the absence of stirring. In particular, the effect of the stirring could be expressed directly as the factor by which the rate of cation supply to the cathode

region was increased as a result of the stirring.

In general, stirring is difficult to standardise and control closely, but it causes an increased flow of liquid carrying cations more rapidly to the regions close to the cathode to replenish cations removed by deposition on the cathode. The more vigorous is the stirring, the more effect it causes.

A brief discussion of diffusion and convection (including natural and forced convection) at electrodes was given by Agar (1947). He quoted the general expression in the case of forced convection, ' δ_f ' = constant. U^{-n} as having been found by many authors to apply in electrode and other surface reactions; ' δ_f ' being the thickness of the diffusion layer adjacent to the cathode surface, U being the stirring velocity and n having a value between 0.5 and 1 depending on the type of apparatus and stirring. ' δ ' is found to be of the order of 10^{-3} cm. For a rotating cathode disc electrode (for which ' δ ' is constant over the disc, with laminar flow) he quoted Levich's theoretical conclusion that with a value of 10^{-5} cm² sec⁻¹ for the diffusion constant ' D ' and a value 10^{-2} cm² sec⁻¹ for the kinematic viscosity gives

$$\delta = \frac{0.022}{\sqrt{\text{rev. per sec}}} \text{ cm.}$$

Vetter (1967), in his recent book "Electrochemical Kinetics", quotes other workers and their views in a discussion of the effect of stirring the electrolyte and has

referred to the cases of both laminar and turbulent flow of liquid.

Even in the absence of stirring, natural convection occurs in the electrolyte during electrodeposition. The natural convection includes gravitational motion due to variations in density associated with ion concentration changes, evolution of gas at the electrode, temperature gradient within the cell and adventitious causes such as vibration.

Changes in concentration within the diffusion layer near the cathode surface with natural convection can be studied, for example, by interferometry (Ibl and Muller, 1955) Ibl and Muller (1955) demonstrated the velocity of flow of the electrolyte parallel to the cathode under such conditions.

Although the general effect of stirring on the electrodeposit structure and growth has been shown by electron diffraction in section 3, there has been only qualitative conclusions derived hitherto. The present results described in section 3 include a new detailed systematic comparison of the structure of nickel electrodeposits when the solution was stirred with that found in absence of stirring. These results allow a direct quantitative estimate to be made of the factor by which the stirring used increased the supply of ions immediately close to the cathode.

1.3.2.2. Studies of Electrodeposits by Optical Microscopy.

Optical microscopy does not provide the details of the deposit structure on the atomic scale, such as crystal structure, habit and orientation, but it gives some useful information in regard to coarser features of surface topography and morphology, sometimes including the crystal size and shape when the crystals are large enough. One advantage is that it can be used in situ to observe progressive changes, e.g. the way in which the crystal form changes with time during electrodeposition (Danjanovic, Paunovic and Bockris, 1963).

Many examples of optical micrographs illustrating electrodeposit structure are given in books and reviews such as those of Blum and Hogaboom (1949), Brenner (1963), Fischer (1954), Gray (1953) and Lawless (1967).

One of the more important features of crystalline structure of electrodeposits was shown by Blum and Rawdon (1923) and Hotherhall (1935). They made carefully polished and etched cross-sections and found that in certain cases the electrodeposit crystals continued the growth of the substrate crystals across the interface, and this was associated with good adhesion of the electrodeposit with the substrate.

A more recent new kind of observation of optical microscopy was the observation of spiral growths, normally

of rare occurrence, in electrodeposits of copper on copper sheets which had been cold-rolled and annealed (Pick, 1955, Pick and Wilcock, 1958, Seiter et al, 1960). Detailed studies have also been made of the more normal stepwise crystal growth (e.g. Pick, Storey and Vaughan, 1960), and of the type of crystallographic faces produced on electrodeposit crystals under defined cases (e.g. Seiter et al, 1960 Pick, Storey and Vaughan, 1960, Storey and Pick, 1960, Danjanovic, Setty and Bockris, 1966). Fuller bibliography and discussions of recent work are available in the recent review by Lawless (1967).

1.3.2.3. Studies of Electrodeposits by X-ray Diffraction.

The earlier studies of electrodeposits by X-rays include those of Glocker and Kaupp (1924), Bozorth (1925), Frolich and Clark (1925), Wood (1931 and 1935), Hume-Rothery and Wyllie (1943), Jacquet and Weil (1949), Clark and Simonson (1951). Usually, the patterns obtained showed the structure of the regions down to a few thousand angstroms below the surface, because of the relatively higher penetration of the X-rays. The patterns did not show the structure of the initial thin layers adjacent to the substrate nor much evidence of the immediate surface region of the deposit.

A summary of texture studies of electrodeposits is

given by Fischer (1954). A more recent extended review on the studies of electrodeposits by X-ray diffraction has been given by Lawless (1967). Mention will therefore be made here only of the demonstration by Wood (1931) that at low c.d. (but not at high c.d.) copper continued the orientation of the carefully cleaned polycrystalline substrate; Leidheiser and Gwathmey's (1951) study of nickel deposits on copper single-crystal (111) and (110) faces, showing parallel orientation of the nickel on Cu (110) face; Oren's (1958) study of the single-crystal growth of Cu on copper crystal (100), (110) and (111) copper faces, at 30 mA/cm^2 ; and Giron and Ogburn's (1961) similar study of copper deposits on these three Cu faces at 10 mA/cm^2 .

Recently, X-ray patterns from polycrystalline electrodeposits have also been used to give information about the grain size and stresses in electrodeposits.

1.3.2.4. Studies of Electrodeposits by Electron Microscopy.

Electron microscopy is another technique available for the study of the electrodeposits. However, there is a limitation in that for direct examination it must be possible to detach the very thin films either mechanically or chemically, without affecting them in any respect. On the other hand, replica techniques have been used to the greatest extent for characterisation of the detailed topography of the deposit at various stages in the growth. The technique of

transmission electron microscopy of a thin film of an electrodeposit or a deposit plus substrate is relatively new, being first used by Weil and Read (1950) in the case of stripped thin nickel deposits from copper and zinc substrates. The thickness of the film prepared was approximately 5×10^{-6} cm. For nickel-plated copper, a solution of 500 gms/l CrO_3 and 50 gms/l H_2SO_4 dissolved the copper, leaving the nickel. A solution of 5% by volume of concentrated HCl in water served for dissolving zinc basic metals.

Reiner (1956) also examined Ni films stripped from polycrystalline copper, and he has discussed the application of electron microscope technique to the study of electro-
Reiner and Ficker
deposits/(1960). Recently, Lawless (1967) has reviewed the studies of electrodeposits by electron microscopy.

Ogawa et al. (1957) were the first to study nickel films (prepared at $22-23 \text{ mA/cm}^2$) using aqueous solution of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 300 gms/l., NaCl 3.1 gm/l, and H_3BO_3 6.2 gms/l., stripped from electropolished single-crystal copper substrates, and they observed much twinning in the lamellar form.

Steinmann and Hintermann (1960) made a detailed study of the effects of substrate structure, and inhibitor concentration, on the structure of copper electrodeposits on Cu foils, at 20 mA/cm^2 , from an acid bath. Stoebe et al.

(1964) also studied Cu deposits (at 11-54 mA/cm²) from various baths, on aluminium substrates.

Dickson, Jacobs and Pashley (1965) studied nucleation and growth of gold electrodeposits on (111) surfaces of Ag films. At an average thickness of 20 Å, the "islands" of gold covered only about 22% of the substrate and were mainly of the order of 200 Å in diameter. At about 80 to 100 Å thickness, the islands had coalesced to form an almost continuous film. (111) orientation parallel to the silver substrate was observed together with mirror symmetrical orientation. They concluded that the kind of nucleation and growth depended mainly on the surface migration of gold atoms over the silver substrate and on the gold islands.

Thompson (1966) studied the early stages of the deposition of gold and nickel on thin single-crystal copper films of (110) and (111) orientations. He also observed isolated nuclei in gold deposits less than 50 Å thick, while the films had become continuous at about 100 Å thickness. The nickel deposits, however, were continuous in the thinnest films observable (< 20 Å), though isolated nickel nuclei were observed in one deposit (< 50 Å thick).

Jesser (1966, cf. Lawless, 1967) examined the nucleation stage of Pt on (111) Au films using transmission electron microscopy. At the early stages (< 50 Å), small

isolated Pt nuclei occurred, but thicker films were continuous.

Some evidence has been obtained (Thompson and Lawless, 1966) suggesting that interfacial dislocations are present between 200 Å nickel deposit and the copper substrate, associated with the lattice misfit.

1.3.3. The Structure and Growth of Electrodeposits on Single-Crystal Substrates.

The nature of the growth of electrodeposits on single crystal substrates depends on the crystallographic form of the surface of the substrate crystal. In most studies, the surface is made highly smooth on the atomic scale by electropolishing, and parallel to a definite crystallographic plane. On the other hand, an etched surface in general tends to be bounded by etch-facets which may be oblique to the mean macroscopic surface.

In epitaxial crystal growth, it is the orientation of the first very thin deposit (a few hundred angstroms or less) that is concerned. As for the other forms of deposition, epitaxy occurs if the deposit and the substrate lattices are not too dissimilar in spacings at the interface. These considerations are discussed in 1.3.3(a). The misfit of the two lattices introduces a corresponding degree of stress in the region near the interface which is probably responsible for disorientation effects such as those

established by electron diffraction and outlined below in 1.3.3(b). On the other hand, systematic electron diffraction studies of electrodeposits on single crystals as a function of thickness and current density, (see 1.3.3(c)) show that new orientations can be developed at above a certain thickness. This can be due to twinning, and secondary or multiple twinning, which then leads soon to random polycrystalline structure and eventually at still higher thicknesses to preferred one-degree orientation with axis normal to the substrate.

1.3.3.(a) Epitaxial Crystal Growth.

The term 'epitaxy' was introduced by Royer (1928) to signify the "arrangement on" or "oriented overgrowth" of one crystalline material on another, in such a way that there are certain orientation relationships between the deposit and the substrate lattices.

Much of the extensive literature on epitaxial crystal growth is reviewed by Van der Merwe (1949), Seifert (1953), Pashley (1956) and Fleischmann and Thirsk (1963). More recent discussions of epitaxy are found in the contributions to certain conferences, e.g. "Single-Crystal Films" edited by Francombe and Sato (1964). Pashley (1965) has given a brief discussion about epitaxy. Lawless (1967) has given a recent review of literature on epitaxial crystal growth of electrodeposits.

In the present case some of the main phenomena and theoretical considerations will be discussed briefly, followed by a more detailed account of epitaxy on electrodeposits on single-crystal substrates.

The first systematic studies of Barker (1906, 1907, 1908) showed a series of epitaxially related structures in the growth of alkali halides upon each other. Some alkali halides grew epitaxially upon each other, while others did not. It was noticed that oriented growth was favoured if the molecular volumes of the two alkali halides are nearly equal.

Royer (1928) repeated much of the work of Barker and extended it to cover many other examples of growth from solution. On the basis of his results, Royer put forward three rules of epitaxy:

(i) Oriented growth occurs only when it involves the parallelism of two lattice planes which have networks of identical or quasi-identical form and of closely similar spacings. The difference between the network spacings is usually expressed in terms of percentage misfit, which is defined as $100(b-a)/a$, a and b being the corresponding lattice spacings in the substrate and overgrowth crystals respectively. The experimental results suggested that the misfits should not be more than about 15% for epitaxy to occur.

(ii) In the case of ionic crystals, the overgrowth atoms or ions should take up positions which corresponding atoms or ions of the substrate material of the same polarity would have occupied had the substrate continued to grow.

(iii) At about the time when Royer carried out his experiments, electron diffraction was discovered. It greatly increased the scope of studies of epitaxy and it soon became apparent that epitaxy occurs with a wide variety of deposits on crystal faces.

In some cases it was found that very thin chemically grown layers (Aminoff and Broome, 1936, Wilman, 1940), electrodeposited metal films (Thomson, 1930, Cochrane, 1936, Finch and Sun, 1936) and metal layers condensed from

the vapour phase (Kirchner and Lassen, 1935, Brück, 1936) were oriented. The results of these experiments showed that Royer's rule concerning a good numerical fit between the substrate and the overgrowth is not always obeyed. A misfit of 38% was observed in the case of metals condensed on to heated rocksalt surfaces (Brück, 1936).

Some attempts were made to explain the occurrence of these large misfits by considering the possibility that the initial layers, i.e. the small initial nuclei, may have grown epitaxially with a low misfit, and upon these other orientations may have been formed at a later stage. A mechanism of this kind, in which the occurrence of twinning played a vital role, was considered in detail by Menzer (1938 a,b,c) for the case of silver on rocksalt.

The results of early diffraction studies led Finca and Quarrell (1933, 1934) to the introduction of a further concept of "basal plane pseudomorphism". This involves the formation of an initial oriented film which has an abnormal crystal lattice dimension (or even structure). It was suggested by them that the bulk structure of the deposit material is constrained so that the lattice plane parallel to and in contact with the substrate surface is close to that of the substrate in size. This hypothesis is now generally agreed to be valid.

Frank and Van der Merwe (1949 a,b,c) followed up

the concept of basal plane pseudomorphism and developed a theory of epitaxy which involves, as a necessary condition of orientation, the formation of an initial pseudomorphic layer.

Van der Merwe (1949) emphasised that crystal orientations are not determined by long-range forces, but by forces between one atomic layer and the next. Hence in order that there shall be a definite orientation in a crystalline overgrowth on a single crystal substrate, there must be formed, as the initial stage, an immobile monolayer of regular atomic pattern, to be called an "embryo". If the formation of a monolayer is regarded as a process of adding atom to atom, it is possible, if the influence of the substrate is strong, for these foreign atoms to take up similar positions to those which the atoms of the substrate material would have occupied in further growth of the substrate crystal. The resulting monolayer homogeneously deformed to fit on the substrate, thus forms an embryo. "Oriented overgrowth" is then obtained when the atomic pattern and orientation of the embryo are preserved throughout the entire lattice of the overgrowth.

The theory developed by Frank and Van der Merwe (1949) led to predictions regarding the necessary conditions under which an embryo can be formed. The theory of Frank and Van der Merwe is based on the properties of one-dimensional dislocation model, consisting of a row of identical balls, connected by identical springs, the balls at the same time

being acted upon by a force, which varies periodically with the position on the substrate. It is found that with this model, the fit or misfit of the monolayer and the substrate is naturally described in terms of dislocations. The embryo in a suitable substrate for the formation of another embryo on it, provided the binding between deposit atoms is not weaker than their binding on the substrate.

If the atomic pattern of the embryo and that of the deposit do not differ in size by more than a certain factor (when the two lattices are isomorphic), it is possible for a stable, macroscopically thick, oriented film to grow by repetition of this process of embryo formation. This assumes, of course, that any flat region of the surface is completely covered by the first monolayer before the second is appreciable.

It is the pattern of potential troughs, i.e. positions of minimum potential energy of the deposit atoms in the substrate force field, rather than the atomic pattern of the substrate surface, which must determine the atomic pattern in an initial atom plane of the deposit structure.

The theoretical ideas of Frank and Van der Merwe are in good general agreement with experimental observations. The fact that pseudomorphic overgrowth is

observed seems to show that there are cases in which slip does not take place during the early stages of growth. Amongst the most striking examples are the cases of aluminium on platinum and zinc oxide on zinc (Finch and Quarrell, 1934) and cobalt on copper (Menzer, 1938) and in the experiments of Finch and Sun (1936) where the abnormal crystal orientations of very thin films were in general such that the atomic population density in the orientation plane of the deposit approached that in the substrate surface.

Smollet and Blackman (1951) made theoretical calculations in the case of alkali halide lattices, using the known elastic constants. They came to conclusions similar to those of Frank and Van der Merwe as to the degree of lattice misfit which can be tolerated.

Van der Merwe (1964) has further discussed theoretically the interfacial misfit and binding between oriented films and their substrates.

Detailed calculations of Menzer (1938), in the case of silver condensed in vacuum on a heated NaCl cleavage face (Kirchner and Lassen, 1935, Brück, 1936) suggested that the initial nuclei of the deposits may have consisted of small crystallites having (221) faces in contact with the substrates. In the bulk of the further growth, these crystallites were considered to have twinned on (111) planes and certain of these twins would have an orientation parallel

to that of the NaCl substrate. The corresponding misfits (9% for Ag, 7% for Ni) in the (211) plane of contact with the substrate would thus also lie within the tolerance limit which is not the case for the misfits (-27% for Ag, -38% for Ni) suggested by the parallel (100) orientation of the bulk of the overgrowths. It was suggested that the orientations of the f.c.c. metallic overgrowths on ionic crystals are not likely to be of this type.

The above orientations are thus such that a better fit can be achieved by other orientations, as was also pointed out by Thomson (1948) for some cases. These considerations together with the fact that deposits on a plane oriented with (parallel to the substrate) inert substrate have a tendency to be a definite plane, show that one cannot be certain that the orientation of the overgrowth is the same as that of the initial embryo.

Thomson and Cochrane (1939, pp.174-5), (see also Thomson, 1953) suggested that epitaxial growth can often be determined by a special line of atoms in the substrate surface, for example at the edge of a crack or at the internal angle at the bottom of a step on the surface. Although initial nuclei can often be seen to grow more or less preferentially at such sites, it is clear that their epitaxial orientation is unaffected by the presence of such features (Drabble, 1949).

It is clearly initiated by the deposit atoms taking

up positions in the potential troughs at the crystal surface. The epitaxial orientation will be initiated by the local atomic fitting of the first small group of deposit atoms on the substrate, as Elleman and Wilman (1949) illustrated in the case of PbCl_2 on a PbS cube face, and as Seifert (1953) has also emphasised. The lattice repetition and misfit are involved only as the nuclei grow larger (cf. Wilman, 1951).

Pashley (1952) has pointed out that care is needed in some cases to define correctly the crystallographic type of the substrate surface on which the epitaxy occurs in a given orientation.

Drabble (1949) showed, however, that considerations of the atomic co-ordination of the Ag^+ and Cl^- ions in AgCl indicate that the silver does indeed grow in its initial nuclei on the NaCl cube faces in a parallel (100) orientation.

Willems (organic materials on inorganic, 1943, 1944, 1948, 1952) having drawn the general conclusion that, for oriented overgrowth to take place, there must exist the possibility of a strong chemical bond between the units (molecules or atoms) of the overgrowth and the corresponding units of the substrate, confirmed it experimentally. Willems particularly showed new cases of epitaxy between crystals of various organic molecular materials and substrates such as NaCl cleavage faces.

From the theoretical considerations of Van der Merwe, one may anticipate that a preferred orientation can exist when one row of the closely packed units in each lattice is parallel, as concluded by Goche and Wilman (1936), Heintze (1937), and Royer (1928). Seifert (1935) in his work on oriented overgrowth of ionic partners, concluded that one-dimensional lattice fitting for a row of closely spaced ions of alternating sign is sufficient to give rise to oriented overgrowth.

In the case of isomorphous natural lattices of the deposit and substrate, the pattern of atoms in the first monolayer of the deposit is identical with that in a plane of the natural deposit lattice, and hence the next monolayer can grow on to this under the conditions similar to those in which the first has grown on to the substrate.

Evidently, this growth process can also take place for non-isomorphic lattices, provided the lattice of the deposit contains planes whose atomic configuration resembles that of the exposed surface of the substrate. This condition can only be satisfied on specific crystallographic surfaces of the substrate. The general problem of oriented overgrowth on various surfaces of a substrate non-isomorphic with the deposit is exceedingly complicated, but from similar theoretical considerations to those above one may anticipate that a two-degree orientation can exist when there is a similarity in spacing in one row of closely packed atoms in

each lattice as remarked by Wilman (1940).

Frank and Van der Merwe (1949) suggested that the same critical misfit is not to be expected for all sorts of substances on all sorts of substrates. The large critical misfit characteristic of the oxides and iodides can be partly accounted for by the greater deformability of oxide and iodide ions respectively. Acharya (1948) in this laboratory, showed epitaxy of f.c. cubic Sb_2O_3 in (111) orientation on the $\text{Sb}^{(111)}$ face, with a lattice misfit of about 80%, i.e. spacings in the ratio 100:180. Wilman (1951) concluded that epitaxy can indeed occur such that x spacings of the deposit lattice nearly match y spacings of the substrate in a parallel direction, x and y being small integers in the same way as occurs in certain crystal groupings.

Engel (1952, 1953) put forward a theory for the orientation of metals upon salt substrates, in which she attempted to explain both the observed degree of lattice fitting and the dependence of the orientation upon the substrate temperatures. This dependence (Brück, 1936) amounts to there being a minimum temperature (the epitaxial temperature) for the occurrence of complete orientation. She suggested that the first stage in the formation of an oriented film is that the atoms in the first layer become ionised, so that a two-dimensional chemical reaction occurs, as indeed Drabble (1949) had considered (see above). A

monolayer of the deposit-metal salt then exists at the interface between the substrate and the overgrowth.

According to Engel's theory, the occurrence of orientation depends upon the possibility of suitable ionisation processes and upon the misfit of the intermediate salt with both the substrate and the deposit.

Pashley (1956) has noted, however, that experimental results of Kehoe (1957) throw doubt upon Engel's theory of the effect of substrate temperature on the orientation of metals on salts. Kehoe found that good orientation occurred at temperatures appreciably lower than Brück's (1936) epitaxial temperature. Ellenan (1948), in this laboratory, had indeed observed epitaxial orientation in silver condensed on a rocksalt cleavage face which had been heated at 500°C and cooled to room temperature. Similarly recent experiments on cleavage of alkali halide crystals in vacuum, followed immediately by condensation of metals, have shown that epitaxy then occurs even at room temperature (e.g. Ogawa et al, 1966). It is now agreed that there is no definite critical temperature for epitaxy. Murr and Inman (1966) in studies of epitaxial growth of Au, Ag, Ni and Al on NaCl substrate, also showed that factors such as rate of deposition, pressure of air in the vacuum, and the condition of the substrate surface in respect of adsorbed impurities affect epitaxy considerably.

Epitaxy of Metal Electrodeposits on Metal Crystal Faces.

With respect to deposits on polycrystalline substrates, Wood (1931), by X-ray diffraction, observed that Ni and Cu follow the orientation of a one-degree orientated Cu (110) substrate. Clark, Pish and Weeg (1944) also observed a definite orientating relationship between Zn and Ni on Cu and Zn on Fe.

The earliest reported electron diffraction examination of an electrodeposit was that of Thomson (1931). He found that silver deposited on an etched copper cube face rigidly followed the orientation of the copper substrate.

Finch and Sun (1936) found by electron diffraction that the first thin layers of electrodeposits growing on random polycrystalline substrates in general also showed polycrystalline structure. For thin deposits on substrates prepared by electrodeposition, parallel growth was observed when the deposit and the substrates nearly had the same lattice dimension. In some cases such as Cu and Ni on (111) Au, some deposit crystals grew in (100) orientation as well as some (111) orientation. This (100) orientation did not appear to give a close fit.

In some cases, no parallel lattice orientation occurred, but the orientation gave approximate fitting in positions of atoms of the substrate and the deposit along one or more lattice rows in their contact planes, such as (110)

Ni and Cu deposits on (111) Fe; (100) Fe on (110) Au, (110) Fe on (111) Au and (110) Sn on (111) Au.

They also found direct evidence of parallel epitaxial growth for Cu, Ni and Co on (110) platinum foil; Cu on (100) Pt-foil; Co on (100) Au-foil; but not with Ni on (100) Au-foil.

Cochrane (1936) made an electron diffraction study of the electrodeposits of Cu, Ni, Ag, Cr, Zn and Cd on etched (110) and (111) copper single-crystal faces. The copper was found to continue the orientation of the copper substrate up to a thickness of at least 40,000 Å, if the c.d. was no greater than a few nA/cm^2 .

The deposits of Zn of various thicknesses were obtained with c.d. from $8 \mu\text{A/cm}^2$ to 1nA/cm^2 . In all the cases the diffraction pattern showed polycrystalline zinc. Cd deposits also gave patterns of rings due to polycrystalline metal, even at low c.d. ($30 \mu\text{A/cm}^2$).

Silver deposited for 18 hours at $15 \mu\text{A/cm}^2$ on etched Cu (111) and (110) faces of Cu single-crystal showed diffraction spots both due to Cu and Ag. There were also faint rings due to Ag and these passed through Ag spots. The Ag was deposited for periods of 34, 51 and 72 hours, at the above c.d. Some features were obtained as before, the copper spots becoming very faint with increasing thickness and the rings, due to polycrystalline Ag observed previously, also became fainter. When Ag had been deposited for 100

hours at 15 μ A, the pattern of spots were entirely due to Ag and the rings were very faint.

A thick layer of Cr (deposited for 20 min. at 0.2 A/cm²) exhibits no orientation and has the ordinary structure of Cr. In the case of thin layers (e.g. deposited from 1/3 sec to 20 sec at 0.06 A/cm²), the patterns showed that there was orientation with (110) planes of Cr parallel to the (111) Cu face, on which the deposit was made. The $\langle 111 \rangle$ spacing in (110) Cr faces only differs by 2% from the $\parallel \langle 110 \rangle$ in Cu (111) faces.

For nickel on the copper, it was claimed that at current densities of 0.3 mA/cm² or greater, the diffraction rings due to polycrystalline nickel passed through the spots from the substrate copper, indicating that the nickel lattice spacing was increased to conform to that of copper. This experiment was repeated by Newman (1956) who found no change in spacing of nickel from its normal parameter. Pashley (1956) has interpreted Cochrane's results as being in fact due to the presence of both oriented and disoriented nickel so that diffraction rings from nickel passed through nickel spots, not copper spots. Such patterns were commonly observed by Lawless (1965) for nickel deposits on the (111) face of a copper single-crystal.

Cochrane found that electron diffraction patterns from deposits of nickel and cobalt of about 60 Å thickness at very low c.d. (0.025 mA/cm²) showed only spots in

positions corresponding to the copper substrate. This was also interpreted in terms of pseudomorphic growth, but this interpretation has been put in doubt by Newman (1956).

In many of the diffraction patterns, strong additional spots occurred, which, Cochrane showed, was due to prominent octahedral twinning of the main crystal orientation parallel to that of the substrate. Groups of "irrational spots" were also observed analogous to those found by Kirchner and Lassen from silver condensed on NaCl cleavage faces.

Thirsk (1939) observed by electron diffraction the epitaxial growth of Au and Ag on a Fe (110) face, with (001) parallel to Fe (110) and a $\langle 010 \rangle$ row parallel to a [001] row of the Fe, when the deposition was carried out at low c.d. He also observed parallel growth of Ag, Ni and Co on approximately (110) and (100) surfaces of Cu.

Finch, Wilman and Yang (1947) showed by electron diffraction that in the first stage of the cathodic crystal growth the deposit structure and orientation were greatly influenced by the substrate. They found that Cu deposit of 200 Å on (100) face of Cu at 20°C and 0.5 mA/cm² from an acid sulphate bath continued closely the structure of the substrate both in crystal orientation and in lattice perfection. As the thickness of the deposit increased to an average value of 500 Å, the electron diffraction showed the same form as before but with fainter Kikuchi lines and

a large number of spots, indicating a rougher deposit surface than the initial substrate had. They also recorded many cases of epitaxial growth of various metals on single crystal faces of Cu and Fe.

Goswami (1950) studied the orientation of Fe, Cd and Zn on electropolished Cu (110) and (100) faces. He found that Fe developed with a (211) plane parallel to the Cu (110) surface and with a $[01\bar{1}]$ row along the Cu $[001]$ direction; and on the Cu cube face the (110) Fe plane was parallel to the cube face, with a cube diagonal parallel to one or other of the Cu cube face diagonals in the surface. These orientations gave a close fitting of the deposit lattice with that of the substrate in at least one direction of the substrate surface. Cd and Zn grew with a (103) and (205) plane respectively parallel to the Cu (110) and with (203) and (101) orientation respectively on the Cu (100) face, in all those cases with a $[100]$ row along a cube-face diagonal of the Cu surface.

Leidheiser and Gwathmey (1951), using X-ray diffraction, studied Ni electrodeposits over a wide range of conditions on Cu (111) and (100) faces. The electrolyte used was a Watts bath containing $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ - 240 g/l, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ - 45 g/l, H_3BO_3 - 30 g/l. No experiment was conducted above 80 mA/cm^2 . In experiments above 8 mA/cm^2 the electrolyte was stirred vigorously. The deposit on the (100)

face was monocrystalline and in parallel orientation to great thicknesses, whereas the deposit on Cu (111) became random polycrystalline at a very low thickness.

Setty and Wilman (1955) studied by electron diffraction the electrodeposits of Ag on Ag single-crystal electropolished (110), (100) and (111) faces. They found that the deposits continued the substrate orientation to a thickness 100,000 Å if the c.d. did not exceed certain limits. They showed clearly that the thickness at which octahedral twinning was first noticeable, decreased systematically with increase in c.d., and that random polycrystalline structure had developed about a similar (thickness, c.d.) locus.

Kumar (1955) found by electron diffraction that in copper deposits of low thicknesses (< 2000 Å) on electropolished (100) and (110) silver faces, the copper crystals grew in parallel orientation to the substrate, though showing some additional octahedral twinning. A "directed" disorientation was observed in some cases (see 1.3.3(b) below). As in the results of Setty and Wilman (1955) for Ag on Ag, strong additional twinning occurred at lower thicknesses the higher the c.d., although a small amount of twinning was present at low thicknesses even at low c.d., probably associated with the lattice misfit and the resultant interface stresses. The epitaxy of Ag deposits on Cu (100)

faces was observed and no cases of directed disorientation occurred.

Oren (1958) studied by X-ray diffraction the epitaxy of Cu electrodeposits at 30 mA/cm^2 with the duration of plating extending even up to 18 hours on electropolished Cu (100), (110) and (111) faces. The general conclusions were (1) that the deposit on Cu (110) was monocrystalline with the same orientation as the substrate; (2) that the deposit on the (100) face consisted of crystallites having the same orientation as the substrate and its four twin orientations; and (3) that the deposit on the (111) face consisted of crystallites having the same orientation as the substrate and an orientation which was twin related to the Cu (111) face.

Reddy and Wilman (1958) examined by electron diffraction the growth of Fe and Cr on (110), (100) and (111) faces of copper single crystal. Within a certain range of c.d. and deposit thickness on all the faces of the copper single crystals used, the growth of Fe was epitaxially related to the substrate. On Cu (110), the Fe deposits grew epitaxially, having a $\{211\}$ type lattice plane parallel to the copper (110) surface. In this plane the most densely populated type of atom row, i.e. of $\langle 111 \rangle$ type (cube diagonal) was parallel to the most densely populated type of lattice row i.e. of $\langle 1\bar{1}0 \rangle$ type of the copper lattice.

On Cu (100) the Fe deposits were strongly epitaxially oriented. A $\{110\}$ plane of the Fe crystals was parallel to the substrate, with again the most densely populated atom row of the Fe, $\langle 111 \rangle$, parallel to that of the Cu, that is, one or other of the two $\langle 110 \rangle$ directions of the Cu cube-face surface. One sided "directed" disorientation was observed prominently in many of these deposits (see below, 1.3.3(b)).

On Cu (111), the Fe deposits were strongly epitaxial with a $\{110\}$ plane of the Fe in contact with the $\{111\}$ Cu substrate, and $\langle 111 \rangle$ of Fe parallel to $\langle 110 \rangle$ in the copper substrate.

At 45°C on all the three faces of the copper single crystal, chromium also developed the same epitaxial orientation as that of Fe.

Giron and Ogburn (1961) investigated by X-ray diffraction the structure of copper electrodeposits from an acid sulphate bath at 10 mA/cm² on Cu (100), (110) and (111) faces. There was evidence of twinning, although for thick deposits some polycrystallinity was present. This was in agreement with Barnes's (1961) results for Cu on Cu (100), (110) and (111) faces up to 15 mA/cm².

Reddy and Wilman (1963) showed clearly the effect of deviation of the substrate surface away from a simple main atomic plane. It was found that on a curved Cu surface, Fe grew with equal preference in each of the two equivalent

epitaxial (211) orientations on the part of the surface approximating closely to the Cu (110) plane. Where the surface curved away from this plane, the Fe (211) orientation (of the above two equivalent one) having a cube-face diagonal most nearly normal to this element of the cathode surface was developed preferentially.

The only other epitaxial study in which deposits on faces other than the three low-index faces were examined appears to be that of Lawless and Garmon (1963; see Lawless 1967). In this study nickel was plated from a Watts bath at 60°C onto electropolished surfaces of large spherical single crystals at current densities from 1 to 10 mA/cm². It was found by electron diffraction that the nickel deposits grew accurately parallel to the substrate copper surface for all orientations. The parallel single crystal orientation extended to 100,000 Å thickness or more on all faces except the (111) which showed double positioning for extremely thin (100 Å) deposits and developed additionally some random polycrystalline structure at about 1000 Å thickness.

Reddy and Wilman (1965) found predominantly parallel growth of thin ($\approx$ 500 Å) nickel on Cu (110) and (111) faces, but with additional twinning becoming increasingly strong with increasing deposit thickness.

Gusminsky (1965) and Sundaram (1966) found "auto" epitaxial growth of Cu (from $M/2 \text{ CuSO}_4 + M/2 \text{ H}_2\text{SO}_4$ bath) on

copper [(100) and (110)] and Ag (from M/2 AgNO_3 bath) on Ag [(100) and (110)] respectively, but octahedral twinning being detected above a (thickness, c.d.) locus similar in form to that observed by Setty and Wilman (1955) for Ag on Ag from a cyanide bath.

Bicelli and Poli (1966), by X-ray diffraction, studied Pb and Cd electrodeposits onto single crystal substrates over a range of current densities for several different compositions of bath, and for a range of thicknesses. Lead deposits on Pb (100) and (110) showed parallel epitaxy at thicknesses of 10,000 to 80,000 Å, and c.d. from 5 to 50 mA/cm^2 . Lead on the (111) surface exhibited twinning for 50,000 Å films formed at c.d. of 30 mA/cm^2 or more, the amount of twinning increasing with the deposit thickness.

Cd deposits on Cd (11 $\bar{2}$ 0) copied the substrate orientation for all conditions studied, whereas deposits on Cd (10 $\bar{1}$ 0) were parallel oriented only for low thicknesses (10,000 Å) and low c.d. (2 mA/cm^2), becoming twinned on the (10 $\bar{1}$ 2) plane at 40,000 Å thickness and 5 mA/cm^2 .

1.3.3(b) Directed Disorientation in Epitaxial Crystal Growth.

The phenomenon of a "directed disorientation" of epitaxially oriented crystals consisting of a range of rotation about a definite axis was first observed by Evans and Wilman (1950).

They observed in the oxidation of a fresh cleavage face of a zinc blende crystal at 520°C , a rotational disorientation of the resulting (103)-oriented ZnO crystals about an axis parallel to the cube-face diagonal of the (110) ZnS substrate face. This was shown by a pronounced arcing (6°) of the spots in the electron diffraction with the beam along ZnS $[1\bar{1}0]$, but no appreciable arcing of the spots with the beam along $[001]$.

They concluded that this rotation of the growing crystals or parts of them must be due to the deformation caused by the epitaxial stress between the substrate and overgrowth crystal lattice, due to the difference of their lattice constants at the interface. They pointed out that though the diffraction pattern did not allow the type of deformation to be established with certainty, it could most simply be explained as indicating a lamellar rotational slip (a process of deformation first defined and conclusively proved to occur by Wilman (1950, 1951)), on planes normal to the rotation axis.

Goswami (1950), in this laboratory, observed a similar range of disorientation, also about a $[110]$ row of the f.c.c. Cu substrate surface, in a Cd electrodeposit on the (110) face of the copper single crystal, again apparently caused by deformation associated with relief of epitaxial stresses caused by the misfit of the two lattices at the interface.

Gharpurey (1950), also in this laboratory, observed a similar case in Ag condensed from the vapour in vacuum upon an NaCl (001) cleavage face at 450°C . The mean sharply defined main orientation being also present was centred on orientations attained from the above by a rotation of $\pm 10^{\circ}$ and 20° respectively, about $[001]$ Ag row.

Pashley (1951) suggested that electron diffraction patterns from AgBr formed by reaction of a Ag (110) face with bromine vapour also showed such a directed disorientation, but this was not conclusively established. The photograph obtained with the electron beam normal to the suggested axis of orientation, however, showed no diffractions other than the spots corresponding to the undisoriented crystals.

Kumar (1955) also observed the interesting result that in the initial parallel growth of silver on copper (100), there was no disorientation, but in the electrodeposits of copper on silver (100) and (110) faces, there was often a disorientation range of several degrees about a densely

populated lattice row of the substrate surface. This kind of rotation was termed a "directed-disorientation". In the case of Cu on Ag, the deposit of Cu is presumably under tension because its lattice spacing (3.608 kX) is less than that of silver (4.078 kX).

Even in the thinnest Cu deposits on Ag (100) and (110) faces, the diffraction patterns showed an arcing of the spots of up to about $\pm 6^\circ$ to 12° , showing a disorientation of the deposit crystals from the initial parallel epitaxial orientation relative to the substrate lattice. The Cu deposits on the Ag (100) face yielded patterns of arcs at all azimuths, but those on the Ag (110) face showed little arcing when the electron beam was along the cube edge, but long arcs when it was along the cube-face diagonal, showing that the disorientation consisted of a range of rotation about the cube face diagonal. Subsequent growth of the deposits to thicker layers also showed similar disorientation in general.

The results of Reddy (1958), and Reddy and Wilman (1958-9) contributed further examples of directed disorientation, here of epitaxial Fe electrodeposits on the Cu (110) and (100) faces, and is strongly suggested in the case of Fe on Cu (111) as shown by the arcing in the diffraction patterns.

In the $\{211\}$ -oriented iron on Cu $\{110\}$, the axis

of rotation is the iron $\langle 110 \rangle$ direction parallel to the surface, the $\langle 110 \rangle$ planes perpendicular to this axis are the most densely populated with atoms, and thus likely to undergo rotational slip on each other most easily. On the other hand, the rotational range might be due to flexural translational slip about this $\langle 110 \rangle$ axis, since this is perpendicular to a $\langle 111 \rangle$ row of the Fe, which is the normal translational-slip direction in b.c.c. iron, and the $\langle 211 \rangle$ plane (parallel to the Cu substrate) is the normal slip plane.

In the $\langle 110 \rangle$ oriented iron on Cu (100), the rotation axis was concluded to be a $\langle 111 \rangle$ iron row parallel to a Cu $\langle 110 \rangle$ surface row.

From the diffraction pattern of Fe on the Cu (111) face, showing "asymmetrical directed disorientation", the rotation axis of disorientation could not be determined, because of the complexity involved in taking into account six geometrically equivalent orientations.

The electrodeposits of Fe on Cu (110), (100) and (111) faces showed, however, a distinctly different type of "directed-disorientation" from that observed so far. The disorientation observed not only consisted of a rotation of the Fe deposit crystals about a definite rotation axis (i.e. directed-disorientation), but that rotational disorientation was asymmetrical, and directed in a specific sense of rotation away from the main epitaxial orientation. The

results (Reddy, 1958, Reddy and Wilman, 1958-9), therefore indicate a type of disorientation of the deposit crystals, which appears to be a new phenomenon. They termed it an asymmetrical or "one-sided" directed disorientation.

The same kind of epitaxial orientation and one-sided rotational disorientation as for Fe were also observed in Cr electrodeposits on copper crystal. This similarity of the results for Fe and Cr is evidently due to these metals having close similarity of the lattice dimension of their b.c.cubic structure.

1.3.3(c) Systematic Studies of the Structure and Growth of Electrodeposits on a Single Crystal as a Function of Current Density and Thickness.

Setty (1953), Wilman (1955), and ^{Setty and} Wilman (1955, 1966) did the first systematic and detailed investigation of the surface structure growth and orientation of electrodeposits of a metal, in this case silver, on single-crystal faces of the same metal, as a function of current density, deposit thickness, bath temperature and concentration, and presence of addition agents. Smooth electropolished (110), (100) and (111) silver single-crystal faces were used as substrates, and the electrolyte contained 35 g AgCN, 30 g KCN and 38 g K_2CO_3 per litre.

These important experimental results provided more precise information on cathodic crystal growth and defined

in detail for the first time the conditions giving rise to the three stages of cathodic crystal growth as suggested by Finch, Wilman and Yang (1947), i.e. an initial epitaxial orientation, then random polycrystalline structure, and finally in still thicker deposits, preferred one-degree orientation. An additional further stage in which the twinning of the deposit crystals occurred was also clearly recognised.

The results shown diagrammatically in fig. 1 suggest that there is always an initially auto-epitaxial orientation, that is, continuing the substrate lattice. The further growth developed twinning, followed by growth of randomly oriented polycrystalline metal. Eventually, further deposition results in the development of preferred orientation characteristic of the bath conditions. Below a certain critical current density, the silver electrodeposits grew parallel to the substrate (in single crystal orientation) even up to deposit thicknesses of several hundred thousand angstroms. Above this "critical current density", often an initial stage of parallel growth, consisting of a continuation of the substrate lattice, there was a region in which the twinning of the deposit crystals on the octahedral planes appeared. The proportion of the twin crystals at the deposit surface increased until in the third region, the crystals were completely randomly disposed relative to the substrate. Finally, there gradually developed a preferred one-degree

orientation in which the deposit crystals have a particular densely populated row normal to the substrate.

Thus, the results showed a distinct region of twinning intermediate between the regions of parallel and random orientation. Setty and Wilman also found that in cathodic crystal growth, beyond the critical current density the upper limit of the deposit thickness corresponding to different regions, e.g. parallel, twinning and random, decreased with increase in current density. In other words, as the current density increased, the electrodeposit followed the orientation initiated by the substrate up to smaller and smaller thickness. The substrate crystal faces [e.g. (110) and (100)] with lower atomic density than for the (111) substrate, were found to have lower "critical current density".

The orientation of the crystals of the electrodeposit was found to depend also on the temperature and concentration of the bath. The increase in temperature or concentration led to an increase of the "critical current density" up to which parallel growth was possible.

Setty (1953) and Setty and Wilman (1966), see also Wilman (1955), also studied the effects of addition agents, such as carbon disulphide, thio semi-carbazide, thio-urea, potassium thiocyanate, and urea, on the growth of silver electrodeposits on the crystal of silver. They found that the addition agents such as these, used for promoting brighter

silver deposits, had widely varying effects on the mode of growth in respect of orientation, size and habit of deposit crystals, especially in deposits on the silver (110) face. At 20°C in deposits up to 10,000 Å thick, on the silver (110) face, the presence of carbon disulphide led to more pronounced twinning probably associated with some co-deposition of Ag_2S . Thio semi-carbazide caused outgrowth of extensive thin lamellae parallel to the $\{111\}$ planes of the substrate crystal but without twinning. Thio-urea caused extensive $\{111\}$ facets in addition to the (110) tips of the ridges along $[1\bar{1}0]$. Urea caused very strong $\{111\}$ twinning at 10 mA/cm^2 and alone gave development of ridges parallel to $[1\bar{1}0]$ at 60°C and 20 mA/cm^2 . Finally, KCNS caused little change except in the shape and size of the ridges observed at low current density. It was concluded that the main action of the addition agents appeared to be chiefly to modify the crystal habit and growth as a result of adsorption on the growing crystal surface.

Kumar (1955), also in this laboratory, used a complex cyanide bath ($\text{CuCN} + \text{KCN} + \text{KOH}$) for the study of the crystal growth of copper electrodeposits on smooth electro-polished silver single-crystal (110) and (100) faces. He also studied the crystal growth of silver deposits from a complex cyanide bath ($\text{AgCN} + \text{KCN} + \text{K}_2\text{CO}_3$) on an electro-

polished silver single-crystal (100) face and a copper single-crystal (100) face. In this case electrodeposits and the substrate both have the same crystal structure (f.c.cubic) but they are dissimilar metals, unlike the case studied by Setty and Wilman (1955).

Kumar found nearly the same general form of dependence of deposit structure on thickness, current density, bath composition and temperature, as was found by Setty (1953) and Setty and Wilman (1955). Some new features were also brought to light. The twinning was observed even at earlier stages of thickness, probably due to lattice misfit between silver and copper. Setty and Wilman did not observe any twinning below a certain c.d. and deposit thickness, when the deposit and the substrate were of the same metal, so that the effect of lattice misfit did not come into play.

It was observed in one case, that though copper starts growing in single crystal orientation parallel to the silver (100) face used as substrate, it was later deposited in a different orientation, that is, two-degree orientation of copper (110) parallel to silver (100) with copper [110] parallel to silver [011] or $[0\bar{1}1]$. Deposit crystals in single-crystal orientation have all three crystallographic axes parallel to the three cube axes of the substrate lattice, whereas, in "two-degree orientation", two lattice directions

are parallel to two directions of the substrate surface and other lattice rows not coplanar with these can take up one of several possible positions relative to that of the substrate lattice. The development of this particular case of a two-degree orientation was suggested as arising from twinning of the initial parallel growth and to a rotational disorientation of the deposit : : lattice. Kumar (1955) also showed that in some cases Cu electrodeposits on Ag showed "directed-disorientation" (see 1.3.4 above).

Reddy and Wilman (1958), and Reddy and Wilman (1963) investigated the structure and growth of iron electrodeposits on copper single-crystal (110), (100) and (111) faces. This was the first extensive systematic study of the cathodic crystal growth of a body-centred cubic metal on a single-crystal substrate of a f.c.c. metal crystal, over a wide range of thickness and current density.

Four main stages of growth of the iron electrodeposits were distinguished, characterised by a predominant type of orientation: (1) epitaxial (two-degree) orientation with a $\langle 111 \rangle$ Fe atom row along a Cu $\langle 110 \rangle$ row in all cases, and with a $\{211\}$, $\{110\}$ and $\{110\}$ plane respectively parallel to the copper $\{110\}$, $\{100\}$ and $\{111\}$ surfaces; (2) as (1), but with $\{211\}$ twinning; (3) either a wide range of orientations or random-polycrystalline structure; (4) development of one-degree $\langle 111 \rangle$ orientation (strongly "outward growth"). The twinning was developed, in deposits of a

thickness, above a critical current density which appeared to be lower on copper $\{111\}$ than on $\{100\}$ and $\{110\}$. This seems to be in reverse order to what was observed in silver deposits on silver by Setty and Wilman (1955). Under certain conditions, a new phenomenon, "one-sided" rotational displacements from the above epitaxial orientations were observed (see above sub-section 1.3.4).

Reddy and Wilman (1958, 1964), also identified $\text{Fe}(\text{OH})_2$ inclusions in some of the Fe electrodeposits. They also studied the structure of chromium electrodeposits at 50°C on copper single crystal substrates and found the same epitaxial orientations and rotational disorientations as for the iron. Reddy (1958) and Reddy and Wilman (1965) briefly studied nickel electrodeposits on copper (110) and (111) faces, and obtained orientations similar in form to those obtained by Kumar (1955) for silver on copper and copper on silver, except that the misfit of nickel on copper is small, thus no "directed" disorientation was noted.

Cusminsky (1965) studied systematically the crystal growth of copper electrodeposits on to the smooth electropolished (110) and (100) faces of copper single crystals, from a bath containing single Cu ions, namely $\{N/2 \text{ CuSO}_4 + N/2 \text{ H}_2\text{SO}_4\}$ electrolyte as a function of c.d. and deposit thickness. Though the deposits grew with the same lattice orientation as the substrate only up to a limiting thickness

before octahedral twinning began to be developed, at any determined c.d., a new surface habit appeared, with oblique plane faces, at an earlier stage well before the onset of twinning was observed. This deposit thickness at which oblique facet development occurred was shown for the first time to be systematically related to the current density. The current density-thickness loci for the stage of oblique facet development were of similar form to that for the development of twinning. The oblique facets observed were mostly at less than 35° to the mean substrate surface, and were different in the deposits on the two substrate faces.

It was also found that the stage of initiation of twinning, ^{and of} the growth with oblique facets occurred at a much lower thickness, at any given current density, in the electro-deposits on the copper (110) face than on the (100) face. This high degree of dependence of the structure of the deposits on the density of atomic packing in the substrate surface is analogous to that of the findings of Setty and Wilman (1955) in the case of silver on silver. Cusminsky's results also showed strongly layer-wise growth of Cu on the (100) face of Cu at 17 mA/cm^2 and 50,000 Å thickness.

Sundaram (1966) studied the habit and orientation of silver electrodeposits on electropolished single crystal (110) and (100) faces using a bath containing simple ions of silver, i.e. $\text{N}/2 \text{ AgNO}_3$. The results showed systematic

changes in the structure of the electrodeposit crystal orientation. At all c.d. investigated for both the faces, the deposits grow initially (up to a limiting thickness) parallel to the substrate, but with increase in the thickness of the deposit, octahedral twinning began to be developed at a deposit thickness depending on the c.d. for the electrodeposition. Like Gusninsky's results, oblique facet development occurred in some cases at an earlier stage prior to the onset of twinning, and in others along with twinning.

The occurrence of twinning and also the oblique-facet development was at a lower thickness for any given c.d. in the deposits on the Ag (110) face than on the Ag (100) face. Thus the structure of the deposit seems to be highly dependent on the density of the atomic packing in the substrate surface.

The close similarity in the curves for Cu on Cu (Gusninsky, 1965), and Ag on Ag (Sundaram, 1966), deposited from their simple salt baths, was established by Sundaram in terms of the number of atoms deposited per site per second and the thickness of the deposits. However, the initiation of twinning occurs at a higher thickness for a given c.d. in the case of copper than for silver ; mainly because copper is doubly charged and silver singly. Moreover, the ionic mobility of silver is greater than that of copper. This causes further minor differences in the condition at which twinning starts.

The results of the present work (see Results section below) provide a further detailed systematic study of the above type, in the case of nickel deposits on copper substrates.

SECTION 2.

EXPERIMENTAL DETAILS.

2.1. Preparation of Polished Polycrystalline Copper Substrates.

In order to prepare smooth flat polycrystalline copper substrates, high conductivity copper rod was used. Small pieces each of nearly 2.5 cms in length and 1.2 cms in diameter cut from a commercial copper rod were used as substrates after careful mechanical polishing and final cleaning.

The flat surface at one end of the copper piece was ground in one direction on emery paper down to 4/0 (5 μ particle size) with isopropyl alcohol as lubricant. After washing with water, the surface was further polished with "Selvyt" cloth wet with "Bluebell" metal polish, mounted on the rotating disc of a polishing machine. While polishing, the surface of the copper piece was kept wet with isopropyl alcohol, and the direction of abrasion was kept the same as it was at the time of abrading with emery paper. In addition, the surface to be polished was kept moving radially, slowly, to avoid deep scratches on the surface.

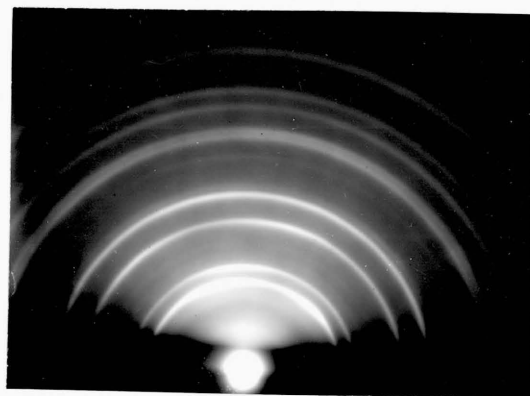
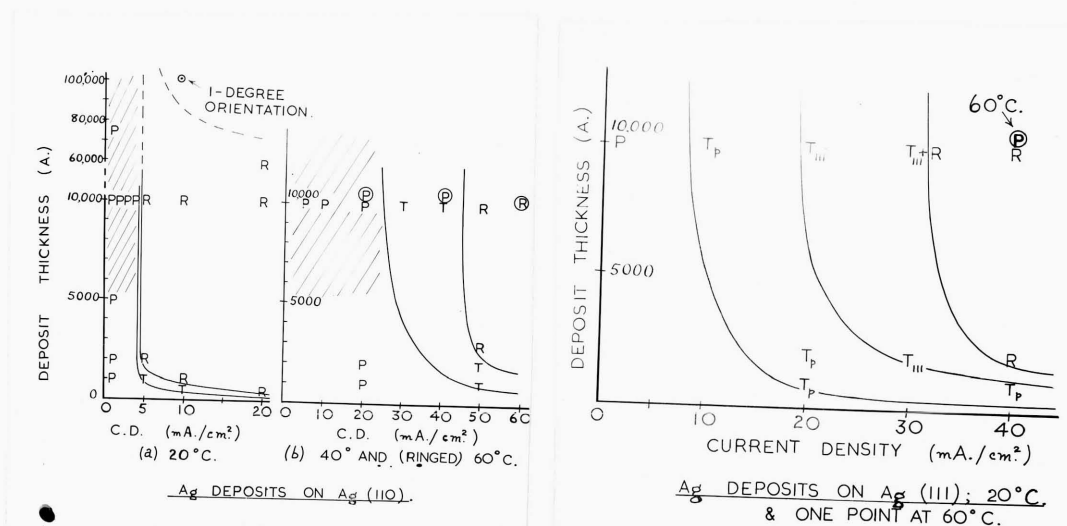
After about twenty minutes of metal polishing, the surface looked very shiny and reflecting. Then it was washed thoroughly with water, followed by dehydration in

isopropyl alcohol and acetone. Since copper is very susceptible to oxidation, the oxide formed on the polished surface was removed by keeping it in concentrated hydrochloric acid for about half a minute, at room temperature.

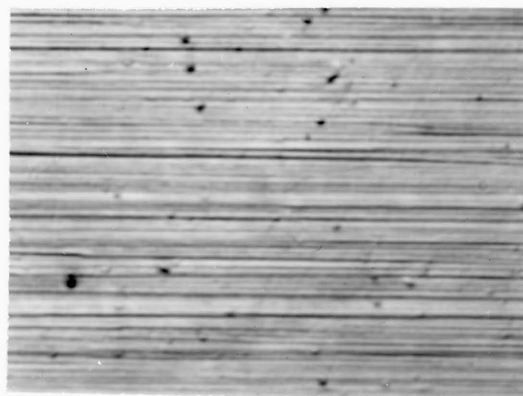
After etching away the oxide, the whole surface of the copper specimen was washed thoroughly with distilled water, avoiding undue delay leading to reoxidation. The surface of polycrystalline copper thus prepared and polished was used as substrate on which nickel was electrodeposited in the systematic studies described below. The electron diffraction photograph from smooth polished polycrystalline copper is shown in Fig.2a. In the electron diffraction photograph there are some faint rings due to silica embedded in the polished substrate. The optical micrograph in Fig.2b shows the smoothness of the polished surface.

2.2. Preparation and Surfacing of OFHC (Oxygen-free, High-Conductivity) Copper Single-Crystal.

Single crystals are usually prepared either from the vapour, from a solution, from solidification of a melt or from a rearrangement of atoms in the solid state (strain and anneal). Different methods for preparing single crystals have been described in the literature by Bridgman (1925), Gwathmey (1948), Lacombe (1951), Chalmers (1953), Setty (1953).



(a)



(b) x 300

Fig. 2. (a) Typical electron diffraction patterns and (b) Optical micrograph from smooth (mechanically polished) polycrystalline copper substrate.

The copper single crystals used in the present experiments were prepared by Dr. ^{E.A.D.} White in the Department of Electrical Engineering, Imperial College. The method followed was by the solidification of the molten metal.

In the present experiments, OFHC copper of very high purity was supplied by British Insulated Callender's Cables Ltd. The copper supplied in the form of a block was sawn into small pieces and put inside a pyrex glass tube of diameter about 1.3 cms, one end of which was closed and drawing it into a narrow drawn-out curving tip. Nearly six inches of the tube was filled with copper pieces. The other end was also sealed after pumping the air out of the tube.

The copper thus sealed under vacuum was melted in a furnace in the Electrical Engineering Department. Then the molten copper was allowed to undergo slow controlled cooling by lowering it through a temperature gradient. When it had attained room temperature, the glass tube was broken and the solidified rod of copper was taken out.

The surface of the copper rod so made was etched with concentrated nitric acid for 10 to 15 seconds and then washed with tap water. When observed carefully, the etched surface showed some reflecting plane facets, without any grain boundary, giving an indication that the copper rod was a single crystal.

The copper rod thus prepared was cut into three pieces each about 3 cms in length. Each of the pieces was examined by electron diffraction in the following way to be sure that it was a single crystal. A flat face was ground on the crystal down to grade 4/0 emery paper; then metal polished and washed in the same way as the polycrystalline substrate after polishing (see above). The polished face of the copper single crystal was etched with 40% dilute HNO_3 till the disoriented metal was completely removed. The crystal was washed with distilled water followed by acetone and finally in isopropyl alcohol in the usual way. The whole of the etched surface after polishing was examined in the electron diffraction camera in order to be sure that it was a single crystal. The uniform spot pattern obtained throughout the surface confirmed that the specimen was a highly perfect single crystal.

With the help of electron diffraction patterns the orientation of the crystal lattice relative to the surface was found. The desired faces were then cut with a fine saw, using isopropyl alcohol as a lubricant and avoiding undue pressure on the crystal in clamping and sawing. The faces thus prepared were (100), (110) and (111). The surfaces were ground to grade 4/0 emery paper, metal polished, washed thoroughly and then electropolished as described below.

2.3. The Electropolishing of the Copper Single Crystal Faces.

The electropolishing of metals has been extensively studied by many workers such as Jacquet (1936, 1938, 1947, 1948 and 1949), Pellissier, Markus and Mehl (1940), Von Hamos (1942), Honeycombe (1944), Courtel (1947), Agar and Hoar (1947), Wein (1948), Epelboin (1949 and 1952), Kawaski (1950), Nagai and Mano (1951), Rowland (1953), Hancher (1954), Sykes, Haddrell, Haines and Mott (1954-55). Wernick (1948) and Tegart (1956) have summarised the results of many investigations in monographs.

Although electrolytic polishing is widely used the exact mechanism has not been fully established in any specific case. Only a general explanation has been developed.

The metal to be electropolished forms the anode in an electrolytic cell, and continued solution of the metal occurs in such a way that irregularities on the surface become smooth and bright. Such behaviour is clearly a special case of more general anodic phenomena, for it is found that, depending on the conditions of operation and the solution used, a metal anode can be either etched, polished, partially passivated, or completely passivated (cf. Evans (1948), Kortum and Bockris (1951)).

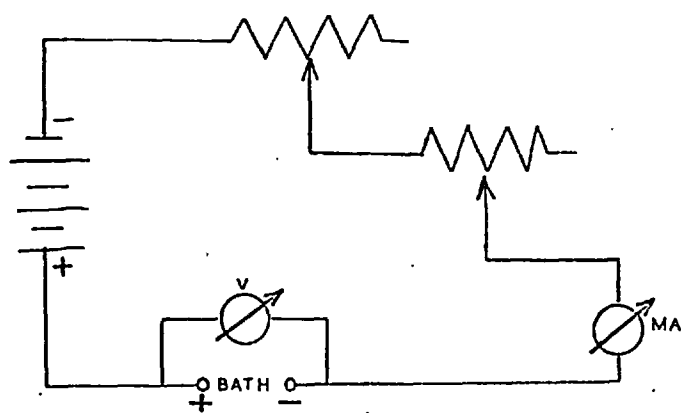
In the present experiments, the electropolishing of the copper single crystal faces was carried out as suggested by Steiner (1953) and used by Kumar (1955), Reddy (1958) and

Cusminsky (1965) in their experiments. The result was found to be very satisfactory, giving a nearly atomically smooth surface.

In the experimental arrangement for electropolishing a 250 ml pyrex beaker of diameter 7 cms was used as an electrolytic cell with nearly 140 c.c. of 50% orthophosphoric acid as the electrolyte. The cathode was a copper plate of about 12 sq cms in area with several holes drilled through it in order to facilitate the escape of gas bubbles formed there. The crystal was kept wholly inside the electrolyte and formed the anode. The surface of the crystal to be electropolished was made to face upward. It was adjusted below and parallel to the cathode plate. The surfaces being parallel and horizontal were kept about 2 cms apart. The cathode plate was also dipped inside the electrolyte. The current density was 0.07 to 0.08 amp/cm², and the voltage 1.9 to 2.0 volts. The electrical circuit is shown in Fig.3.

It has been observed that best polishing occurs when the solution becomes blue due to its high Cu⁺⁺ concentration. Before working with the single crystal a high Cu⁺⁺ concentration was obtained by dissolving polycrystalline copper sheet in place of copper single crystal as the anode.

When the electrolyte turned fairly deep blue, the single crystal was electropolished. Keeping the electrolyte



CIRCUIT DIAGRAM

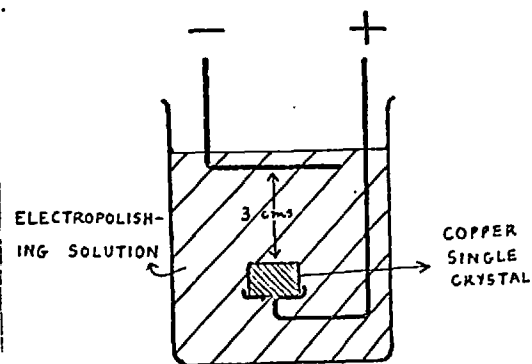
ARRANGEMENT OF ELECTRODES
IN THE ELECTROPLATING BATH

Fig. 3.

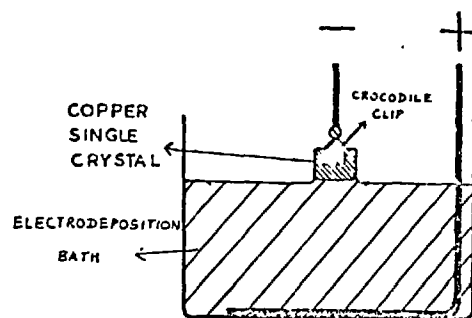
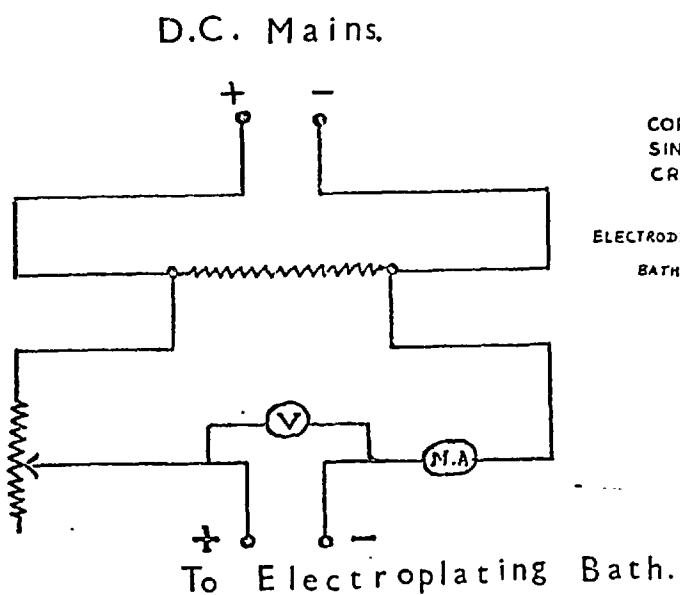
ARRANGEMENT OF ELECTRODES
IN THE ELECTRODEPOSITION BATH

Fig. 4 .

at room temperature ($\simeq 20^{\circ}\text{C}$), the time for adequate polishing was found by trial to be 20 to 30 minutes. Before arriving at the right conditions of electropolishing the specimen was electropolished and examined in the electron diffraction camera a few times until an atomically highly smooth surface was obtained.

In all cases of electropolishing, the switch in the circuit was switched on, keeping the cathode plate out of the electrolyte. Then the cathode plate was dipped into the electrolyte and electropolished. The crystal was taken out after polishing it for the requisite time, without switching off the current. It was washed in tap water for 30 seconds, then in 10% orthophosphoric acid (to avoid any precipitate of basic phosphate) and finally in a large amount of distilled water, followed by acetone to remove the water from the surface. After this washing procedure, the surface was etched with concentrated HCl for 30 seconds to remove the cuprous oxide from the surface if there was any. In later experiments, the etching chemically in conc. HCl was replaced by 10% potassium cyanide solution.

After removing the oxide, the specimen was washed quickly with distilled water followed by acetone, and lastly the surface was covered with a less volatile liquid, isopropyl alcohol, so as to avoid exposing the clean surface to air during its transference to the electron diffraction camera

and evacuation of the apparatus.

Though the copper single crystal faces thus electropolished were very bright and smooth, still for the confirmation that they were atomically highly smooth they were examined in the electron diffraction camera. The electropolished (100), (110) and (111) faces of the copper single crystal were used as substrates on which nickel was deposited. The diffraction patterns Figs. 5 to 10 obtained from these electropolished crystal faces, all showing well-defined Kikuchi bands and vertically elongated spots, indicate that the crystals had an atomically highly smooth surface.

2.4. Electrodeposition of Nickel from the Standard Nickel Sulphamate Solution.

$\text{Ni}(\text{SO}_3 \cdot \text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$	350 gm/litre
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	5 gm/litre
$\text{B}(\text{OH})_3$	35 gm/litre.

The standard nickel sulphamate solution of the above composition, supplied by British Insulated Callender's Cables Ltd., was used as electrolyte for nickel electrodeposition. The solution was of 'Analar' grade. The electrical circuit used for electrodeposition is shown diagrammatically in Fig. 4 . It is almost of the same type as that used for electropolishing, with the difference that the crystal has now been made the cathode. Since the

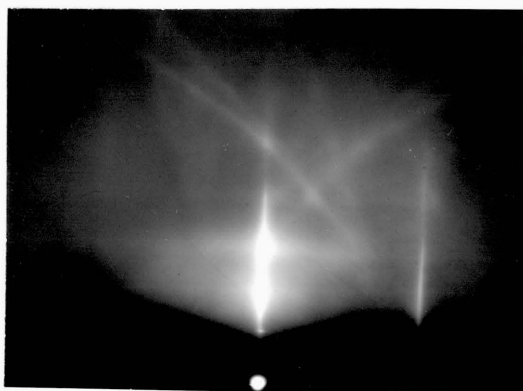


Fig.5. Beam along $\langle 210 \rangle$.

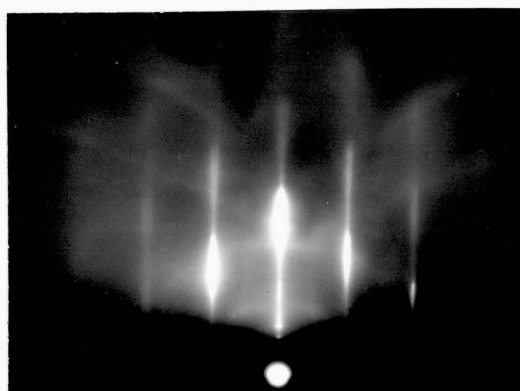


Fig.6. Beam along cube-face diagonal.

Figs.5 & 6. Patterns from smooth electropolished Cu (100) face.

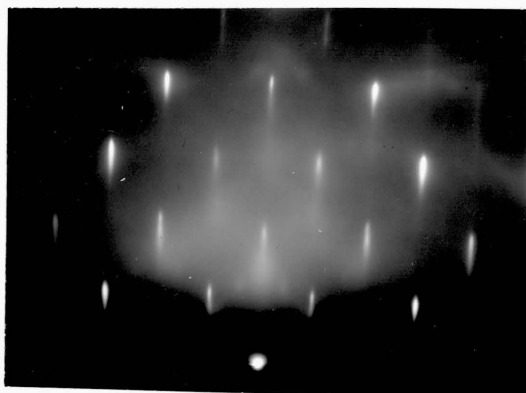


Fig.7. Beam along $\langle 110 \rangle$



Fig.8. Beam along $\langle 211 \rangle$

Figs. 7 & 8. Patterns from smooth electropolished Cu (110) face.

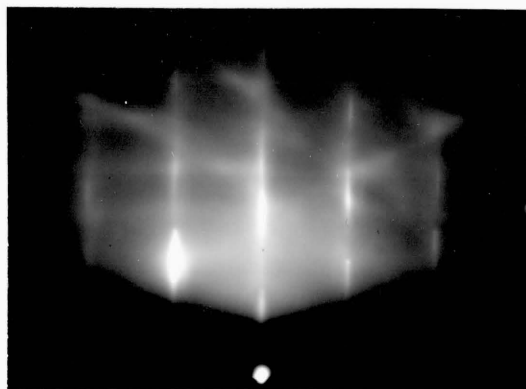


Fig.9. Beam along $\langle 110 \rangle$

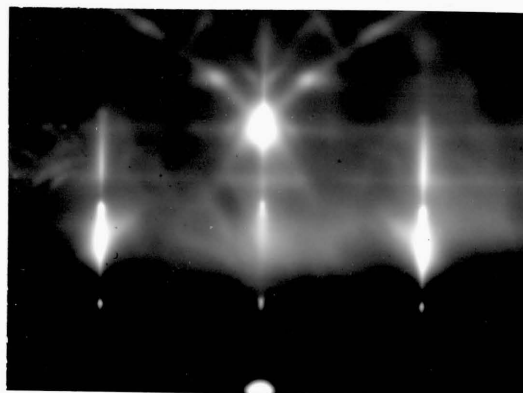


Fig.10. Beam along $\langle 211 \rangle$

Figs. 9 & 10. Patterns from smooth electropolished Cu (111) face.

electrodeposition involved mostly higher current density, the current was taken from the D.C. mains.

A carefully cleaned 100 ml. pyrex beaker of diameter 5 cms with nearly 60 c.c. of the electrolyte was used as the electrolytic cell. It was surrounded by a water jacket. A nickel sheet of diameter about 4 cms with its plane horizontal was made the anode.

Before using the polished substrate as cathode for electrodeposition at 50°C , it was kept immersed in nickel sulphamate solution at 50°C for 5 mins, so that the substrate may acquire the bath temperature. The polished copper substrate surface, facing downward, was immersed two mm. in the electrolyte, holding the crystal (by its other end in the air) with a crocodile clip. The surfaces of the anode (nickel sheet) and cathode (polished crystal) were made horizontal to each other. They were kept nearly 3 cms apart. The temperature of the bath was maintained as desired.

After making the adjustments as described above, the current already calculated and adjusted for a particular current density, was switched on. The electrodeposition was carried out at a particular temperature for a known time to give a desired deposit thickness at the desired current density.

Then the specimen was taken out of the electrolyte without switching the current off. It was immediately given a thorough wash with distilled water followed with acetone.

Finally it was covered with isopropyl alcohol and then transferred to the electron diffraction camera without any avoidable delay, and this was evacuated.

As for the variation of the temperature of the bath, there was hardly any change observed more than $\frac{1}{2}^{\circ}\text{C}$ at the lower current densities ($< 300 \text{ mA/cm}^2$) and for short periods of deposition (< 30 seconds). However, at higher current densities ($> 300 \text{ mA/cm}^2$) and for longer times of deposition, the change observed was found to be round about 8°C . Still, the temperature at which the electrodeposition started was that nominally associated with the deposit for practical purposes.

After transferring the specimen into the electron diffraction camera, the whole surface of the specimen was examined to see whether the same diffraction pattern was seen from all parts of the surface or not. The diffraction photographs were taken from different parts of the specimen at different azimuths. Subsequently, some of the specimens were also examined in the optical microscope under vertical and oblique illumination of the surface.

The thickness of the electrodeposit was calculated from Faraday's law, but taking into account the estimated current efficiency, E :-

$$\text{Deposit thickness} = \frac{EW}{A\rho}$$

theoretical

where w = weight of the electrodeposit in gms, A = area in sq.cms. and ρ = density of the metal in g/cm^3 .

This method gives the average thickness of the deposit.

Deviation from 100% current efficiency only occurred above a certain current density. The experiments and results on current efficiency are discussed further in section 3, below.

In the present work, using electropolished (100), (110) and (111) faces of the copper single crystal as substrates, in addition to the mechanically polished polycrystalline copper, the structure of nickel electrodeposits has been studied systematically by varying the current density, temperature, deposit thickness and the degree of stirring.

For stirring, a glass stirrer with a flat and slightly twisted part at its end was used. Its other end was rotated by a motor at nearly 1200 revolutions/minute. The speed of rotation was also controlled by a rheostat in series with the motor.

After performing the necessary electron diffraction examination of the surface of the nickel electrodeposit, nickel was removed from the copper substrate by boiling in orthophosphoric acid. The surface was repolished in the usual way and used as substrate again.

2.5. Special Precautions Necessary for Preparing Substrates and Electrodeposits for Electron Diffraction Examination.

(i) . For sawing, the crystal should be clamped lightly in between two wooden pieces inside the vice to avoid undue pressure on the crystal. It should be kept wet by isopropyl alcohol which serves as lubricant, and at the same time it does not allow the temperature to rise much due to the frictional heat developed in sawing.

(ii) The electron diffraction pattern from the face of a single crystal should be carefully studied in order to bring the desired plane on the surface. One should ascertain correctly from which side and end how much of the crystal has to be removed off before getting the required plane. At the same time the azimuth should be chosen so that there is minimum waste of the single crystal. For adequate accuracy the surface of the crystal should be marked with a line where the desired plane meets the surface, after studying the initial diffraction pattern.

(iii) After sawing the crystal judiciously, the following operations were followed in succession. (1) The surface was made smooth with emery paper, starting at grade 2 and ending up to 4/0 (5 μ particle size), followed by washing with tap water. (2) It was then polished with "Bluebell" metal polish, keeping the surface wet with isopropyl alcohol

to avoid heating, then thoroughly washed with tap water.

(3) This surface was etched in 40% HNO_3 solution, washing with tap water was followed by acetone and then the surface was covered with isopropyl alcohol. If etching is not sufficient to remove all the disoriented and deformed metal, rings or arcs will also be seen in the electron diffraction pattern. In that case, further metal should be removed by further etching until a clear and well-defined spot pattern is obtained, which proves that the specimen is a single crystal.

(iv) Better electropolishing is attained when the electrolyte has become blue due to ~~high~~ Cu^{++} concentration. After electro-polishing, the surface should on no account be either touched or rubbed.

(v) The part of the crystal surface other than the polished face over which nickel has been deposited should also be taken into consideration for calculating the current density and the corresponding deposit thickness.

(vi) The specimen of the electrodeposit prepared should not be touched or rubbed during washing; otherwise there might be deformation and disorientation of the crystal structure.

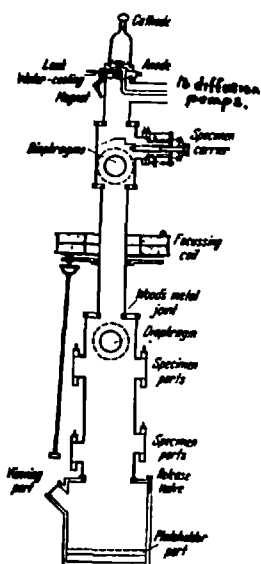
2.6. The Electron Diffraction Technique.

The electron diffraction technique has been evolved since its discovery in 1927. Thomson (1928) designed and built the first apparatus for the photographic recording of diffraction patterns, using fast electrons (accelerating potential of the order of a few tens of kilovolts).

The electron diffraction camera used in the present work (Fig.11) is of the type designed and used by Finch and Wilman (1937) except that the mercury diffusion pump was replaced by oil diffusion pumps.

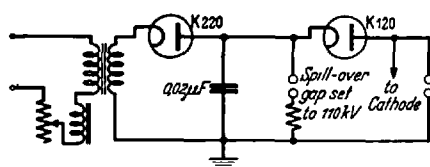
For high tension supply a typical half-wave rectification circuit and saturated-diode constant-current output is described by Finch and Wilman (1937) and Finch, Quarrell and Wilman (1935), Fig. 12. It is intended for cold-cathode discharge generation of an electron beam and the saturated diode supplies constant current to the discharge tube. If the gas pressure does not alter, this means that the voltage is steady across the discharge tube. The spark-gap method of measuring the electron accelerating voltage has been followed, using 10 cm diameter brass spheres. The voltage at which the electron diffraction studies of the specimens were carried out was in the range of 50-60 KV.

The source of electrons is the cold cathode discharge. The anode block is provided with a diaphragm in



C

Fig. II. Diagram of the Electron Diffraction Camera.



High-tension circuit with constant current output.

Fig. I2.

the form of a pin-hole of about 0.1 mm diameter in thin nickel sheet. A fine and nearly monochromatic beam of high energy electrons is obtained by allowing the electrons to pass through the anode diaphragm.

The focussing of the electron beam on the fluorescent screen is done by the coaxial focussing coil. The current ~~th~~^r_hrough the focussing coil is adjusted until the electron image of the anode pin-hole is formed on the fluorescent screen at a distance of 47-50 cms. from the specimen. When a current is passed through the focussing coil a magnetic field is produced perpendicular to the direction of the electron beam, and the coil serves as a converging magnetic lens. The focal length of such a magnetic lens is given by

$$f = \frac{8P}{i^2 \eta \int_{-\infty}^{+\infty} (H_z)_0^2 dz}$$

where i is the current in the coil, $(H_z)_0$ is the value of the magnetic field H on the axis of the coil when unit current flows, $\eta = e/m$ and P is the accelerating voltage in e.m.v. The z -axis is taken along the axis of the coil with origin at the centre. The ordinary lens formula $\frac{1}{f} = \frac{1}{u} + \frac{1}{v}$ applies, where u is the distance from anode aperture to the coil and v is the distance from coil to screen.

It may be noted that rays initially lying in one axial plane also lie in one axial plane after passing through

the lens, but the plane is turned through an angle ϕ about the axis, where

$$\phi = \frac{i}{2} \sqrt{\frac{n}{-2P}} \int_{-\infty}^{+\infty} (H_z)_0 dz$$

By altering the tilt of the coil a well focussed electron beam is allowed to fall on the specimen at a grazing incidence of the order of $\frac{1}{2} - 1^\circ$ in order to obtain the diffraction pattern from the specimen. The electron diffraction pattern is recorded on a photographic plate by lifting the fluorescent screen, which is hinged at one side. The lifting operation is carried out from outside the camera with a rotatable knob. After exposing the plate, the inside of the camera is brought to atmospheric pressure by letting in air, and the plate is removed and developed.

2.7. Methods of Interpretation of Electron Diffraction Patterns.

Reviews of electron diffraction techniques have been given by Thomson (1930), Mark and Wierl (1931), Finch, Quarrell and Wilman (1935), Beeching (1936), Finch and Wilman (1937), Thomson and Cochrane (1939), Laue (1944), and Pinsker (1949, 1953).

The method of interpreting electron diffraction patterns from rotating crystals or one-degree-oriented polycrystalline specimens developed by Wilman (1952) in this laboratory has been found to be very useful and convenient.

In addition to this, methods of interpreting the Kikuchi line patterns from single crystals (Wilman, 1948 a,b) and spot patterns from single crystal groupings (Wilman, 1950, 1951) have also been developed by him in this laboratory. The electron diffraction patterns of diffuse maxima from molecular crystals were discovered and interpreted in this laboratory by Charlesby, Finch and Wilman (1939) and maxima of a less diffuse nature of the type recognized in X-ray diffraction as due to thermal oscillations in the lattice were recognized by Charlesby and Wilman (1942).

A further special type of electron diffraction pattern is that associated with a continuous or discrete "directed-disorientation" which appears to be related with stresses in epitaxial layers on single crystal substrates due to lattice misfits (Evans and Wilman, 1950; Goswami, 1950; Gharpurey, 1950; Kumar, 1955; Reddy and Wilman, 1959).

In the present work the reflection electron diffraction technique was used to study electrodeposits at polished copper (polycrystalline, single crystal) substrates. The diffraction patterns obtained were in the form of either continuous rings from randomly oriented crystals, or spot patterns or arc patterns on the ring positions due to preferentially oriented crystals. The methods of interpreting the above patterns have been discussed below in detail.

(i). The Method of Interpreting a Ring Pattern.

In the case of diffraction from a polycrystalline specimen as in fig. 13, AB represents a plane of a given crystal. The electron beam is incident on that at the Bragg angle of grazing incidence θ . The incident waves strike the crystals oriented at all possible angles and the beams reflected from all lattice planes which are at the Bragg angle θ to the primary beam reach the screen S. Due to the presence of crystals oriented at all angles, the diffracted electron beams form cones of various radii due to various parallel sets of planes. This leads to the formation of a ring pattern on the screen. A particular set of planes (hkl) represented by AB in the diagram, gives rise to a ring of radius R on the screen :-

$$R = L \tan 2 \theta \quad (1)$$

where L is the distance between the specimen and the screen ("camera length").

Again, the Bragg's condition of reflection from net planes with spacing 'd' gives

$$2 d \sin \theta = n \lambda \quad (2)$$

where λ is the wavelength of the electrons and n is the order of reflection.

From equations (1) and (2),

$$d \approx n [\lambda L/R] \quad (3)$$

when θ is very small.

A multiplying factor $[1 + \frac{3}{8} \frac{R^2}{L^2} + \dots]$ is used to give a still closer approximation.

For any crystal, the net plane spacings are related to the Miller indices h, k, l ; the axial lengths a, b, c , of the unit cell, and the angles α, β, γ between the axes.

The mathematical formulae for the net plane spacings of some of the symmetrical crystal systems are as follows:

$$\begin{array}{ll}
 \text{Cubic} & \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \\
 \text{Tetragonal} & \frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \\
 \text{Orthorhombic} & \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \\
 \text{Hexagonal} & \frac{1}{d^2} = \frac{4}{3a^2} (h^2 + k^2 + hk) + \frac{l^2}{c^2} \quad (4)
 \end{array}$$

From equation (3), the net plane spacings 'd' of a crystal can easily be calculated by measuring the ring radii 'R' of the diffraction pattern.

The Miller indices hkl can also be worked out either mathematically from the above equations or graphically after calculating the net plane spacing 'd'.

The Determination of λ

De Broglie gave a relation that the wavelength of the electrons is given by

$$\lambda = \frac{h}{mv} ,$$

where h is Planck's constant, m and e the mass and charge of the electrons respectively, v their velocity and V the accelerating potential for the electrons.

The energy of the electrons is expressed by

$$eV = \frac{1}{2} mv^2 .$$

Substituting the approximate values of h , m and e ,

$$\lambda = \frac{h}{\sqrt{2meV}} = \sqrt{\frac{150}{V}} \text{ Angstroms.}$$

Applying relativistic correction, the electron energy formula changes to

$$eV = \frac{m_0 c^2}{\sqrt{1 - v^2/c^2}} - m_0 c^2$$

where c is the velocity of light. Hence,

$$\lambda = \frac{hc}{\sqrt{eV (eV + 2 m_0 c^2)}}$$

Thus, knowing all the terms in the right hand side of the above expression λ can be calculated.

(ii) Method of Interpreting a Spot Pattern.

The electron diffraction spot pattern from a single crystal can be interpreted in three ways:- in terms of (a) Bragg reflection of the primary beam from the net planes in the crystal; (b) Laue zones of reinforcement of the spherical wavelets scattered from successive lattice points along any

lattice row; and (c) Ewald's reciprocal-lattice construction for the directions of the diffracted beams.

Bragg's law gives the condition of appearance of diffraction maxima as a specular reflection of the primary electron beam in any net plane of the crystal. Mathematically it is expressed as $n\lambda = 2d \sin \theta$, where 'd' is the distance between the net planes, θ is the angle of grazing incidence λ , the wavelength and n is an integer.

In the conception of Laue (1912), the primary beam is considered as equivalent to a plane wave, and when this is diffracted from a three dimensional lattice, spherical diffracted wavelets are sent out by the atoms, and the mutual interference of these from the atoms in three sets of non-coplanar atom rows is considered. A regular network of diffraction spots is obtained on the fluorescent screen or photographic plate from the two-dimensional lattice which is normal to the incident beam or nearly so. A third atom row which is parallel to the beam or nearly so, gives a set of concentric circular reinforcement zones called "Laue zones" with their common axis on this lattice row. The spots of the two-dimensional pattern are then superimposed on these circular Laue zones of reinforcement. The spots become brighter when they lie on one of the circular zones as shown in fig. 14.

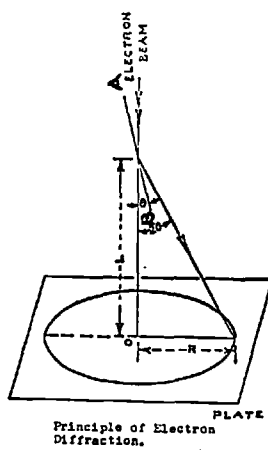


Fig. I3.

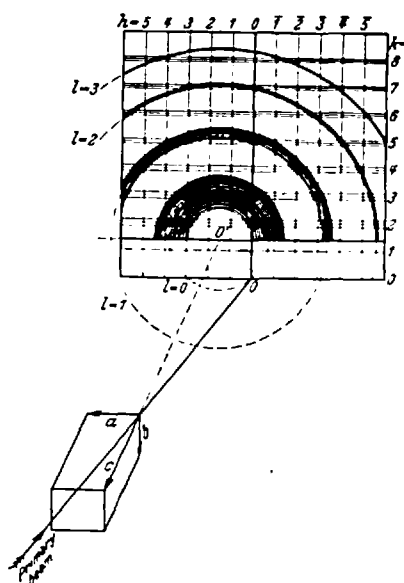


Fig. I4. Diagram of Laue Zones.

The third method of interpretation is the Ewald reciprocal lattice method. The reciprocal lattice is based on three vectors $\underline{a}^*$, $\underline{b}^*$, $\underline{c}^*$, as axes, such that $\underline{a}^*$ is perpendicular to $\underline{b}$ and $\underline{c}$ and of length $(bc \sin \alpha)/V$, $\underline{b}^*$ is perpendicular to $\underline{c}$ and $\underline{a}$ and of length $(ca \sin \beta)/V$, and $\underline{c}^*$ is perpendicular to $\underline{a}$ and $\underline{b}$ and of length $(ab \sin \gamma)/V$, where V is the volume of the unit cell having axes $\underline{a}$, $\underline{b}$, $\underline{c}$. Ewald showed that if a distance $1/\lambda$ is marked out from the origin in a direction opposite to the primary electron beam and if a sphere of radius $1/\lambda$ is drawn round that point, then the strong diffracted beams occur in directions joining the sphere centre to any reciprocal lattice point which lies on the sphere.

For fast electrons, 50-60 KV, λ is of the order of 0.05 Å. The radius, $1/\lambda$, of the 'sphere of reflection' is small compared with the distances apart of the reciprocal-lattice points. Thus, the spot pattern on the photographic plate, which is distant L from the specimen, approximates to the array of reciprocal-lattice points in the plane which is perpendicular to the primary beam, but enlarged in scale by ratio $\lambda L : 1$. When this sphere surface deviates away from the tangent plane at the origin, it will intersect consecutive parallel reciprocal lattice planes in circular regions. This corresponds to circular zones of increasing radii on which diffracted beams occur as observed on the plate.

Finch and Wilman used the term "one-degree orientation" when the crystals in a polycrystalline specimen have a certain type of lattice row $[UVW]$ in common, but otherwise randomly disposed azimuthally about this common axis. The electron diffraction pattern obtained from such specimens is analogous to that which is formed by rotating a single crystal round the $[UVW]$ lattice row placed parallel to the orientation axis. Usually, the one-degree orientation pattern is in the form of arcs due to some spread of orientation away from the mean orientation axis. This leads to the formation of arcs instead of spots.

In order to analyse a reflection electron diffraction pattern of this type, the specimen is rotated ^{about its surface normal} λ and the pattern is checked ^{as to} whether it is the same at all azimuths. If so, the orientation axis must be normal to the specimen surface and the Laue indices hkl of the arc which is centred on the plane of incidence are next determined from the relative radii of the set of diffractions observed. This strong arc corresponds to a Bragg reflection from the (hkl) crystal planes which are parallel to the mean substrate surface.

For the construction of theoretical pattern for an orientation with an (hkl) plane parallel to the substrate, the knowledge of $U:V:W$, of the lattice direction perpendicular to the (hkl) planes, is necessary. Wilman(1952)

derived an expression for the ratio $U:V:W$ for the general triclinic case. The ratio for crystals of higher symmetry are expressed as follows:

$$\begin{array}{ll}
 \text{Hexagonal} & U:V:W = (2H+K):(H+2K):\frac{3}{2} \frac{L}{(c/a)^2} \\
 \text{Tetragonal} & U:V:W = H:K:L/(c/a)^2 \\
 \text{Orthorhombic} & U:V:W = H/a^2:K/b^2:L/c^2 \\
 \text{Cubic} & U:V:W = H:K:L.
 \end{array}$$

One can easily draw the scale diagram showing the ring positions and the layer lines or Laue zones associated with the $[UVW]$ lattice row. The layer lines are practically straight and normal to the projections of the $[UVW]$ axis on the plate. The spacing between two consecutive layer lines being the same is given by $\lambda L/T_{[UVW]}$, where λ is the wavelength of the electron beam, L the camera length and $T_{[UVW]}$ the lattice translation vector along the $[UVW]$ direction. Diffraction maxima of any given type with indices hkl occur at the intersection of hkl ring and layer line of h^{th} order where

$$h' = hU + kV + lW.$$

While drawing the theoretical pattern, the points satisfying the above conditions are marked. It is also supposed that all the symmetrically equivalent planes of the type $\{hkl\}$ lead to the formation of diffractions on the ring position concerned. The theoretical pattern thus drawn is compared with the experimental one.

The present work involves the study of orientation and habit of electrodeposited crystals by electron diffraction techniques. The effective depth of penetration of electrons without loss of energy and thus losing their power for interference depends mostly on the condition of the surface. The depth of penetration of electrons in the case of a flat surface at grazing incidence is very small, whereas for rough surfaces, the depth of penetration below the tips of the projected part is larger. Finch and Wilman (1937) showed that the depth of penetration of electrons at $\sim 1^\circ$ grazing incidence in atomically smooth surfaces is of the order of 40 Å for crystals of light elements, such as Si, O, C, etc. This is equivalent to a penetration of about 5000 Å in the beam direction before much inelastic scattering occurs.

The horizontal Laue zones on which the spots lie are considerably broadened as a result of small depth of penetration of the beam normal to the surface. But the vertical Laue zones due to the atom rows parallel to the surface are, on the other hand, relatively very narrow Laue zones. The elongation of spots from an atomically smooth surface is greater the nearer the spots are to the shadow edge, as in Fig.14.

Sometimes the refraction of the diffracted beams at the smooth surface causes the displacement of the centres

of the spots towards the shadow edge. An atomically rough surface without faces gives rise to a transmission type of pattern whereas those with projecting facets form arrow head shaped spots if inclined faces are nearly parallel to the electron beam. In the case of smooth but corrugated surfaces the number of spots in a diffraction pattern is larger when the electron beam is incident along the corrugation.

(iii) Identification of a Material.

The identification of the material by electron diffraction technique is based on the formula $d = \lambda L/R$. From our experimental observations of λ , L and R , the values of d are calculated. Then a set of values is compared with the net plane spacings of known materials and the unknown material is identified when there is agreement between the two. But this is subject to some error in the measurement of R and λL . In order to avoid the error involved in determining λL , the diffraction pattern from the unknown material is obtained in the presence of a material of known lattice dimension, from which, with its R values, λL can be calculated. Then the lattice dimension of the unknown material is calculated with accuracy.

RESULTS.

The electrolyte used throughout these experiments consisted of $\text{Ni}(\text{SO}_3 \cdot \text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$ - 350 g/l, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ - 5 g/l, $\text{B}(\text{OH})_3$ - 35 g/l. It was supplied by British Insulated Callender's Cables Ltd., who obtained it commercially from Messrs. Albright and Wilson Ltd. In all cases the nickel electrodeposits had the face-centred cubic structure.

3.1. Current Efficiency Measurements.

The current efficiency of a reaction is the ratio of the actual amount of material deposited to that expected theoretically on the basis of Faraday's laws of electrolysis. In the following experiments the measured rate and the theoretical rate of deposition are plotted against the c.d., and the current efficiency is thus the ratio of the ordinates of these loci.

For the study of the variation of current efficiency with respect to current density, the electrolysis was carried out in a pyrex crystallising dish of diameter 8 cm., see Fig. 15. The depth of the electrolyte was 4.2 cm. The cathode was a polished polycrystalline copper disc of diameter 4.7 cm. and thickness 3 mm. A nickel sheet nearly 0.5 mm. thick and 5.2 cm in diameter forming the anode was adjusted horizontal with its plane almost in the bottom of the bath. The cathode plate with its polished lower face inside the bath faced downward towards the anode.

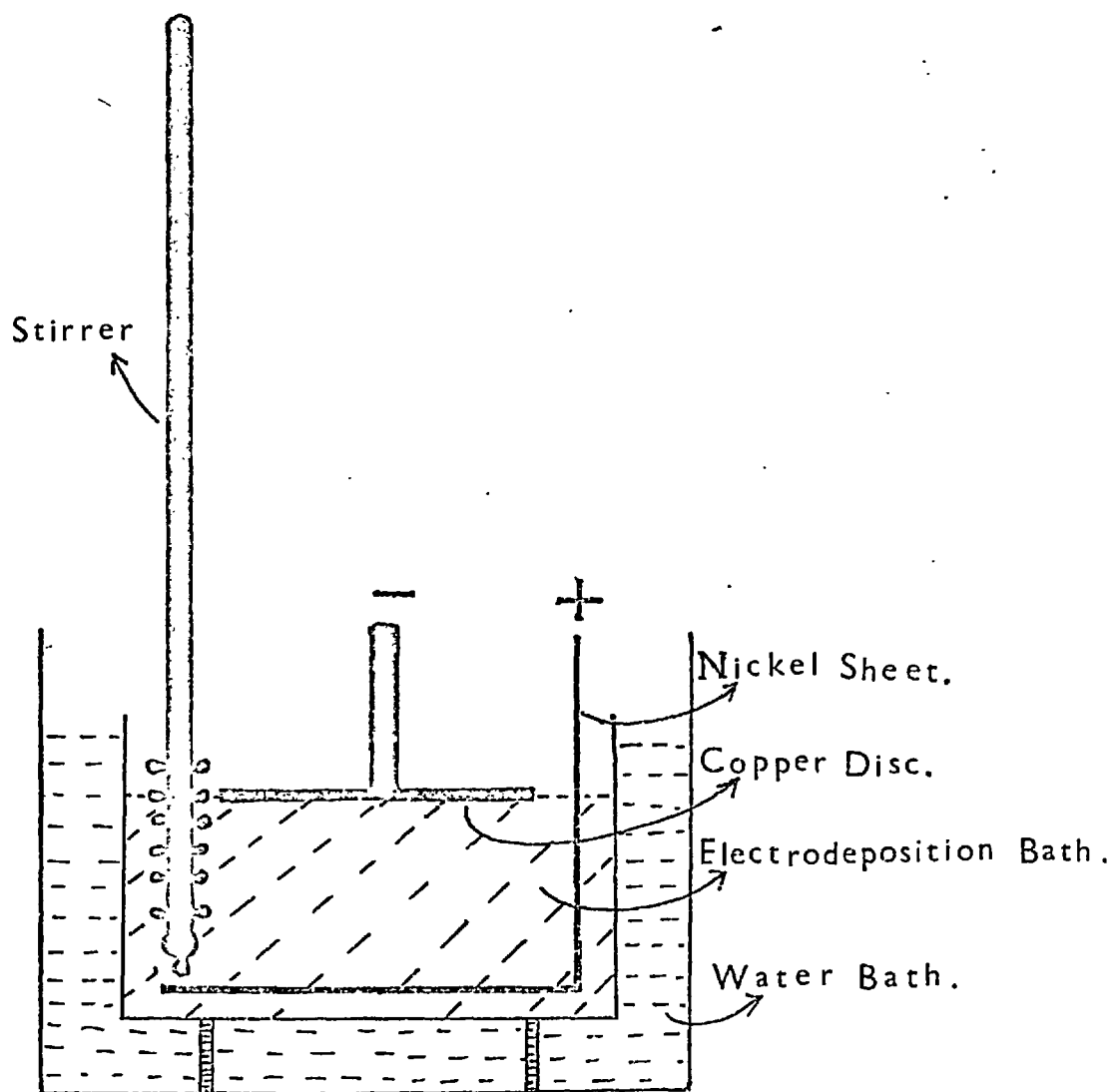


Fig. 15.

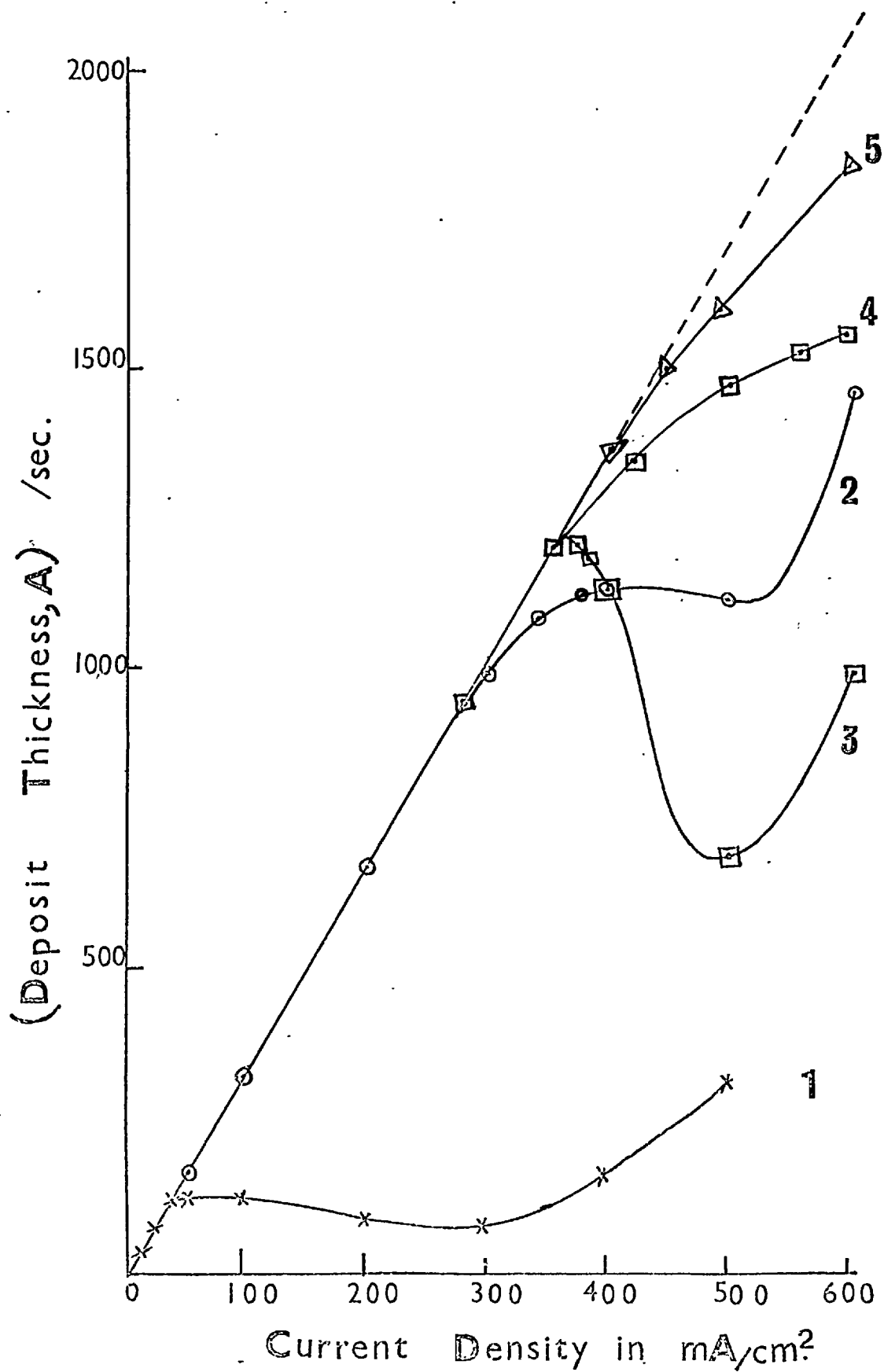


Fig. 16(a).

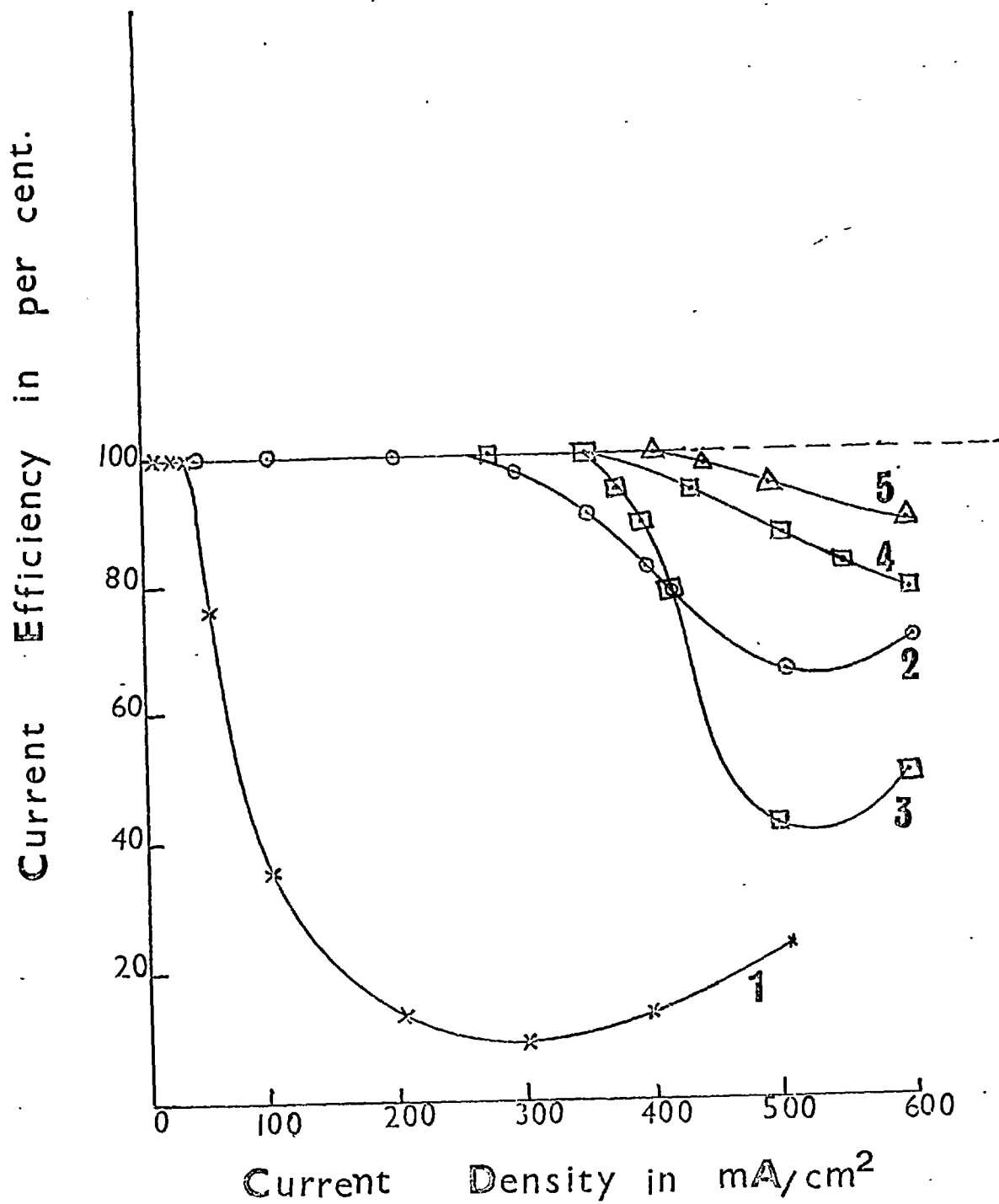


Fig. 16 (b).

Their faces were adjusted parallel or nearly so, to each other. The cylindrical sides of the cathode were also in contact with the electrolyte to 3 mm height, and deposition of the metal occurred on that also.

The electrolysis was carried out for one minute, nickel being deposited on the weighed cathode. From the increase in the weight of the cathode, the thickness of nickel deposited in angstroms per second was calculated. This experiment was done at various c.d. and the corresponding rates of deposition were determined.

Results were obtained at 20° and 50°C with the unstirred bath, and 50° and 60°C with the stirred bath. While stirring the electrolyte, the axis of the spirally twisted glass stirrer was adjusted vertically at about 1.8 cm from the side of the bath (see Fig.14). The stirrer rotated at about 1,200 r.p.m. The four sets of results are shown in Fig.16(a). The variation of current efficiency with c.d. at temperatures 20°C (bath unstirred), 50°C (bath stirred and unstirred) and 60°C (bath stirred) is shown in Fig.16(b).

In all these sets of results the fall in current efficiency below 100% was accompanied by evolution of oxygen at the anode and hydrogen at the cathode, and formation of a greenish hydroxide layer on the cathode.

3.1(a). Current Efficiency with the Nickel Sulphamate Bath at Room Temperature ($\approx 20^{\circ}\text{C}$) and Unstirred.

Observed rates of deposition are shown by curve 1 in Fig.16(a). It is seen that there is 100% current efficiency up to nearly 40 mA/cm^2 c.d. At higher c.d. the experimental curve starts to branch off below the theoretical straight line, with a gradual rise to its maximum peak round about 45 mA/cm^2 . Then it falls to its lowest value at about 300 mA/cm^2 . With further increase in c.d. the curve again rises.

3.1(b). Current Efficiency with the Nickel Sulphamate Bath at 50°C and Unstirred.

The observed rates of deposition are shown by curve 2 in Fig.16(a). In general nature, curve 2 resembles curve 1 with the difference that the current efficiency is found to be 100% up to about 270 mA/cm^2 . After that it starts to branch off below the theoretical straight line, i.e. there is less than 100% efficiency.

The measured rate of deposition becomes a maximum at around 375 mA/cm^2 and then starts to decrease. The trend in decrease continues up to about 480 mA/cm^2 . After that, the curve shows an abrupt rise.

3.1(c). Current Efficiency with the Nickel Sulphamate Bath at 50°C and Stirred.

Curves 3 and 4 in Fig.16(a) were obtained in two sets of experiments, and show a variation. The upper curve 4 is near to the straight line graph of the theoretical rate of deposition. This disagreement between the two curves 3 and 4 is attributed to a difference in the degree of stirring, presumably associated with an appreciable difference in the position of the stirrer. In the case of curve 3, above about 360 mA/cm^2 , an extensive greenish deposit (nickel hydroxide) was seen on the cathode, increasing in amount with increase in c.d. For curve 4, much less of this hydroxide was observed at similar c.d., thus it seems clear that the large fall in efficiency is associated with much of the cathode becoming covered with oxide and the effective c.d. being very much increased.

The branching of both the curves 3 and 4 from the theoretical line starts at about 360 mA/cm^2 . The maximum of curve 3 is at about 380 mA/cm^2 c.d. and the curve then falls to its lowest possible position at around 500 mA/cm^2 and then rises rapidly. The upper curve 4 after separating from the theoretical line does not show any marked peak and trough like curves 1, 2 and 3. It simply rises continuously below the theoretical line.

3.1(d). Current Efficiency with the Nickel Sulphamate Bath at 60°C and Stirred.

Curve 5 was obtained with the stirred bath at 60°C. The deviation of the experimental curve 5 from that of the theoretical line starts at about 400 mA/cm². The curve rises always below the theoretical straight line without forming any crest and trough unlike the curves 1, 2 and 3.

3.2. Electrodeposition of Nickel on a Rotating Cathode.

The substrate used as cathode was a solid cylindrical piece of polycrystalline copper of 1.2 cm in diameter and nearly 2.5 cms long. The lower end of the axis of the driving motor was attached to a small hollow metallic cylinder of length nearly 2 cm and inner diameter 1.4 cm. One of the flat surfaces of the copper substrate was mechanically polished, cleaned and made oxide free, in the usual way (see 2.1). It was kept in nickel sulphamate solution at 50°C for 5 minutes.

The copper piece was then fixed by screws to the lower end of the vertical axis of the driving motor, so that the polished copper surface faced downward parallel to the horizontal anode. The distance between the electrodes was kept about 3 cm. The height of the cathode was adjusted in such a way that only 2 mm of its length was inside the electrolyte in addition to the horizontal surface facing the anode. During the experiment the electrical connection to

the rotating cathode (at about 1200 r.p.m.) was made through a slip ring. The results on the stationary cathode on unstirred and stirred baths were also obtained under similar conditions.

The experimental results are shown in Table 1, and also, for comparison, the results under similar conditions on a stationary cathode in the unstirred and stirred baths at 50°C. Typical electron diffraction photographs are shown in Fig.17.

It is seen that both the stirring and cathode rotation have similar type of effect in promoting the lateral growth type of orientation, with (100) plane parallel to the cathode.

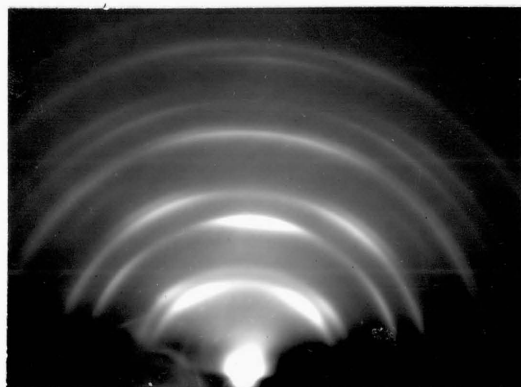
Table 1.

Current Density mA/cm ²	Deposit Thickness A	Nickel Orientation *		
		Cathode Rotated Solution Unstirred	Bath Stirred Cathode Stationary	Bath Unstirred Cathode Stationary
240	49,000	S(100) [‡] + tr (210)	S(100) [‡]	S(100) [‡]
300	10,200	S(100) [‡] + tr {111, twin. or (111)	S(100) + M(210) + tr. {111} twinning or (111)	S(110)
300	15,300	S(100) + M{111} twin. or (111)	S(100) + M{111} twinning or (111)	S(110)
300	81,600	S(100) [‡] + F(110) + F(210)	S(100) [‡]	Random
400	22,000	S(100) [‡] + F(110) + F(210)	M(100) + M(210) + F(110)	S(110) [‡] + (210) [‡]

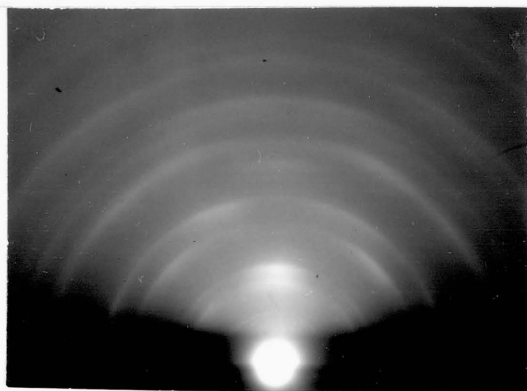
* S=strong, M = medium, F = faint, tr = trace.

‡ = Strong refraction of the electron beams by smooth plane surface of this type.

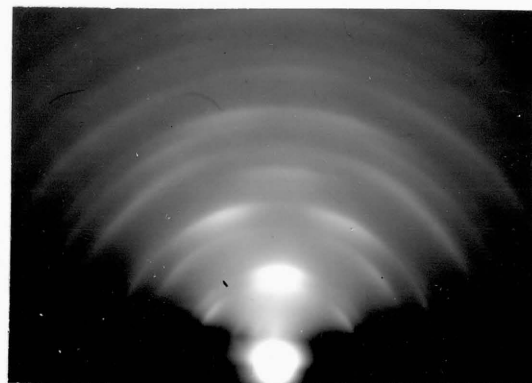
‡ = Observed after etching away the oxide on the rough deposit, with 5% H₂SO₄ for 10-15 secs.



(a)



(b)



(c)

Fig.17. Ni electrodeposits 15,300 Å thick at 300 mA/cm^2 on polycrystalline copper, at 50°C .

- (a) using the unstirred bath and a stationary Cu cathode
- (b) using the unstirred bath and a rotated Cu cathode
- (c) using the stirred bath and a stationary Cu cathode.

3.3. The Degree of Uniformity of Current Density Over the Cathode Surface.

In all the present experiments, the electron beam was used at grazing incidence of about $\frac{1}{2}$ to 1° to determine the deposit surface structure. The beam thus impinges on a length of about 2 to 1 cm respectively, from the bottom edge of the specimen upwards; as compared with the diameter of the specimens used of the order of 1 cm. The diffraction pattern is thus contributed to by both the central region and the outer edge region of the cathode, which may in some cases have different crystal orientations. The experiments (P. 127) below were made to test this possibility in several cases. In the present case, it appears that the c.d. is appreciably higher near the edge than in the main central area, as indicated by visual appearance. (roughness and in certain cases greenish hydroxide deposits).

Such considerations have been noted by Finch and Dayton (1951). They indicated that the complexity in their electron diffraction results of copper deposit was due to the inequality of the c.d. distribution.

The degree of lack of uniformity depends upon c.d., e.g. Wagner (1951) showed that greater uniformity of c.d. at different parts of the cathode is to be expected at low c.d. As the mean c.d. is increased, a larger proportion of the current is carried by the edges and corners of the cathode; since the current lines pass in part outside the space

between the electrodes. Likewise, non-uniform current distribution results if the electrodes are not plane.

In addition, the current distribution depends on the composition of the bath. As first pointed out by Pfannhauser (1901), the higher the polarisation, i.e. the slope of the potential-c.d. curve for the cathodic process, the more uniform is the current distribution.

Consequently, as explained by numerous authors, notably by Foerster (1923), Barth (1923), Haring and Blum (1923), Gardam (1937) and Agar and Hoar (1947), the current distribution in an electrolytic cell is determined by (a) the polarisation curve (electrode potential plotted versus c.d.); (b) specific electrical conductivity; and (c) linear dimensions, such as breadth of electrodes, distance between anode and cathode and distance between crests and troughs of profiled electrodes. Moreover, Kasper (1940, 1942) showed how the current distribution can be calculated quantitatively if a linear relation between electrode potential and current density is assumed.

Using an unstirred bath at 50°C the nickel deposits on polycrystalline copper substrates always show lateral growth of (100) type at c.d. up to 220 mA/cm².^(See Fig 18) Beyond that, very minute traces of outward growth type of orientations, such as (210) or (110) start appearing with the main (100) orientation in some cases. Evidently at this stage the

outer edge region of the cathode (of higher c.d.) begins to show traces of a more outward growth type of orientation. In the stirred bath, the other conditions remaining the same, this stage occurs at about 300 mA/cm^2 , again giving traces of (210) with the main (100) orientation as is evident from the diagram, Fig.38.

In the above transition regions, the outer part of the deposit surface roughly within 2 mm from the edges of the 1.2 cm diameter cathode looks rougher than the central part. Some blackish rough deposits are also observed near the edges. The electron diffraction patterns from the central and edge regions of the deposit surface show indeed appreciably different orientations (see Table 2). The orientation of the nickel in the central region is of the type which would have been expected towards the lower side of the transition c.d., whereas in the edge region the nickel crystal orientation is the same as on the higher side of the transition c.d. This agrees with the suggested increase in c.d. from the central to the edge region of the cathode surface.

When the electron beam was incident across the middle region of the deposit it gives mainly the diffraction pattern from the main central region of nearly uniform c.d., together with a minor component from the narrow outer part of the deposit surface where the c.d. is higher. If the

same deposit surface is examined by allowing the beam to graze the surface near the edge, it gives patterns predominantly showing the orientations which were common towards the higher c.d. side of the transition region.

Some of the typical experimental results are shown in Table 2.

Some typical electron diffraction photographs corresponding to the central and the edge region of the same deposit surfaces are shown in Fig.19.

TABLE 2.
UNSTIRRED BATH.

Temp. °C	Substrate	c.d. mA/cm ²	Deposit thickness A	Orientation of the nickel deposit.	
				Central part	Outer part
50	Polycryst Cu	270	10,000	(100)	(100)+(110) + (210)
50	"	270	30,000	(100)	(100)+(110)+(210)
50	"	300	45,000	(110)	R*
20	"	30	30,000	(100)	(110)+(210)
50	Cu(110)	320	60,000	P+T*	R*
50	Cu(110)	260	61,000	(100)	(110)+(210)

STIRRED BATH					
Temp °C	Substrate	c.d. mA/cm ²	Deposit thickness A	Orientation of the nickel deposit	
				Central part	Outer part
50	Polycryst Cu	440	30,000	(110)+ (210)	R*
50	"	400	30,000	(100)	(110) + (210)
20	"	50	10,000	(100)	(110) + (210)
50	Cu(111)	460	47,000	(100)	(100) + (110) + (210)

* P+T = parallel growth with strong twinning.

* R = random polycrystalline nickel after etching away
the surface hydroxide.

Symbols Used in Figs. 18, 38, 54, 64, 68, 79, 87, 102, 108, 116, 122, 126 and 131.

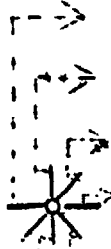
 = Parallel (100) single-crystal orientation on the Cu (100) face.

 = Parallel (110) single-crystal orientation on the Cu (110) face.

 = Parallel (111) single-crystal orientation on the Cu (111) face.

R = Random polycrystalline surface structure.

 = Surface hydroxide layer; the structure observed after etching away the hydroxide is denoted by the symbol inside the circle.



 - - -> Small amount or much random polycrystalline Ni.

 - - -> One-degree (111) orientation.

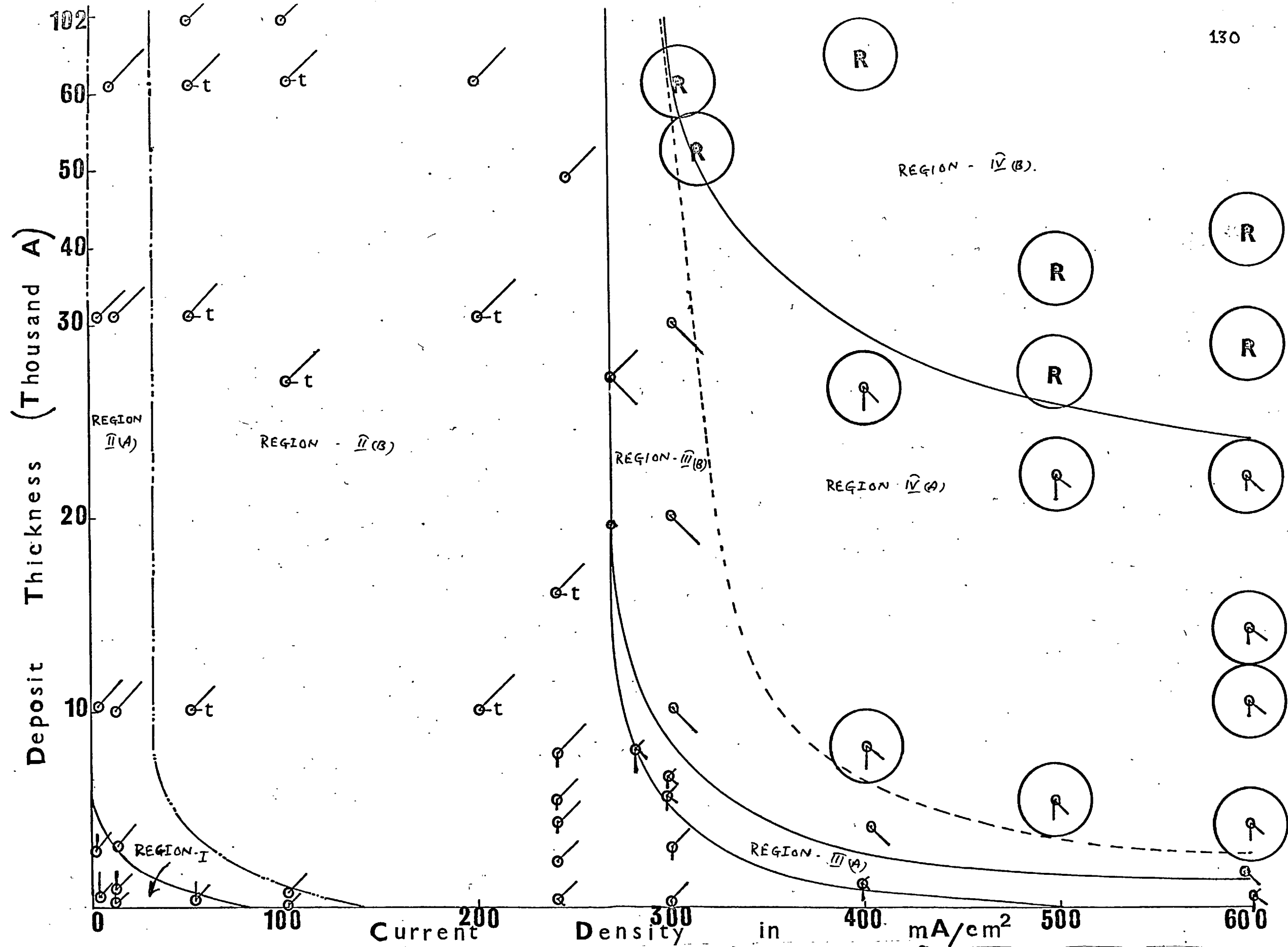
 - - -> One-degree (100) orientation.

 r or R - - - t or T - - - Little or much {111} twinning.

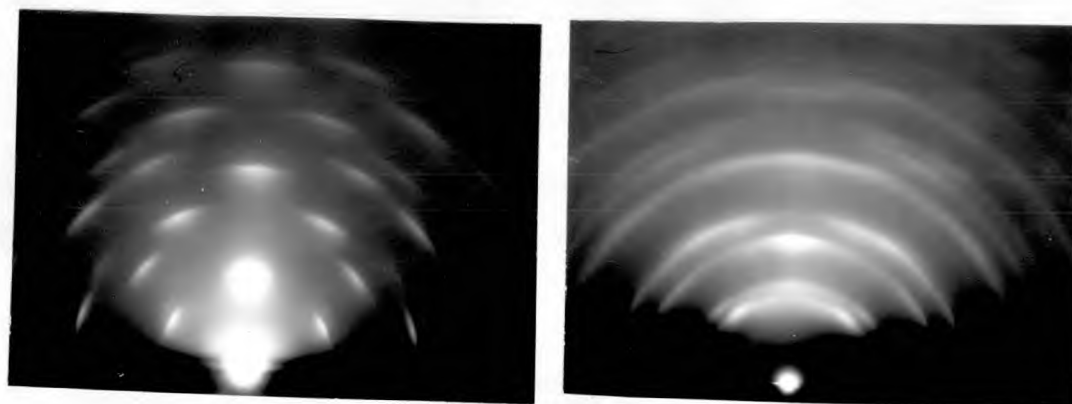
 - - -> One-degree (110) orientation.

 - - -> One-degree (210) orientation.

 - - -> Close-packed hexagonal structure (only observed in one deposit).



Fi .18. Ni on Polycrystalline Cu, Unstirred, 50°C. For symbols see page 130(A).



(a)

(b)

Fig.19. Nickel electrodeposit 30,000 Å thick at 270 mA/cm^2 on polished polycrystalline Cu, unstirred bath, 50°C .

(a) Pattern from the central part.

(b) Pattern from the outer part.

3.4. The Structure and Growth of Nickel Electrodeposits on Mechanically Polished Polycrystalline Copper Substrates, from the Standard Nickel Sulphamate Solution at 50°C.

An electron diffraction study was made of the structure, growth and orientation of nickel electrodeposits on smooth mechanically polished polycrystalline copper substrates, with a wide range of current densities from 1 to 600 mA/cm², and deposit thickness from 200 to 102,000 Å. The results at room temperature ($\approx 20^{\circ}\text{C}$) are described later in section 3.8.

Fig.2(a,b) shows the typical electron diffraction pattern with its optical micrograph from the smooth mechanically polished polycrystalline copper used as substrate.

3.4.1. Nickel deposits on polycrystalline copper, using the sulphamate bath at 50°C, and unstirred.

Fig.18 shows diagrammatically the orientation of the nickel crystals in the surface region (to a depth of the order of 100 Å) of the electrodeposits at the various c.d. and thicknesses studied. This makes clear the nature of the dependence of the structure of the nickel electrodeposits on the current density and thickness.

On the basis of the results obtained, the whole diagram has been divided into four main regions marked in

Fig.18 as I, II, III and IV. In each region the nickel has a particular type of crystal orientation. The lines indicate the positions of the relatively narrow zones of transition of the deposit structure from that of one region to that of the neighbouring region. The region II has been further divided into the two sub-regions II(A), II(B); and region III into III(A), III(B); and region IV into IV(A), IV(B).

The spread of the electrodeposit crystal orientation from the mean, as shown by the angular spread of the arcs from their mean positions in the electron diffraction pattern, has been found to decrease with increasing deposit thickness, for the types of orientations observed. The shortening of the arcs, as the deposit thickness increased, is more rapid below 40,000 Å thickness. Beyond that, it gradually tends to become constant. Fig.20 (a to f) show the variations of the angular spread of the arcs for the orientations $(100)^{(210)}$ and (110) , in relation to deposit thickness, at various current densities. Fig.21

shows the angular spread of the arcs (i.e. of (100) orientation) in relation to current density, at constant thickness.

The deposit thicknesses plotted in Fig.18 were estimated taking into account the current efficiency, at each c.d., as estimated in section 3.1.

Region I; Nickel in a mixture of (111) and (100) orientations

This is a very small region extending from 1 to 75 mA/cm², and deposit thickness up to about 5,000 Å at 1 mA/cm² and decreasing as the c.d. increases, to zero at about 75 mA/cm² (see Fig 18).

The diffraction patterns such as Figs. 22 and 23 show an arc centred on the plane of incidence, on both the 111 and 200 ring positions. This indicates that some of the nickel crystals were oriented with a (111) and some with a (100) plane parallel or nearly so to the substrate surface. The other arcs in these photographs correspond to one-degree (111) and (100) orientations respectively, that is, with random azimuthal crystal orientation. At 1 mA/cm² and 500 Å thickness (or presumably less), the (111) orientation is more pronounced than the (100), see Fig.22. At higher thickness or c.d. the converse is found, e.g. Fig.23. Fig. 24 (a and b) shows the theoretical diffraction positions for one-degree (111) and (100) orientations.

In the diffraction patterns, the arcs centred on the plane of incidence have an angular spread from the mean positions which decreases with increasing thickness. The deposit is very bright up to about 3,000 Å thickness at 1 mA/cm². Thicker deposits are less bright, due to their rougher surface.

Region II(A); Nickel in (100) orientation without twinning.

Figs. 25, 26 and 27 show typical diffraction patterns. This region ^(see Fig.18) was studied up to 102,000 Å deposit thickness and occurs above region I. Here, the results show very strong one-degree (100) orientation of the nickel crystals, without any other orientation being also present. In deposits thicker than 5,000 Å, it occurs in a narrow region of c.d. up to 30 mA/cm².

As before, the spread of the arcs corresponding to (100) orientation becomes shorter with increasing deposit-thickness, as shown in Fig.20. The surface becomes rougher with increasing thickness and so less bright. On the other hand, deposits of the order of 30,000 Å or more in thickness show diffraction arcs strongly drawn out vertically towards the shadow edge, indicating relatively smooth cube faces on the (100) oriented crystals (see Fig.27)

Region II(B); Nickel in (100) orientation with different amount of {111} twinning.

Representative photographs of deposits in this region are shown in Figs. 28 to 32. This is a wider region ^(see Fig.18) lying between c.d. 30 and 270 mA/cm². The thicknesses studied extend up to 102,000 Å. It is a region predominantly of one-degree (100) orientation. The (100) orientation is accompanied by {111} twinning, as shown by the two arcs on the 111 ring position below the 200

arc on either side of the plane of incidence.

Fig.24(c) shows the theoretical pattern to be expected from the twins which combine to form one-degree (221) orientation. Besides the 111 arcs referred to, the expected arcs on the 200 and 220 ring positions are seen in Fig.28(a). The $\{111\}$ twinning occurs sometimes in small amount and in other cases in a larger amount.

Fig.28(b) shows an optical micrograph from the deposit which yielded the diffraction photograph shown in Fig.28(a). This shows an appreciably rough surface with projections of the order of 2 microns in diameter. The surface of the deposits is very smooth and bright up to about 30,000 Å. Thicker deposits become duller and less bright, due to increasing degree of roughness, but the diffraction patterns then show arcs strongly drawn out vertically towards the shadow edge, indicating smooth (100) faces on the (100) oriented nickel crystals (see Fig.27).

Figs. 29 (a,b) and 30 (a, b) show typical electron micrographs from carbon replicas of Ni deposits at 200 mA/cm² and thickness 10,200 Å and 61,200 Å respectively. The deposit surface is seen to be uneven and no well defined crystals faces can be recognised. Fig. 30(b) seems to show crystal grains of about 400 Å. diameter.

Region III(A); Nickel mainly or partly in (210) orientation with small amount of (100) and (110).

Fig.33(a) is typical of the deposits in this narrow region between c.d. 270 and 600 mA/cm² (see Fig 18). The diffraction patterns obtained from deposits show a mixture of (100), (110) and (210) orientations (see Figs. 18 and 24). The deposit surface, even at a few thousand angstroms thickness, is less bright above 300 mA/cm². The optical micrograph corresponding to the diffraction pattern in Fig.33(a) is shown in Fig.33(b).

Region III(B); Nickel mainly in (110) orientation.

Fig.34 shows the (110) orientation of nickel electrodeposits in this region (cf. Figs. 18 and 24). In the lower part of it extending between c.d. 270 and 600 mA/cm², and above sub-region III(A), mainly one-degree (110) orientation occurs with a trace of (210) at lower thicknesses. The deposit surface becomes rougher above 300 mA/cm².

The upper part of this sub-region is a region where one-degree (110) orientation occurs exclusively, lying at the higher thicknesses, mainly between 270 and 320 mA/cm², but decreasing in width with increase in deposit thickness.

Region IV; Nickel deposits showing a surface hydroxide layer.

In this region which lies on the right hand side of the broken line curve in Fig.18, there was evolution of gas during electrodeposition of nickel. The surface of the

deposits was covered with a greenish rough coating, probably nickel hydroxide. Sometimes, around the edges, black deposits were also observed. The diffraction patterns obtained from these rough surfaces were diffuse haloes, e.g. Fig.35. The pattern does not correspond to NiO (f.c.cubic, $a = 4.17 \text{ \AA}$), but indicates the presence of nickel hydroxide.

The two strongest rings have radii of 0.88 and 1.50 cm, corresponding to spacings of 2.80 and 1.65 $\text{\AA}$ (both $\pm$ a few %). The ratio of these is close to 1.73, thus these rings could be the 100 and 110 diffractions of Ni(OH)_2 agreeing well also with the spacings calculated from $a = 3.117 \text{ \AA}$ for Ni(OH)_2 . Two very faint additional diffuse rings occur at radii about 1.0 and 1.3 cm, presumably correspond to 10 $\bar{1}$ and 11 $\bar{1}$ type of diffractions. Germer (1938) found indeed by electron diffraction that Ni(OH)_2 is formed when German silver (a nickel alloy) is immersed in water.

After the deposits had been etched in 5% dil. H_2SO_4 for 15-20 sec., the underlying metal surface was exposed and yielded electron diffraction patterns characteristic of f.c.cubic metal.

This region sets in roughly at 320 mA/cm^2 around 24,000 $\text{\AA}$ deposit thickness and extends to 600 mA/cm^2 or more. The orientation of the metallic electrodeposits is different in the two sub-regions IV(A) ((110)-oriented nickel with (210)) and IV(B) (random nickel), which are discussed below separately.

Region IV(A); Nickel in mainly (110) orientation below the surface hydroxide.

(see Fig 18)

In the lower part of this region, the deposits were rough surfaced and showed strong (110) orientation, with either a small proportion or much of the nickel in (210) orientation as in Fig.36. Above about 11,000 Å and 500 mA/cm², there is only very little (210) orientation. This region extends from nearly 320 to 600 mA/cm² and deposit thicknesses of about 6,000 to 30,000 Å.

Region IV(B); Nickel in random orientation below the surface hydroxide.

This sub-region occurs at higher deposit thicknesses than sub-region IV(A) and continues up to large thicknesses (~70,000 Å or more) with the same structure. The deposit surface was rough and the diffraction photograph from it is shown in Fig.37. Here, the metal crystals in the surface region of the deposit are randomly oriented, giving a ring pattern. Thus it is evident that the nickel crystals, though oriented in the lower part of the deposit, are no longer deposited preferentially in any definite orientation at deposit thicknesses like those defined by the lower limit of region IV(B) (joining the points roughly at 300 mA/cm², 46,000 Å and 600 mA/cm², 24,000 Å). The deposit thickness above which the nickel crystals grow in random orientations decreases with increasing c.d.

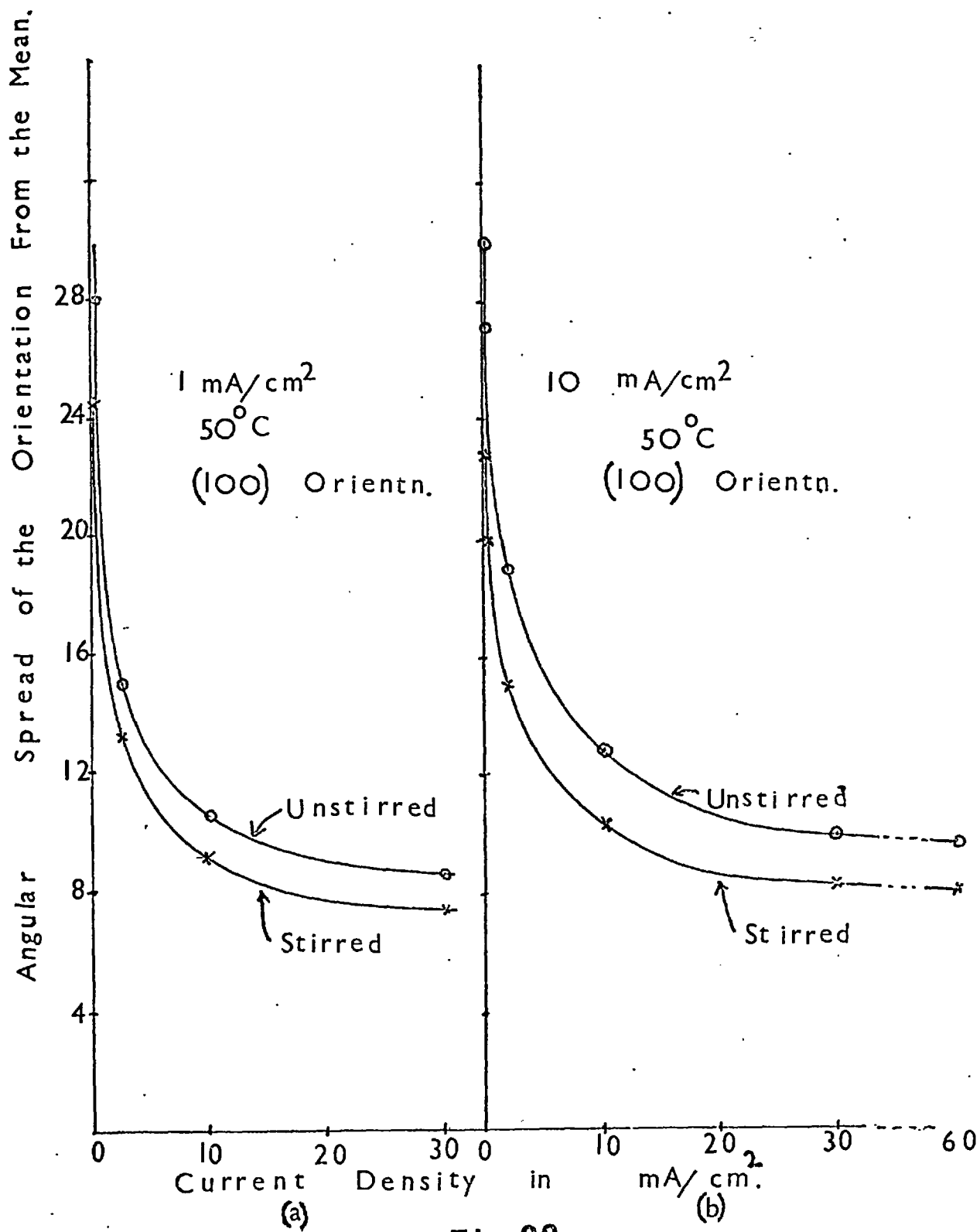


Fig. 20.

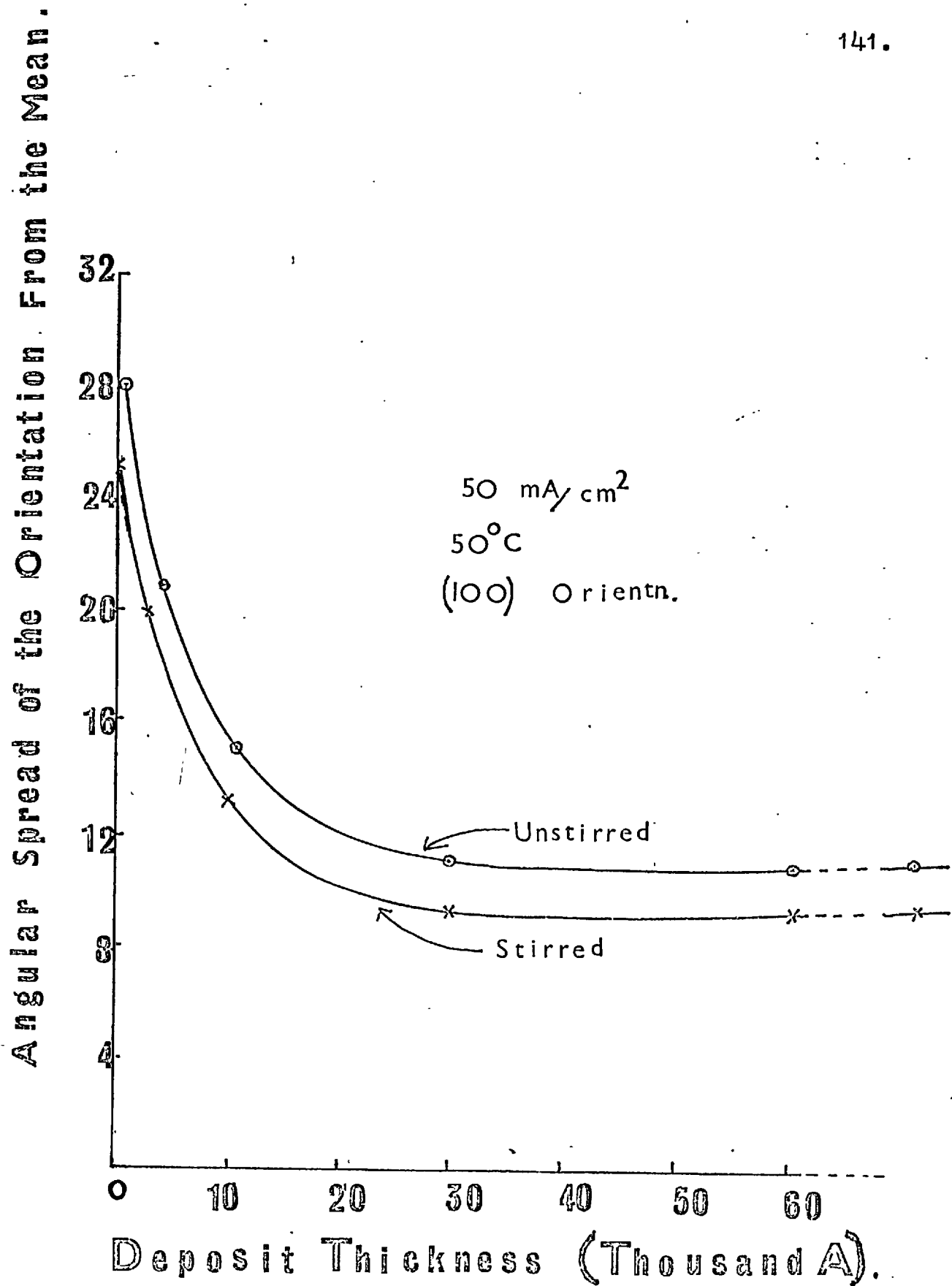


Fig. 20 (c).

Angular Spread of the Orientation From the Mean.

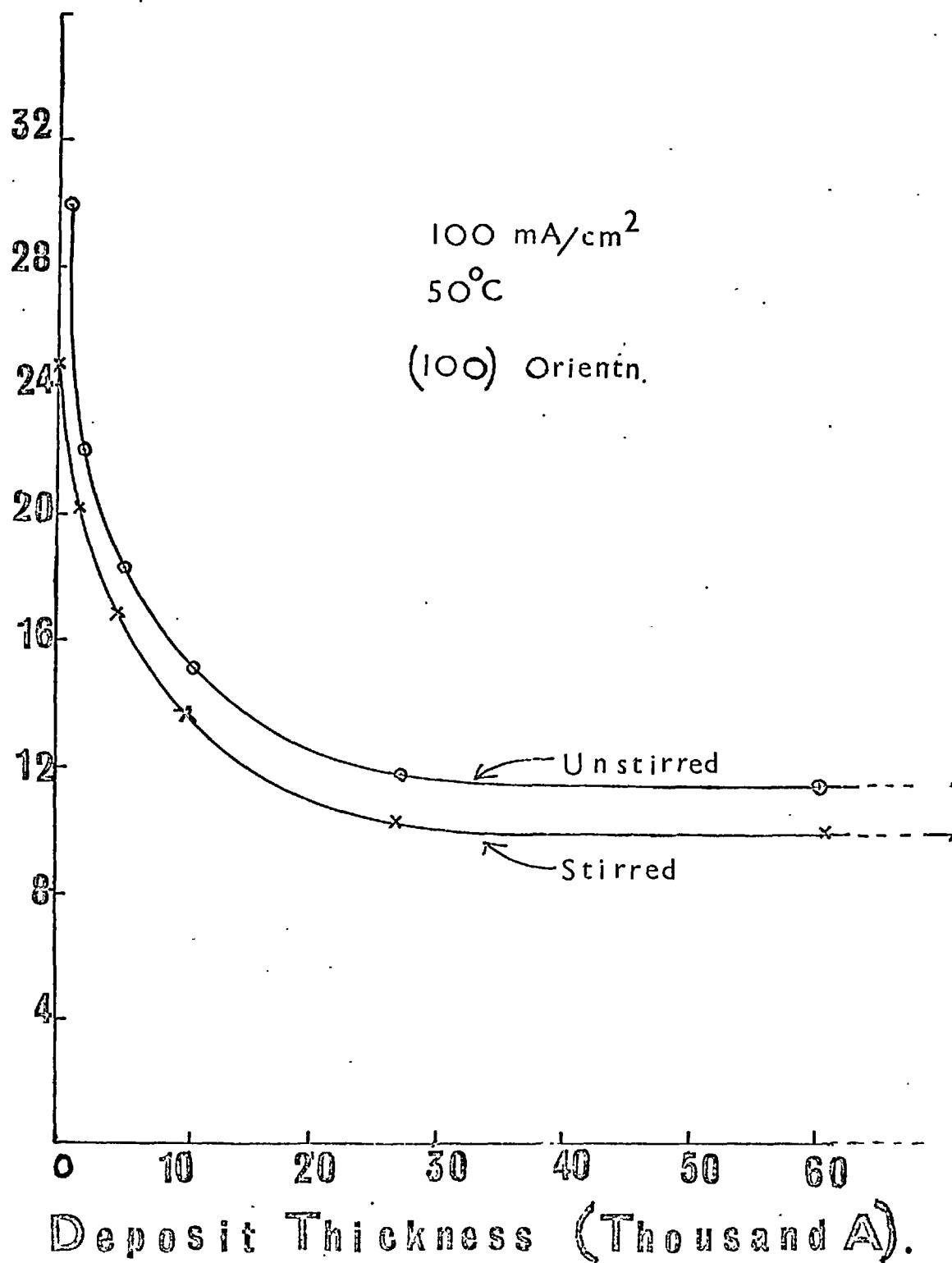


Fig. 20 (a).

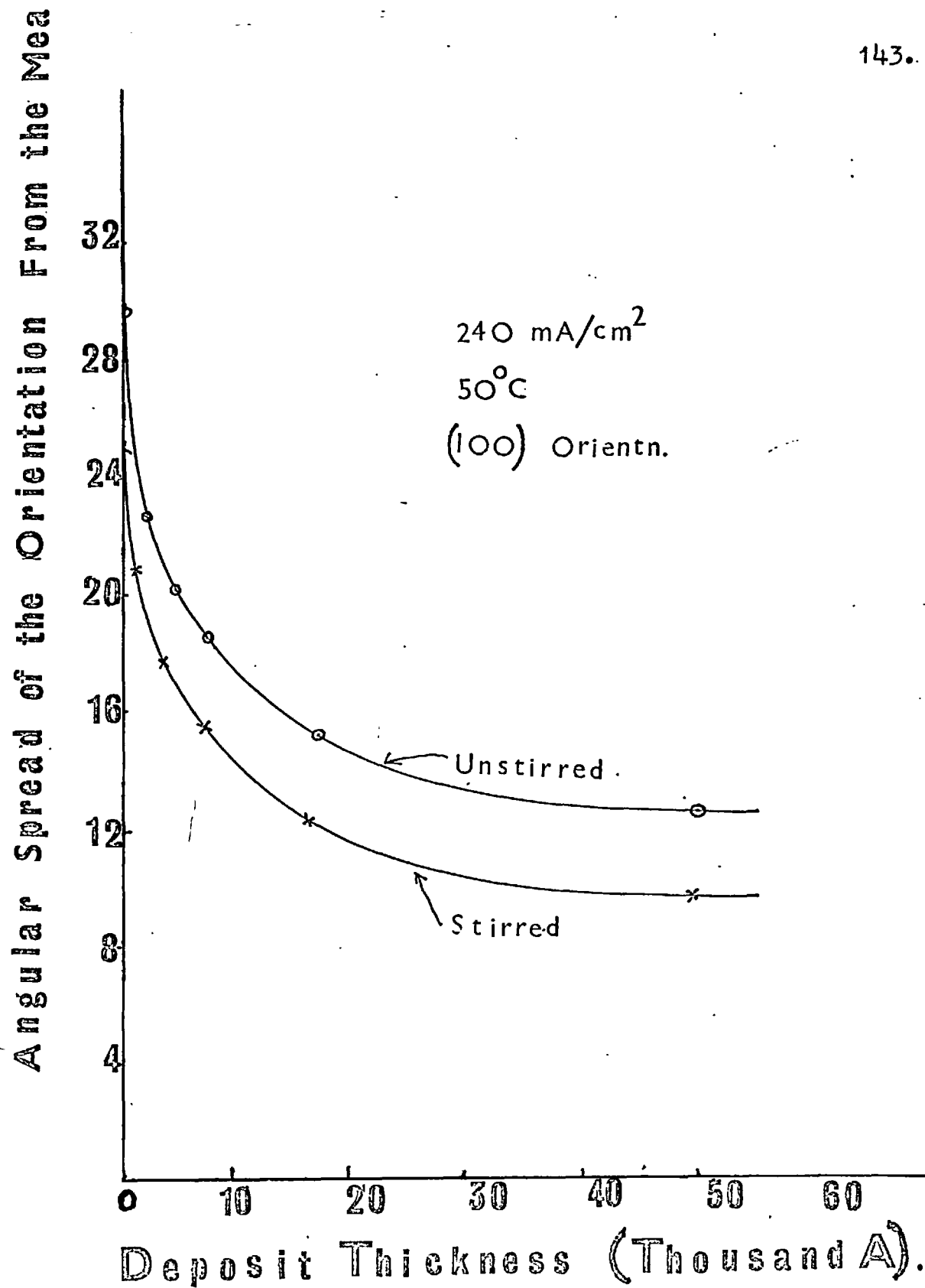


Fig. 20 (e).

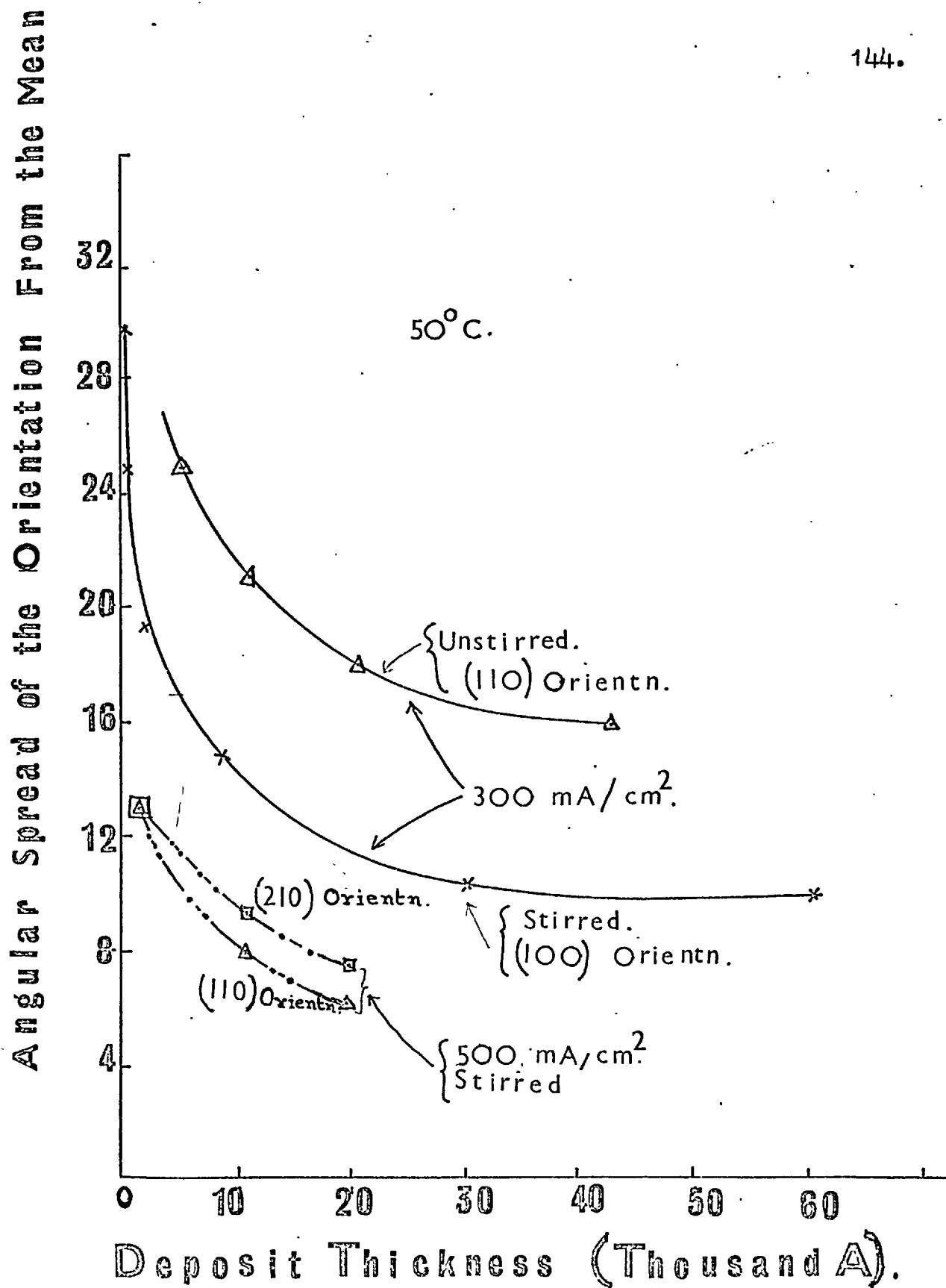


Fig. 20 (f).

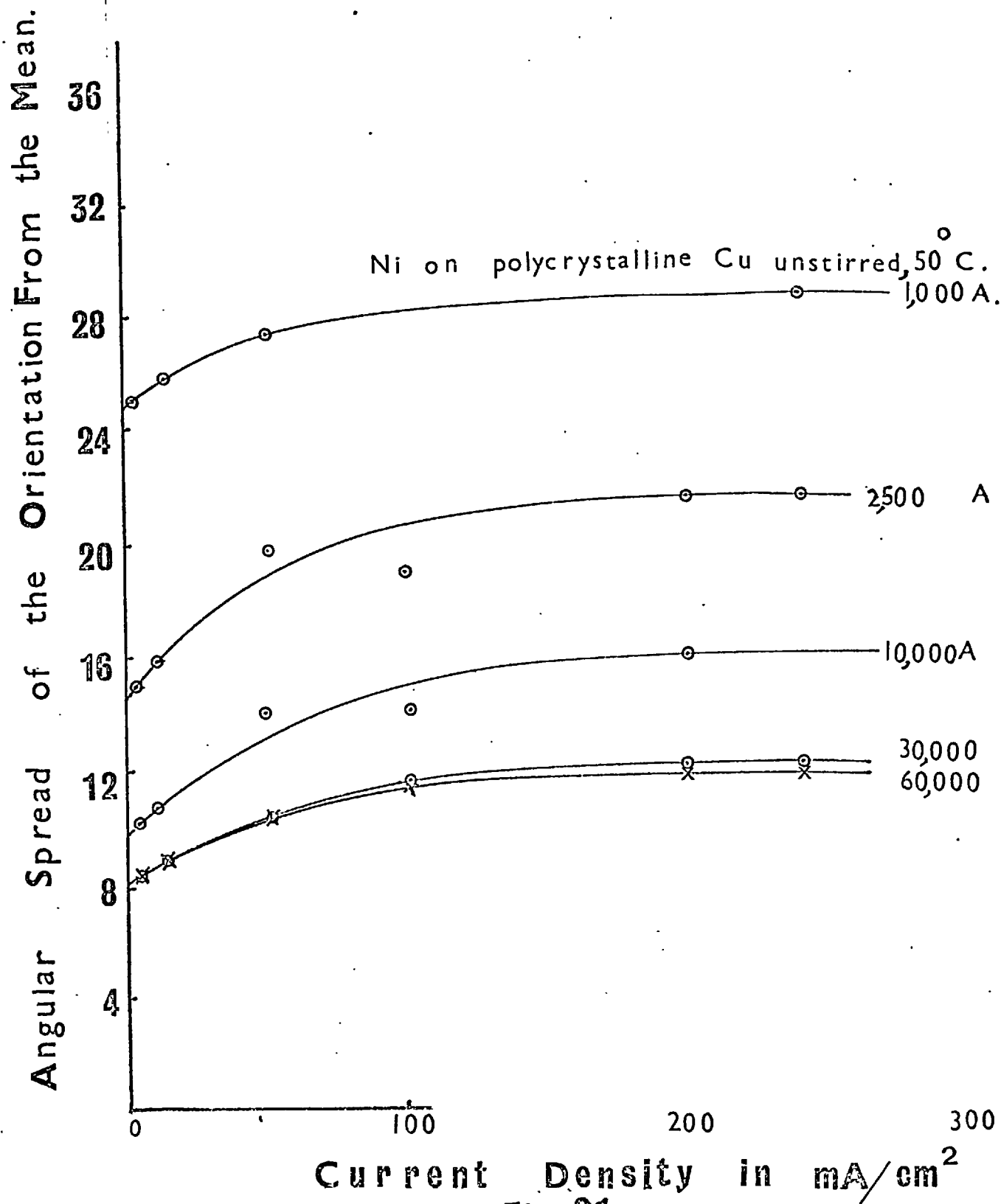


Fig. 21.

REGION I OF FIG. 18.

(Polished polycrystalline Cu, unstirred bath, 50°C.)

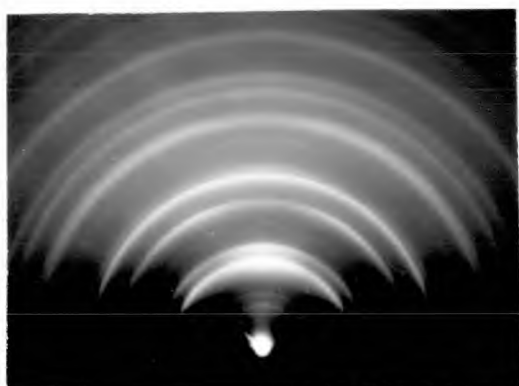


Fig.22

510 Å Ni at 1 mA/cm² on
polished polycrystalline
Cu, bath unstirred,
50°C.

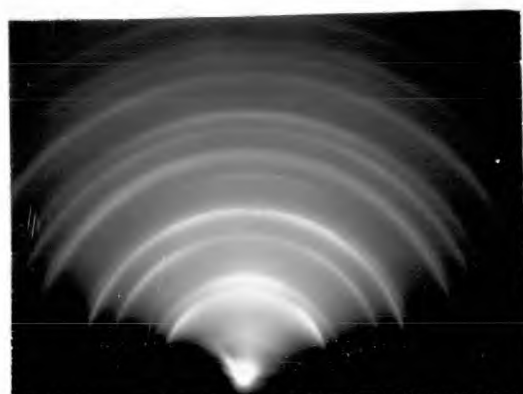


Fig.23.

510 Å Ni at 10 mA/cm² on
polished polycrystalline
Cu, bath unstirred,
50°C.

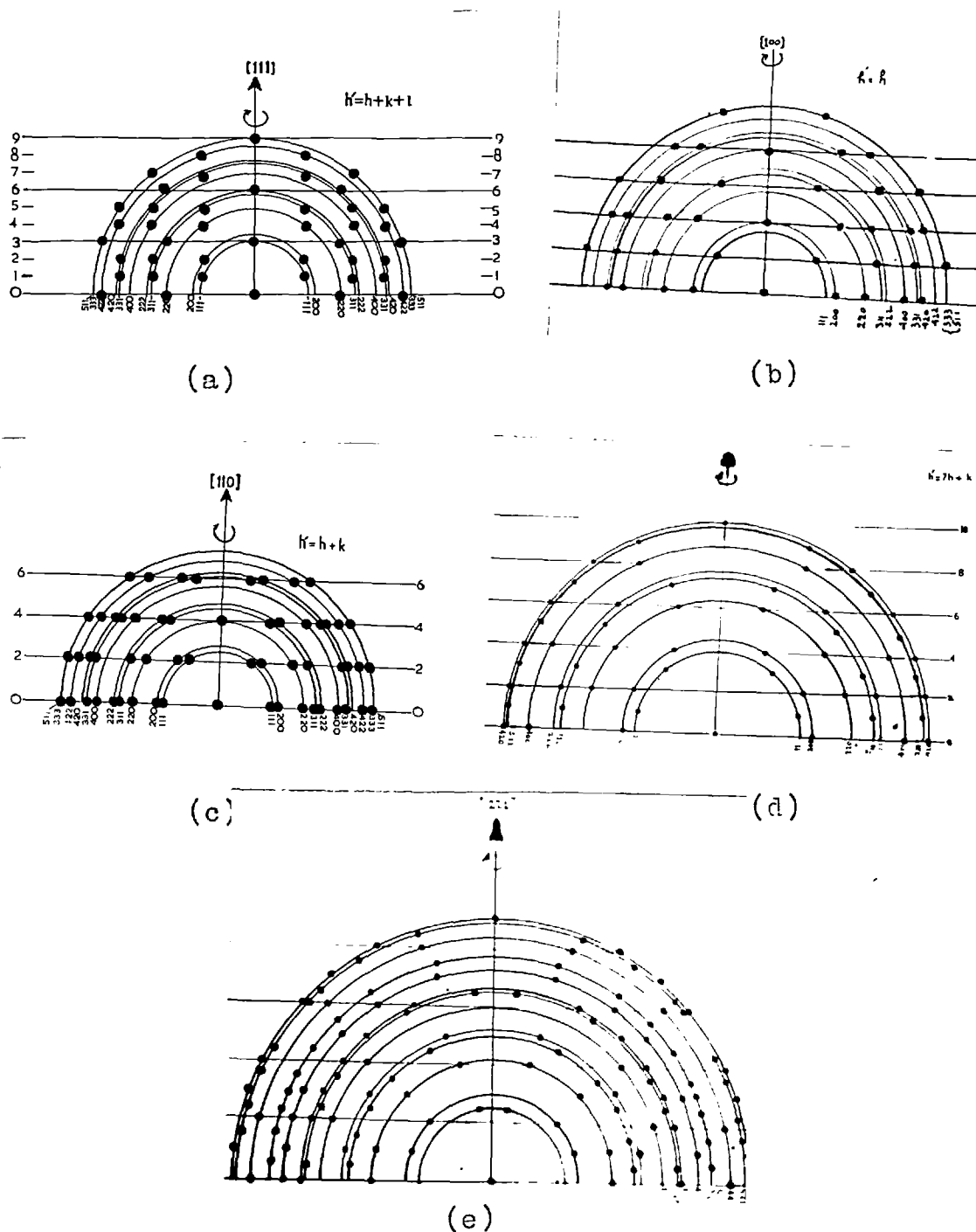


Fig.24. Theoretical patterns of diffraction.

- (a) One-degree (111) orientation.
- (b) One-degree (100) orientation.
- (c) One-degree (110) orientation.
- (d) One-degree (210) orientation.
- (e) One-degree (221) orientation equivalent to $\{111\}$ twinning of the (100) oriented crystal.

REGION II(A) OF FIG. 18.

(Polished polycrystalline Cu, unstirred bath, 50°C.).

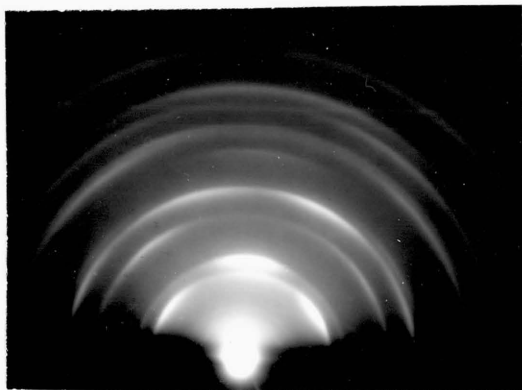


Fig.25.

680 Å Ni at 100 mA/cm² on polished polycrystalline Cu,
unstirred bath, 50°C.

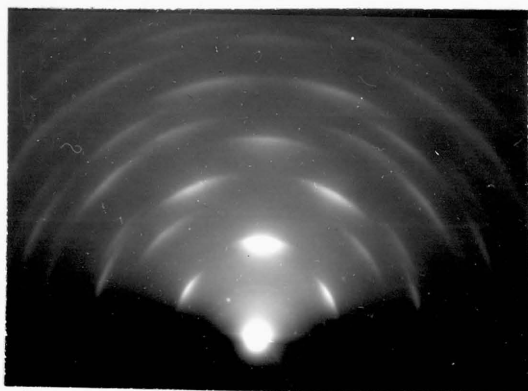


Fig.26.

10,200 Å Ni at 1 mA/cm² on
polished polycrystalline Cu,
unstirred bath, 50°C.

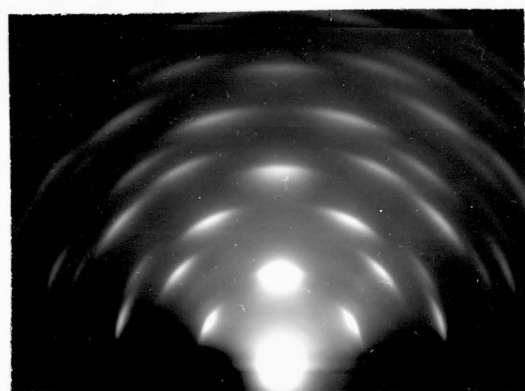
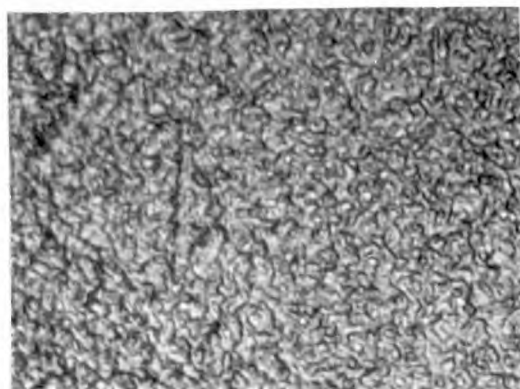
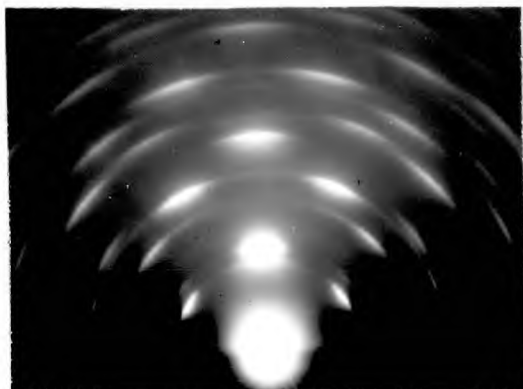


Fig.27.

61,200 Å Ni at 10 mA/cm²
on polished
polycrystalline Cu,
unstirred bath, 50°C.

REGION II(B) OF FIG. 18.

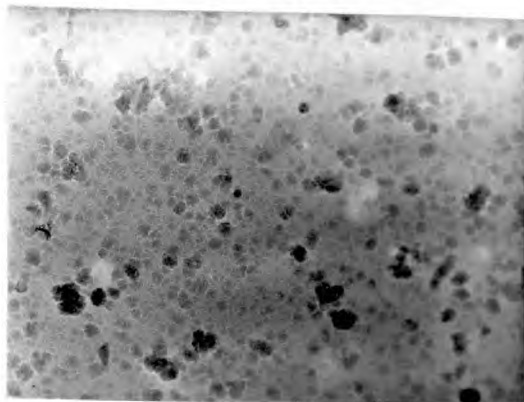
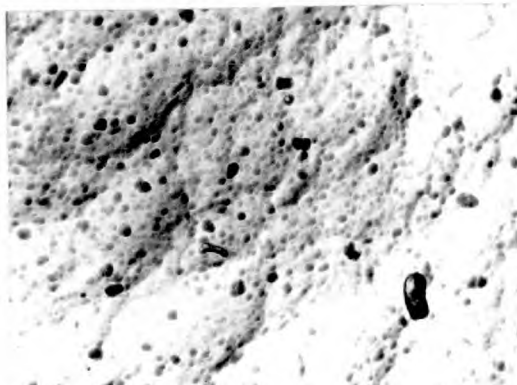
(Polished polycrystalline Cu, unstirred bath, 50°C).



(a)

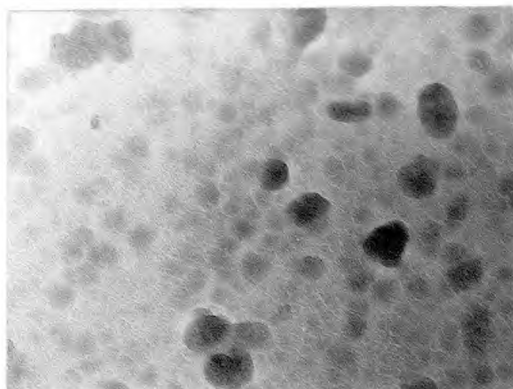
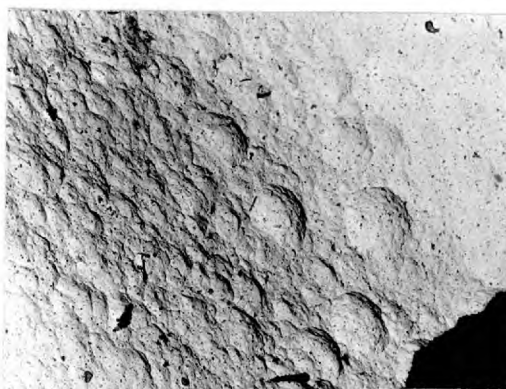
(b) Opt. Micro. x 1130

Fig. 28. 61,200 A Ni at 100 mA/cm² on polished polycrystalline Cu, unstirred bath, 50°C.



(a) Electron Microgr. x 20,000. (b) E.M. x 50,000

Fig. 29. 10,200 A Ni at 200 mA/cm² on polished polycrystalline Cu, unstirred bath, 50°C.



(a) Electron Microgr. x 50,000. (b) El. Micro. x 100,000

Fig. 30. 61,200 A Ni at 200 mA/cm² on polished polycrystalline Cu, unstirred bath, 50°C.

REGION II(B) OF FIG. 18.

(Polished polycrystalline Cu, unstirred bath, 50°C).

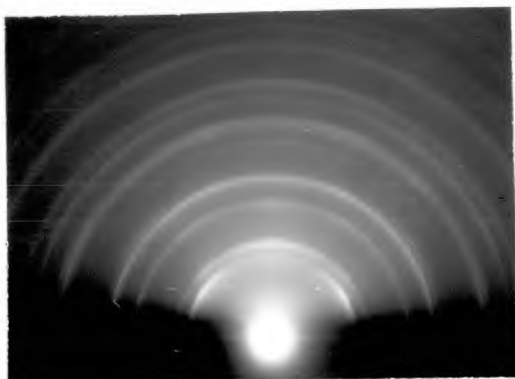


Fig.31.

408 Å Ni at 240 mA/cm² on
polished polycrystalline Cu,
unstirred bath, 50°C.

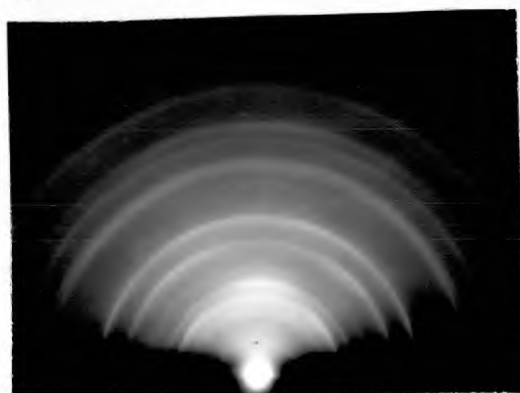
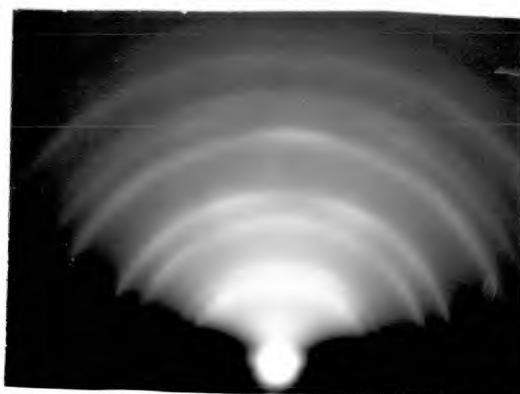


Fig.32.

500 Å Ni at 300 mA/cm² on
polished polycrystalline
Cu, unstirred bath, 50°C.

REGION III(A) OF FIG. 18.

(a)



(b)

Fig.33. 6,000 Å Ni at 300 mA/cm² on polished polycrystalline
Cu, unstirred bath, 50°C.

Optical micrograph x 300

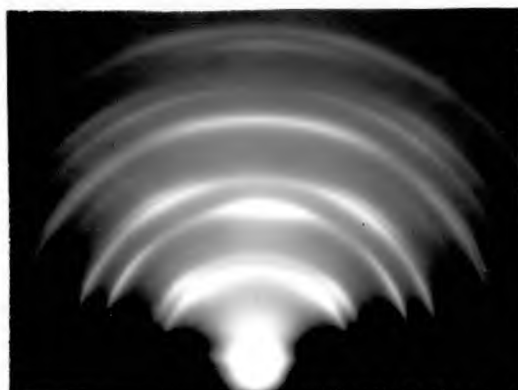


Fig.34. 20,000 Å Ni at 300 mA/cm^2 on polished polycrystalline Cu, unstirred bath, 50°C .

REGION IV OF FIG. 18.

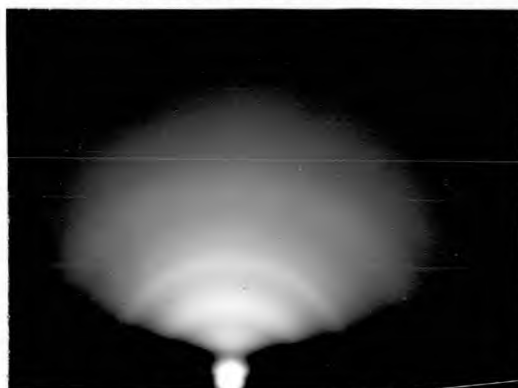


Fig.35. 2,000 Å Ni at 600 mA/cm^2 on polished polycrystalline Cu, unstirred bath, 50°C .

REGION IV(A) OF FIG.18

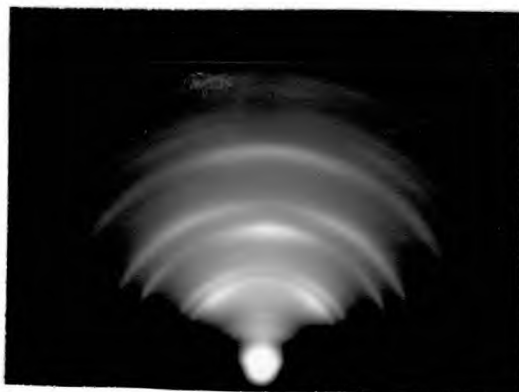


Fig.36. 26,500 Å Ni at 400 mA/cm^2 on polished polycrystalline Cu, unstirred bath, 50°C .

REGION IV(B) OF FIG.18.

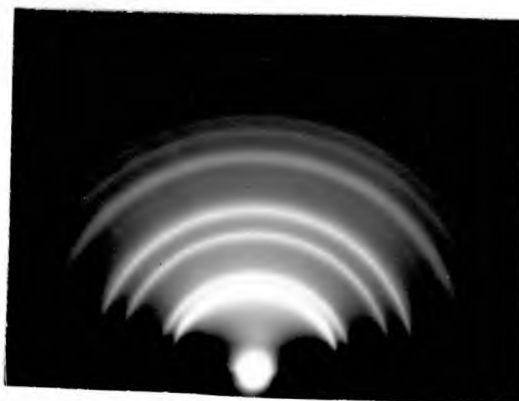


Fig.37. 61,200 Å Ni at 600 mA/cm^2 on polished polycrystalline Cu, unstirred bath, 50°C .

3.4.2. Nickel deposits on polycrystalline copper, using the sulphamate bath at 50°C and stirred vigorously.

Using the stirred bath, the surface orientation of the deposits was studied systematically from 1 to 600 mA/cm² and up to 102,000 Å deposit thickness, and the results are shown in Fig.38. It is found that the variation in structure, growth and orientation of nickel electrodeposits on polycrystalline copper substrates at 50°C is a function of c.d. and deposit thickness, as in the case where the unstirred bath is used. The nature of the deposit surface orientation is different in the four divisions of the entire diagram marked as regions I, II, III and IV. Each region is discussed separately below.

The angular spread of orientation away from the mean orientation is found to decrease with increase in thickness at any particular c.d. This variation is shown in Fig.20(a to f). Fig.21 shows the variation of orientation-spread with increase in c.d. at any particular deposit thickness.

The deposit thicknesses plotted in Fig.38 were estimated, taking into account the current efficiency, at each c.d., as estimated in section 3.1.

Region I; Nickel in a mixture of (111) and (100) orientations.

Figs. 39 and 40 are characteristic diffraction patterns from deposits in this region. ^(see Fig.38) This region occurs only at low c.d. and deposit thickness. Here the one-degree (111) orientation is developed together with the cube-face orientation. At low deposit thickness (from about 1,000 Å at 50 mA/cm² to 4,000 Å at 1 mA/cm²) the (111) and (100) orientations are about equally represented (see Fig.39).

With increasing thickness and/or c.d. the amount of (111) orientation is reduced (see Fig.40) and ultimately disappears (giving place to region II). Roughly, region I extends from 0 to 140 mA/cm². The deposit thickness exhibiting the characteristic structure of the region goes on decreasing with increasing c.d. It extends up to 4,000 Å at 1 mA/cm² and tends to zero thickness near 140 mA/cm².

Region II; Nickel mainly in (100) orientation, but sometimes with traces of {111} twinning and/or one-degree (210) orientation.

Figs. 41, 42, 43(a), 44(a) and 45 are the typical electron diffraction photographs. Figs. 43(b) and 44(b) are the optical micrographs corresponding to Figs. 43(a) and 44(a). Figs. 46, 47 and 48 are the scanning electron micrographs of the deposit surfaces.

These electron diffraction photographs and micrographs define the surface crystalline structure and the

degree of surface roughness respectively. The optical micrographs (see Fig. 43(b) and 44(b)) evidently consist of projections about 4 microns in diameter in the case of deposits about 50,000 to 102,000 Å thick. In this region II, the crystals developed mainly cube-face orientation, i.e. the nickel crystals tend to grow preferentially with (100) planes parallel to the mean substrate surface or nearly so.

The refractive drawing out of the arcs vertically in the case of thick deposits ($>40,000$ Å) indicates that the crystals have developed smooth cube faces (see Figs. 43(a), 44(a) and 45). The specimens are bright even up to 35,000 Å and 400 mA/cm^2 , unlike those from the unstirred bath, where the roughening sets in earlier. This region covers a wide range of c.d. (410 mA/cm^2) and thickness (102,000 Å). At the earliest stage ≈ 400 to 1,000 Å thickness, the diffraction patterns were closely similar to Fig. 41 up to 350 mA/cm^2 in region II. Though the (100) orientation is the most pronounced, some small traces of other orientations accompany it in many cases at c.d. between 300 and 410 mA/cm^2 .

Below 286 mA/cm^2 small traces of $\{111\}$ twinning of the main cube-face oriented crystals may be indicated by several faint additional arcs in some cases. Above 280 mA/cm^2 , traces of one-degree (210) orientation occur in

varying amount, with or without the small traces of {111} twinning of the main (100) orientation (see Figs. 44(a) and 45).

Comparing the diagrams Figs. 13 and 38, it appears that stirring the bath has had an appreciable effect in extending the region of (100) orientation to higher c.d. as well as reducing the degree of roughness of the deposit. Using the unstirred bath, the region II extends mainly up to 270 mA/cm^2 , whereas in a stirred bath it goes up to 410 mA/cm^2 . This shift of 140 mA/cm^2 is due to the stirring causing the maintenance of the supply of cations to the solution near the cathode surface. This favours the "lateral" type of growth, in cube-face orientation, up to higher c.d.

Region III; Nickel in (110) and (210) orientations without surface hydroxide.

Figs. 49, 50 and 51 show the typical surface structures in different parts of this region. ^(see Fig. 38) In this region the cube-face orientation no longer occurs. Some of the nickel crystals tend to grow with one-degree (110) and with (210) orientations. In the narrow part of this region above 20,000 Å deposit thickness and within the c.d. range ⁽¹¹⁰⁾ 410 to 445 mA/cm^2 , the one-degree is less pronounced than the (210). Below 20,000 Å, and between 410 and 580 mA/cm^2 , (210) and (110) orientations are nearly equal in amount.

Region IV; Nickel deposits showing surface hydroxide layer.

This region lies on the right hand side of the broken line curve in Fig.38. At c.d. within this region, there was evolution of gas during electrodeposition of nickel. The surface of the deposit was covered with a greenish rough coating, probably nickel hydroxide, as explained in the case of the unstirred bath. The electron diffraction pattern from the nickel hydroxide coated surface was similar to Fig.35.

This region sets in roughly at 450 mA/cm^2 and above $30,000 \text{ \AA}$ thickness and extends to 600 mA/cm^2 or more. The orientation of the metallic electrodeposits after etching away the nickel hydroxide layer with 5% H_2SO_4 for 15 secs. is different in the two sub-regions IV(A) ((110) oriented nickel with (210)) and IV(B) (random nickel), which are discussed below.

Region IV(A); Nickel in (110) and (210) orientations below the surface hydroxide.

This sub-region lies between the lower part of region III and sub-region IV(B). The underlying metal surface after etching away the nickel hydroxide layer shows that some of the nickel crystals grow with one-degree (110) and some with (210) orientations as shown by the diffraction photograph in Fig.52. Below $5,000 \text{ \AA}$ deposit thickness the orientations (110) and (210) are nearly equal in amount, but above $5,000 \text{ \AA}$, the (210) is more pronounced than (110).

Region IV(B); Nickel in random orientation below the surface hydroxide.

This sub-region occurs at higher deposit thickness than the sub-region IV(A) and continues to large thicknesses (60,000 Å or more). The diffraction photograph from the deposit surfaces in this region is as shown in Fig.53. In this sub-region, the nickel crystals in the surface region of the deposit (after etching away the hydroxide) are randomly oriented and give a ring pattern. Thus it is evident that the nickel crystals, though oriented in the lower part of the deposit, are no longer deposited preferentially in any definite orientation at deposit thicknesses defined by the lower limit of sub-region IV(B) (joining the points roughly at 450 mA/cm^2 , 30,000 Å and 600 mA/cm^2 , 11,000 Å). The deposit thickness above which the nickel crystals grow in random orientation decreases with increasing c.d.

REGION I OF FIG. 38.

(Polished polycrystalline Cu, stirred bath, 50°C).

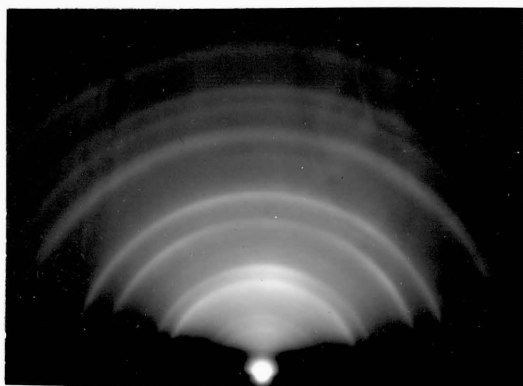


Fig.39.

510 Å Ni at 10 mA/cm² on
polished polycrystalline
Cu, stirred bath, 50°C.

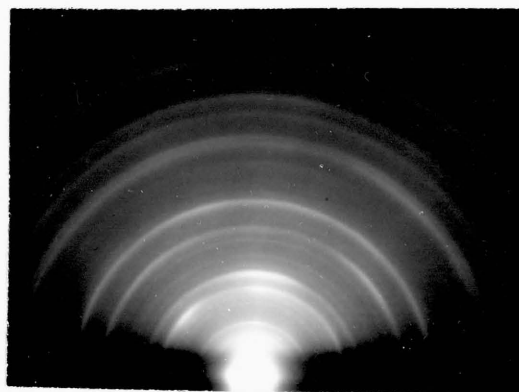


Fig.40.

170 Å Ni at 100 mA/cm² on
polished polycrystalline
Cu, stirred bath, 50°C.

REGION II OF FIG. 38.

(Polished polycrystalline Cu, stirred bath, 50°C.).

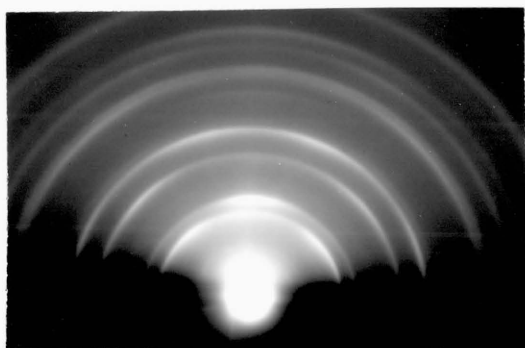


Fig.41. 400 Å Ni at 240 mA/cm² on polished polycrystalline Cu, stirred bath, 50°C.

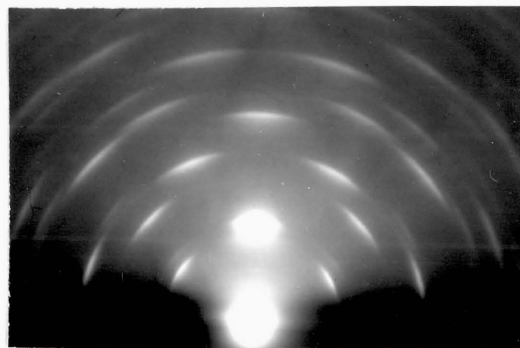
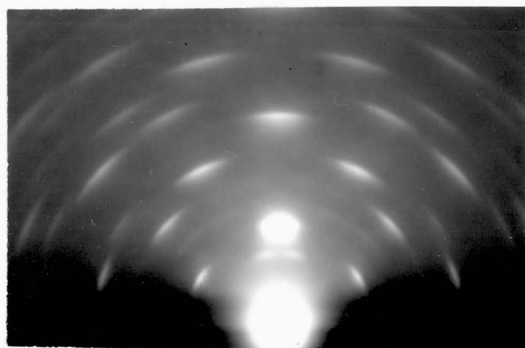
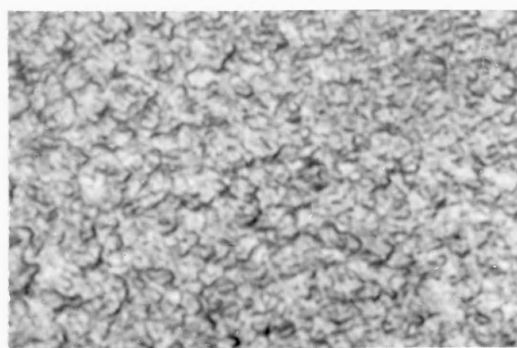


Fig.42. 29,000 Å Ni at 100 mA/cm² on polished polycrystalline Cu, stirred bath, 50°C.

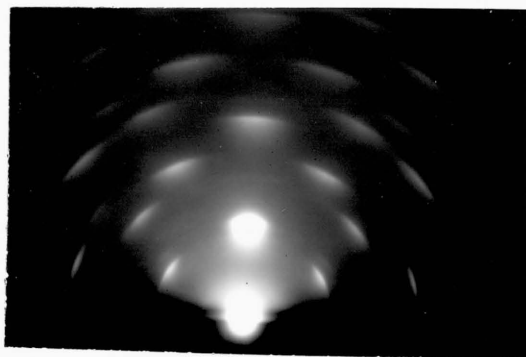


(a)

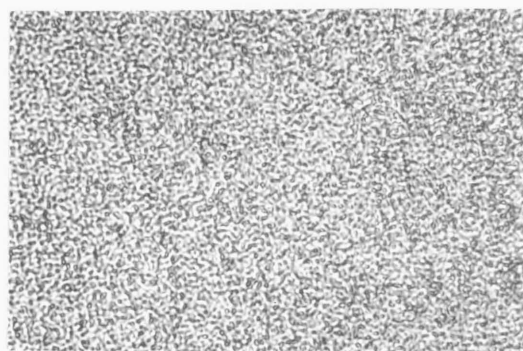


(b) optical micrograph
x 1200

Fig.43. 102,000 Å Ni at 100 mA/cm² on polished polycrystalline Cu, stirred bath, 50°C.



(a)



(b) optical micrograph x500

Fig.44. 49,000 Å Ni at 240 mA/cm² on polished polycrystalline Cu, stirred bath, 50°C.

REGION II OF FIG. 38.

(Polished polycrystalline Cu, stirred bath, 50°C).

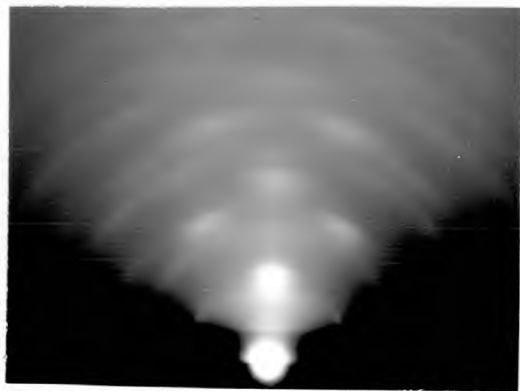


Fig.45.

54,500 Å Ni at 400 mA/cm²
on polished polycrystalline
Cu, stirred bath, 50°C.

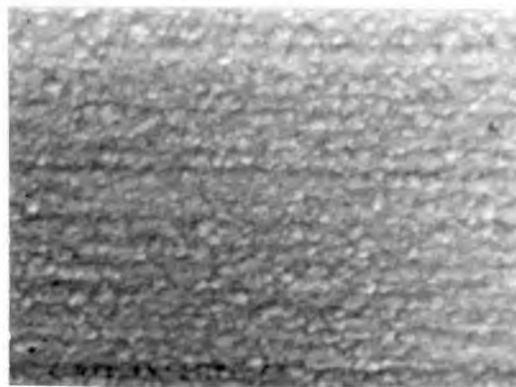


Fig.46.

Stereoscan electron
micrograph, x 2750.
16,200 Å Ni at 240 mA/cm²
on polished polycrystalline
Cu, stirred bath, 50°C.

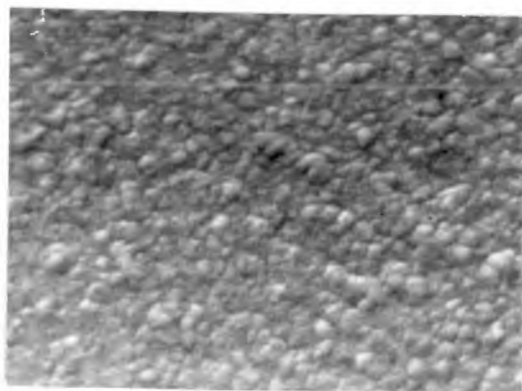


Fig.47.

Stereoscan electron
micrograph x 2850.
15,200 Å Ni at 300 mA/cm²
on polished polycrystalline
Cu, stirred bath, 50°C.

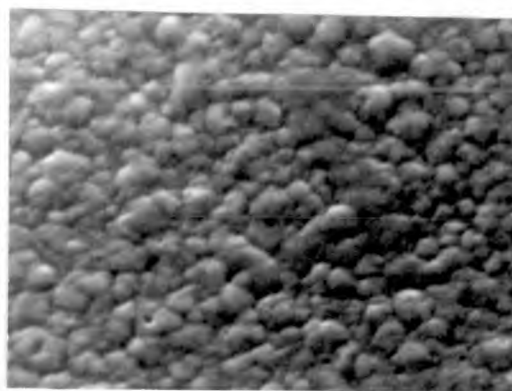


Fig.48.

Stereoscan electron
micrograph x 2500.
61,000 Å Ni at 300 mA/cm²
on polished polycrystalline
Cu, stirred bath, 50°C.

REGION III OF FIG. 38.

(Polished polycrystalline Cu, stirred bath, 50°C).

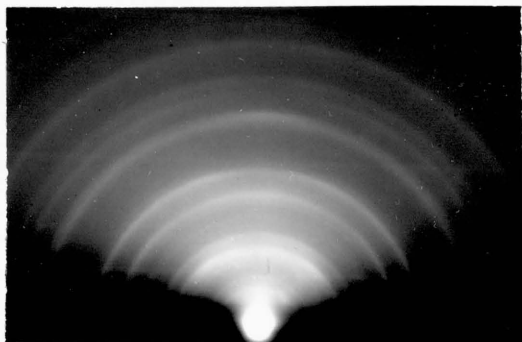


Fig.49. 1500 Å Ni at 500 mA/cm² on polished polycrystalline Cu, stirred bath, 50°C.

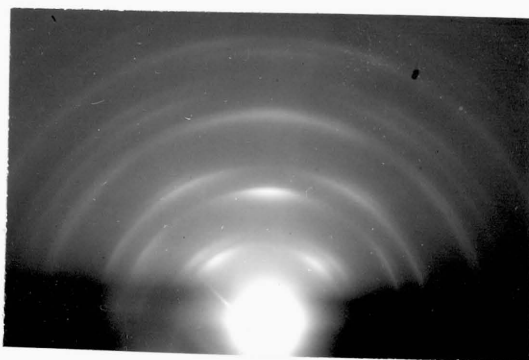


Fig.50. 19,500 Å Ni at 440 mA/cm² on polished polycrystalline Cu, stirred bath, 50°C.

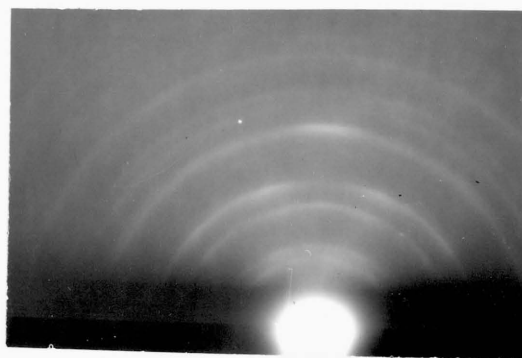


Fig.51. 27,000 Å Ni at 440 mA/cm² on polished polycrystalline Cu, stirred bath, 50°C.

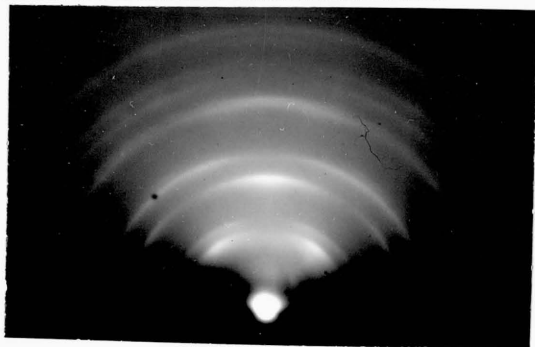
REGION IV(A) OF FIG. 38

Fig.52 17,000 Å Ni at 600 mA/cm² on polished polycrystalline Cu, stirred bath, 50°C.

REGION IV(B) OF FIG. 38.

Fig.53. 27,000 Å Ni at 460 mA/cm² on polished polycrystalline Cu, stirred bath, 50°C.

3.5. The Structure, Growth and Orientation of Nickel Electrodeposits on an Atomically Smooth Electro-polished (100) Face of a Copper Crystal from the Standard Nickel Sulphamate Solution at 50°C.

The electron diffraction study of the structure, growth and orientation of nickel electrodeposits on an atomically smooth electropolished (100) face of a copper single crystal was made over a wide range of c.d. and thickness, i.e. 0-600 mA and 0-61,000 A respectively. Figs. 5 and 6 show typical electron diffraction patterns illustrating the atomically smooth nature of the electropolished copper (100) face used as substrate. Two sets of results obtained with unstirred and stirred baths are shown in Figs. 54 and 61, and are discussed separately.

3.5. 1. Nickel electrodeposits on the copper (100) face, from the sulphamate bath at 50°C, when the bath is unstirred.

Fig. 54 shows diagrammatically the experimental results. It shows the surface structure, growth and orientation of the nickel electrodeposits at various stages of thickness and c.d. The change of the structure above a certain c.d. divides the whole diagram into two main regions as described below.

Region I; Nickel only in a single crystal orientation, with axes parallel to those of the copper single crystal.

Figs. 55 to 59 show typical electron diffraction photographs. Fig. 59 also shows the optical micrograph corresponding to its nickel deposit diffraction pattern.

(see Fig. 54)
This region I_λ extends mainly up to 250 mA/cm² (see Fig. 54). Beyond 250 mA/cm², its upper limit of deposit thickness decreases with further increase in c.d. and finally is practically nil beyond 390 mA/cm². At all thicknesses investigated from 100 to 61,000 Å, the nickel deposits show single-crystal structure with the cube-axes parallel to those of the copper single crystal used as substrate.

The square arrangement of spots when the electron beam is parallel to the cube edge is obtained in Figs. 55(a) to 59(a). The "centred $\sqrt{2}$ -rectangle" spot patterns with $\sqrt{2}$ -side horizontal, when the electron beam is along the cube-face diagonal, are shown in Figs. 55(b) to 59(b). The diffraction spots lying in the plane of incidence have Laue indices 200, 400, ... showing that the cube face is parallel to the surface or nearly so, i.e. parallel to the Cu(100) face.

The diffraction pattern at 300 mA/cm² and 500 Å is similar to that at 200 mA/cm² and 340 Å (cf. Fig. 57). The diffraction pattern at 100 mA/cm² and 200 Å (cf. Fig. 55) is

nearly similar to those at lower c.d. ($\approx 20 \text{ mA/cm}^2$) up to 30,000 Å.

The deposits at very low thickness, of the order of a thousand angstroms, gave patterns in which spots are vertically much elongated normal to the shadow edge. This elongation is due to refraction at, and low penetration into, the atomically highly smooth crystal surface, which is evidently parallel to the copper (100) face of the substrate. At thicknesses of a few thousand angstroms, up to 30,000 Å or more, the electron diffraction spots are still mainly of this form, but show increasingly some degree of fanning out radially from their upper ends which correspond to the unrefracted spot positions (as in transmission). This indicates an increasing waviness (roughening) of the surface form. The slopes of the more or less undulations tend to be near to (311) (or (411)?) and (310) planes, though no extensive facet development is indicated until much higher thickness of the order of 60,000 Å.

Fig.59(c) is the optical micrograph of the 61,000 Å deposit surface. Though there are noticeable projections, the surface is not very rough. In appearance, the deposit surfaces in this region I were very bright and shiny throughout. At 61,000 Å, the "arrow-head" shape of the diffraction spots is evidence of the development of extensive oblique faces parallel to the particular types of planes, i.e. (511) and (310).

Region II; Nickel deposits showing the surface hydroxide layer.

This region lies on the right of the broken line i.e. mainly above 250 mA/cm^2 in the vicinity of 30,000 Å in Fig.54. In this region, the electrodeposition is accompanied by evolution of gas, this being more vigorous with increasing c.d. The deposit surface was coated with a rough greenish deposit, probably nickel hydroxide. The diffraction patterns from the hydroxide-coated surfaces were diffuse (cf. Fig.35). The underlying metal surfaces after etching away the hydroxide layer in 5% dil. H_2SO_4 for 15-20 seconds gave clear f.c.c. nickel patterns. On the basis of the structure results, this region has been further subdivided into sub-regions II(A) and II(B), which are discussed below.

Sub-region II(A); The nickel just below the hydroxide layer in parallel single-crystal growth to the copper crystal substrate.

Fig.60 shows typical diffraction results in this sub-region, which is enclosed between the broken and continuous lines in Fig.54. At low thicknesses, up to $\approx 500 \text{ Å}$, this sub-region lies between 390 and 490 mA/cm^2 . Here the nickel deposits after etching away the surface hydroxide layer, show very smooth single-crystal surface in parallel growth to the substrate crystal, without any other additional structure. The diffraction pattern from a thin

deposit of the order of 700 Å at 400 mA/cm² was similar to that in Fig.60.

Sub-region II(B); The nickel just below the hydroxide layer mainly in parallel growth to the copper crystal, with a little {111} twinning, in some cases a little one-degree (110) orientation, plus an increasing proportion of randomly oriented crystal.

Typical diffraction photographs are shown in Figs. 61 to 63. Within the c.d. range investigated, this sub-region extends mainly between 250 and 600 mA/cm² or more (cf. Fig.54). The underlying metal surface after etching away the hydroxide layer in 5% dil. H₂SO₄ for 15-20 seconds, show single-crystal structure in parallel growth to the copper crystal substrate. However, there are additional {111} twinning and random orientation both in small amount, at below 30,000 Å (cf. Fig.61). The amount of random nickel and {111} twinning increases with increase in deposit thickness and c.d., with consequent decrease in amount of single-crystal growth (cf. Fig.63). Above 30,000 Å, between 250 and 320 mA/cm², the parallel growth together with small amounts of {111} twinning and random nickel, is accompanied by some one-degree (110) orientation also (cf. Fig.62). In some cases around 10,000 Å, the extension of the diffraction spots in part, obliquely towards the shadow edge, indicates the more or less smooth but undulating form of the nickel crystal surface.

In Fig.61(a), the square arrangement of spots is obtained when the electron beam is along the cube-edge direction, whereas Fig.61(b) shows the "centred $\sqrt{2}$ -rectangle" pattern, the $\sqrt{2}$ -side horizontal, when the beam is incident along the cube-face diagonal. The diffraction spots 200, 400, ..., lie on the plane of incidence, showing that the cube-face was parallel to the surface or nearly so, i.e. parallel to the Cu (100) surface.

In Fig.61(b), the $\{111\}$ twinning is concluded by the presence of additional spots, e.g. two on the 111 ring position, one on each side of, and close to the plane of incidence, i.e. near the 11 o'clock and 1 o'clock positions. The same is true for Fig.62, but there is presence of some one-degree (110) oriented nickel crystals

3.5:2. Nickel electrodeposits on the copper (100) face, from the sulphate bath at 50°C, when the bath is stirred vigorously.

Fig.64 shows diagrammatically the experimental results on the surface structure of the nickel electrodeposits, up to deposit thicknesses of 52,000 Å and c.d. up to 600 mA/cm². The change in the structure of the nickel electrodeposits above a certain c.d. results in the division of the whole diagram into regions I and II, discussed below.

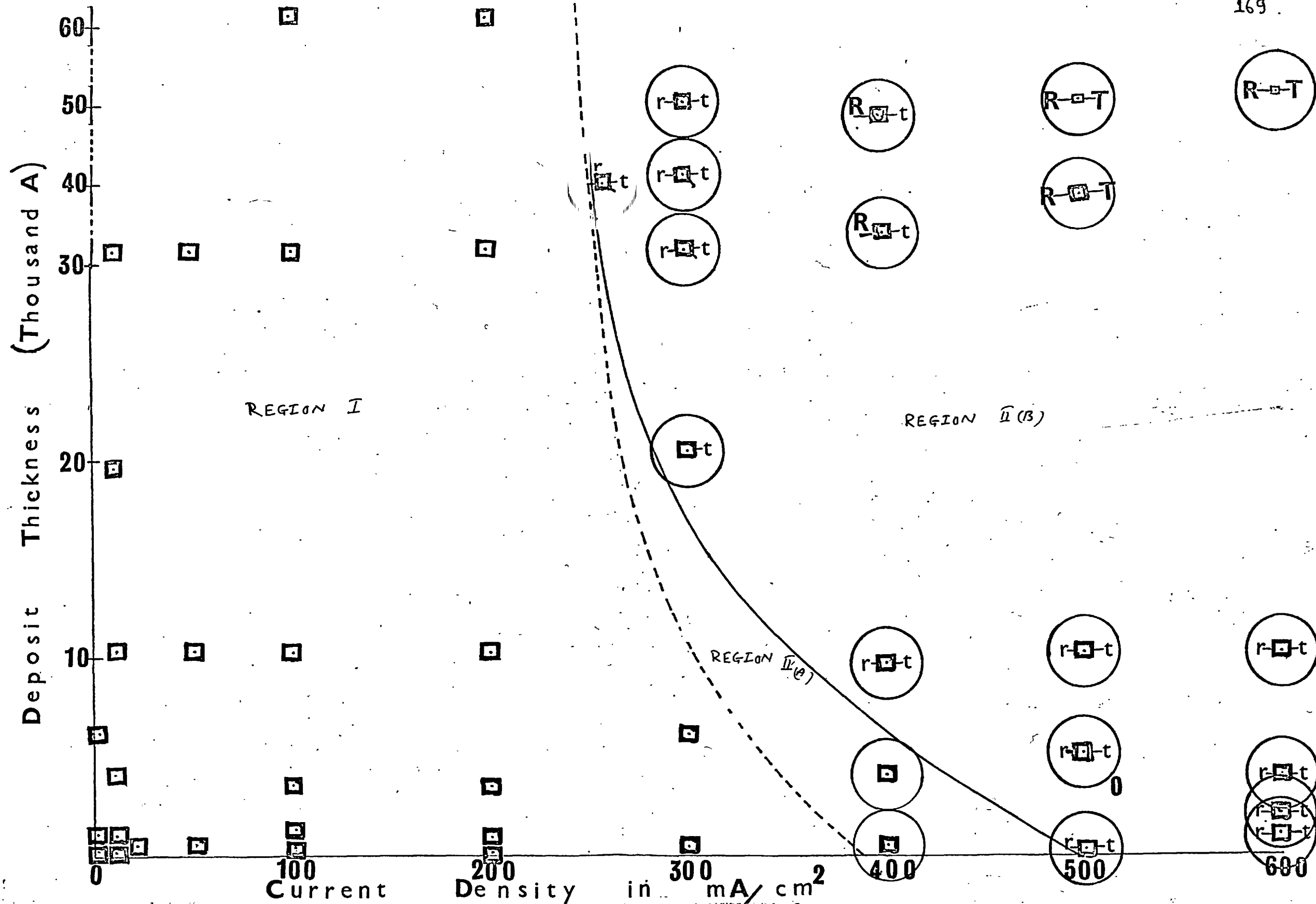
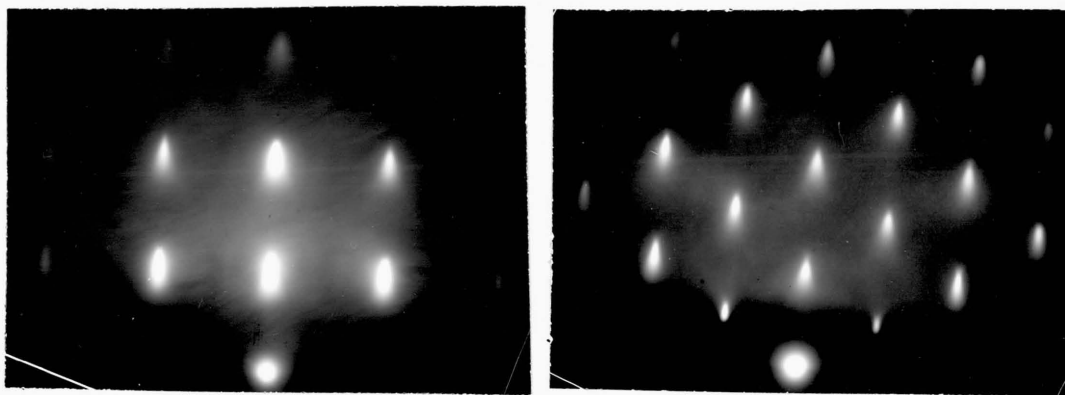


Fig. 54. Ni on Cu (100), Unstirred, 50°C. For symbols see page 130(A).

REGION I OF FIG. 54.

(Cu (100), unstirred bath, 50°C).



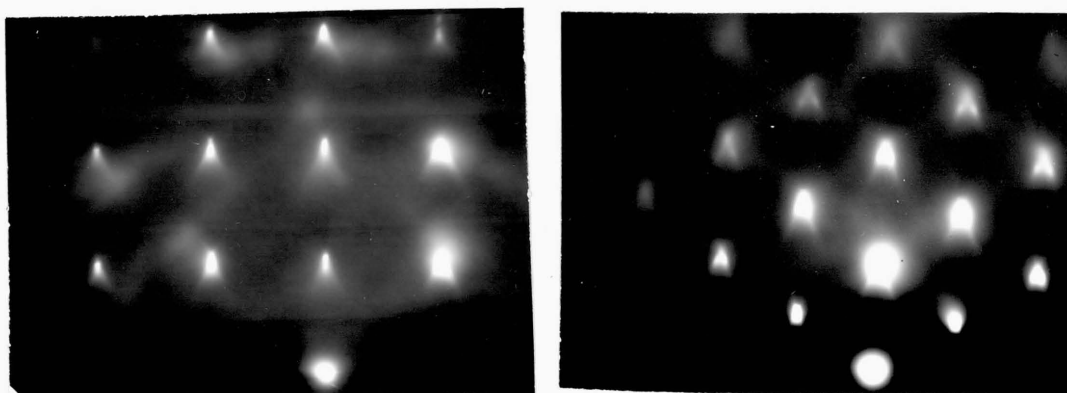
(a)

(b)

Fig.55. 170 Å Ni at 100 mA/cm^2 on electropolished Cu (100) unstirred bath, 50°C .

(a) Beam along cube edge

(b) Beam along cube-face diagonal.



(a)

(b)

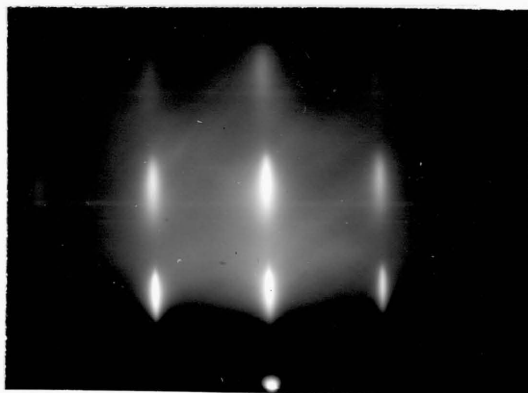
Fig.56. 61,000 Å Ni at 100 mA/cm^2 on Cu (100), unstirred bath, 50°C .

(a) Beam along cube edge.

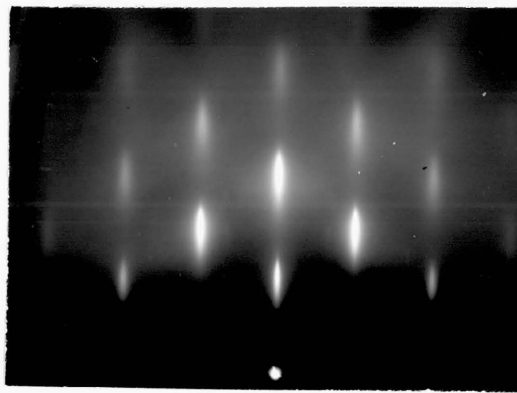
(b) Beam along cube-face diagonal.

REGION I OF FIG. 54.

(Cu (100), unstirred bath, 50°C.)



(a)

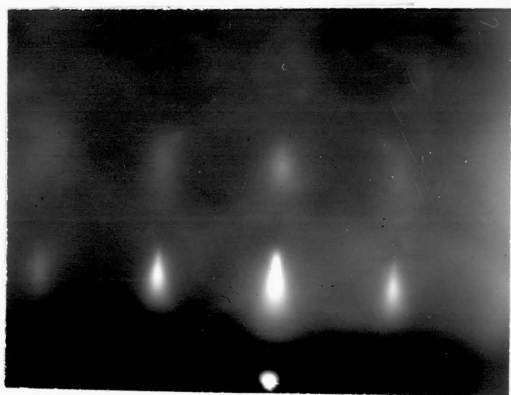


(b)

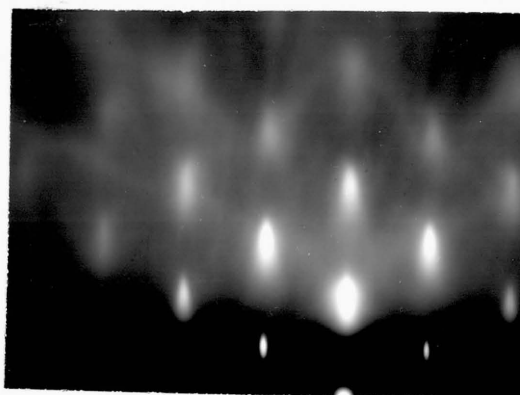
Fig. 57. 340 Å Ni at 200 mA/cm² on Cu (100), unstirred bath, 50°C.

(a) Beam along cube edge.

(b) Beam along cube-face diagonal.



(a)



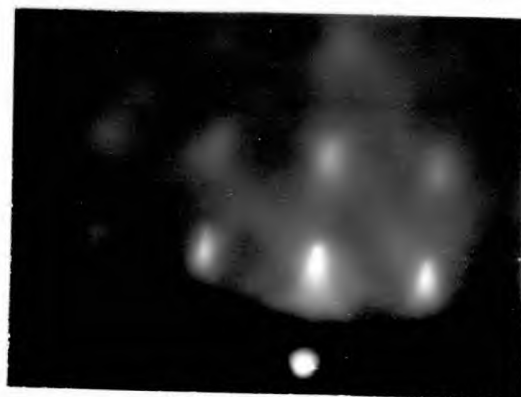
(b)

Fig. 58. 30,600 Å Ni at 200 mA/cm² on Cu (100), unstirred bath, 50°C.

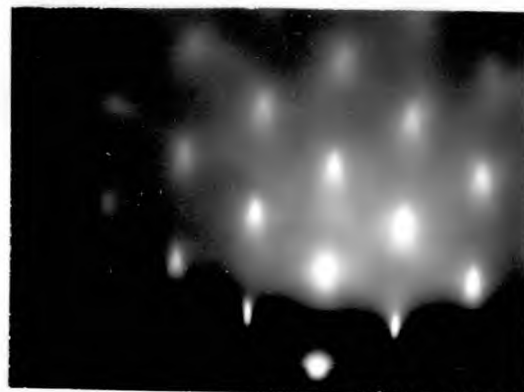
(a) Beam along cube edge.

(b) Beam along cube face diagonal.

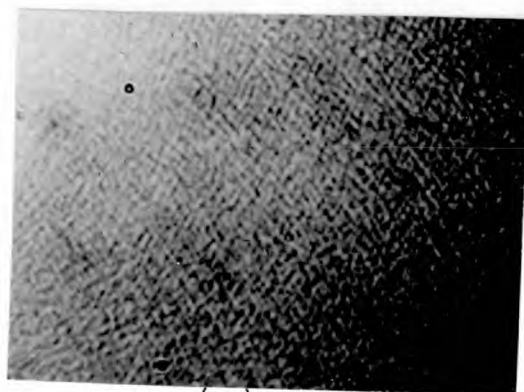
REGION I OF FIG. 54.
(Cu (100), unstirred bath, 50°C).



(a)



(b)



(c)

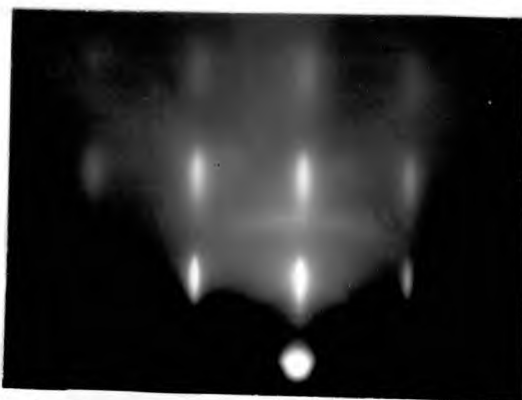
Fig.59, 61,000 Å Ni at 200 mA/cm² on Cu(100), unstirred bath, 50°C.

(a) Beam along cube edge.

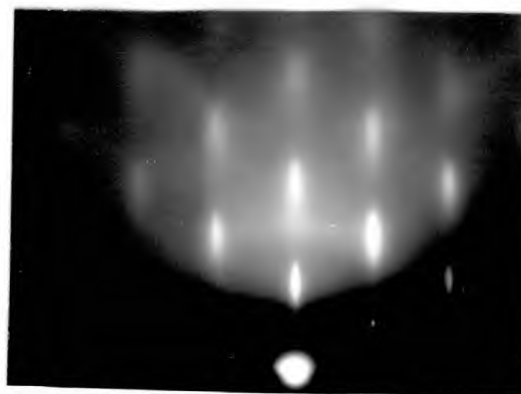
(b) Beam along cube face diagonal.

(c) Optical micrograph x 300.

REGION II(A) OF FIG. 54.



(a) Beam along cube edge

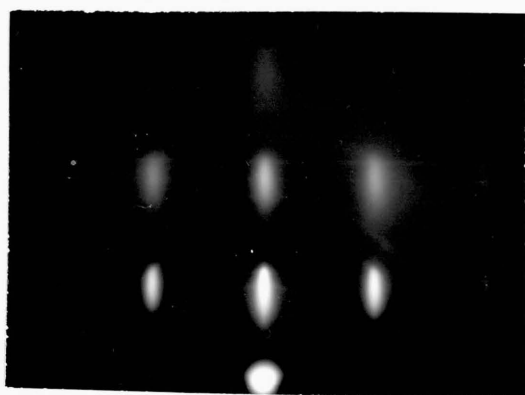


(b) Beam along cube face diagonal.

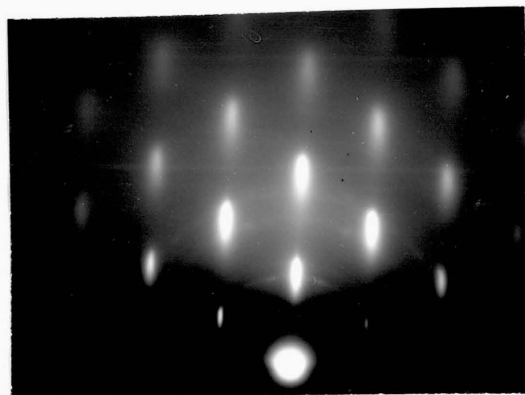
Fig.60. 4,000 Å Ni at 400 mA/cm² on Cu(100), unstirred bath,

REGION II (B) OF FIG. 54.

(Cu (100), unstirred bath, 50°C).



(a)



(b)

Fig.61. 850 Å Ni at 500 mA/cm² on Cu (100), unstirred bath, 50°C.

(a) Beam along cube edge.

(b) Beam along cube-face diagonal.

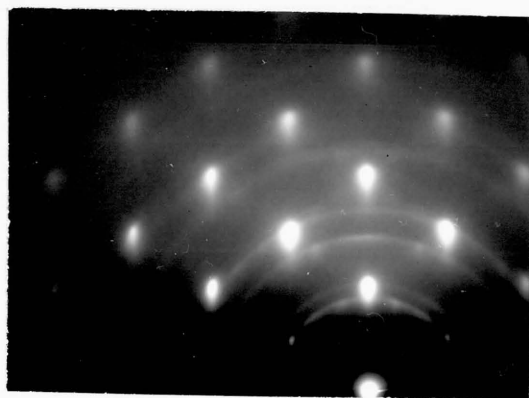


Fig.62

30,600 Å Ni at 300 mA/cm²
on Cu (100), unstirred bath
50°C.

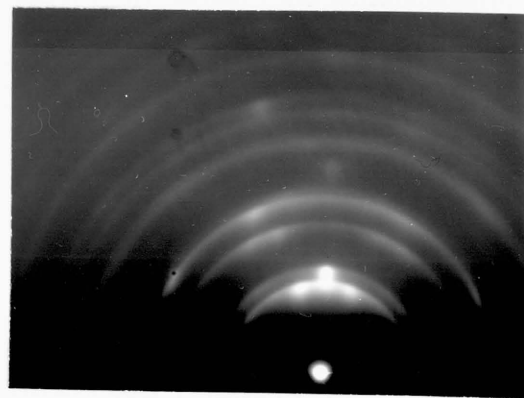


Fig.63.

51,000 Å Ni at 500 mA/cm²
on Cu (100), unstirred bath
50°C.

Region I; Very smooth nickel deposits having a single crystal structure with arcs parallel to those of the copper crystal used as substrate.

Fig.65 shows a typical electron diffraction photograph from deposits corresponding to this region (cf. Fig.64). Fig.65(a) showing square arrangement of spots is the diffraction pattern when the electron beam is incident along a cube-edge direction. Fig.65(b), showing a centred $\sqrt{2}$ -rectangle pattern with $\sqrt{2}$ -side horizontal, is obtained when the electron beam is along a cube-face diagonal. In both the patterns, the diffraction spots lying on the plane of incidence show that the cube face is parallel to the surface or nearly so, and therefore parallel to the Cu (100) face.

The single crystal growth of nickel parallel to the copper substrate crystal even up to 52,000 Å has a fairly smooth surface. The elongation of the electron diffraction spots also shows a highly smooth surface on the atomic scale, the surface being a cube face parallel to the substrate surface. None of the deposits show any other additional orientation. The diffraction patterns from all the deposits in this region are nearly the same. This region extends nearly up to 550 mA/cm². At 600 mA/cm², however, this region lies below 15,000 Å.

Using the unstirred bath at 50°C, region I, showing parallel growth with the substrate, goes up to

250 mA/cm² (cf. Fig.54). The stirring increases the upper limit of c.d. for region I from 250 to 550 mA/cm² (cf. Fig.64)

Region II; Nickel in decreasing proportion of single crystal structure with minute traces of {111} twinning and increasing proportion of random oriented nickel.

Figs. 66 and 67 show the typical nickel structure in this region, which starts at about 550 mA/cm² and extends towards higher c.d. (cf. Fig.64).

Fig. 66 was obtained when the electron beam was incident along the cube-face diagonal of the deposit surface. The spot pattern is of the centred $\sqrt{2}$ -rectangle form with the $\sqrt{2}$ -side horizontal characteristic of parallel growth. In addition a little {111} twinning and much randomly oriented nickel is present. The {111} twinning is shown by the presence of additional spots, e.g. the two on the 111 ring position, one on each side of, and close to, the plane of incidence, i.e. near the 11 o'clock and 1 o'clock positions.

The single crystal growth of the nickel parallel to the copper substrate crystal decreases in amount with deposit thickness, whereas the proportion of random nickel increases. A very minute trace of {111} twinning is also present before one structure is completely random.

There is still a tendency for the (100) oriented nickel crystals to be bounded by a cube face parallel to the substrate surface, as is shown by the noticeable elongation

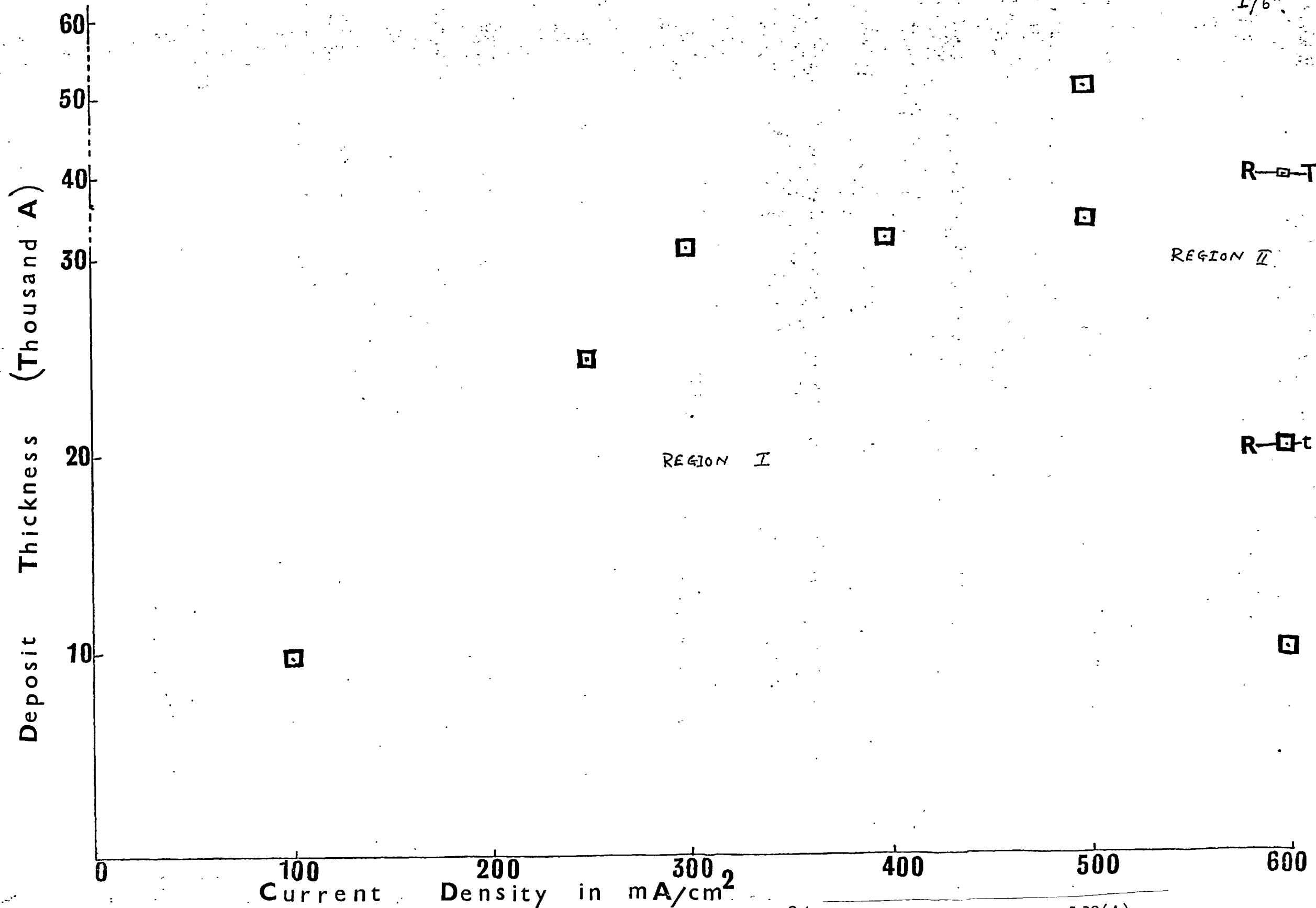
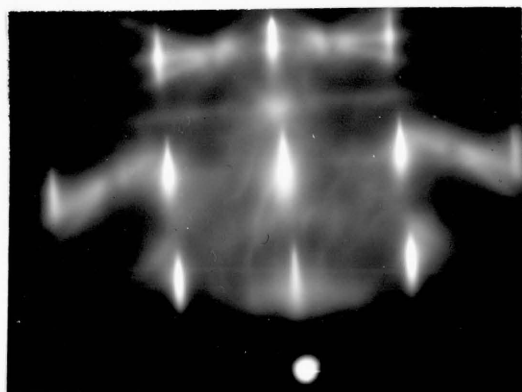


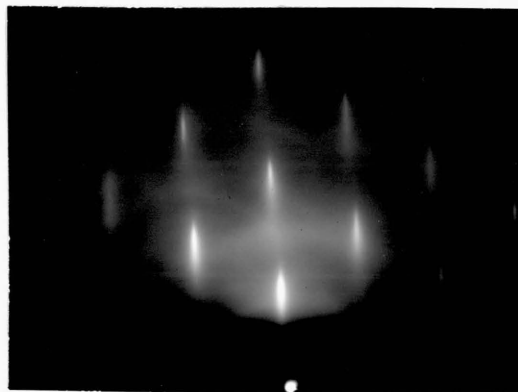
Fig. 64. Ni on Cu(100), Stirred, 50°C. For symbols see page 130(A).

REGION I OF FIG. 64.

(Cu (100), stirred bath, 50°C.



(a)



(b)

Fig.65. 51,000 Å Ni at 500 mA/cm² on Cu (100), stirred bath, 50°C.

(a) Beam along cube edge.

(b) Beam along cube face diagonal.

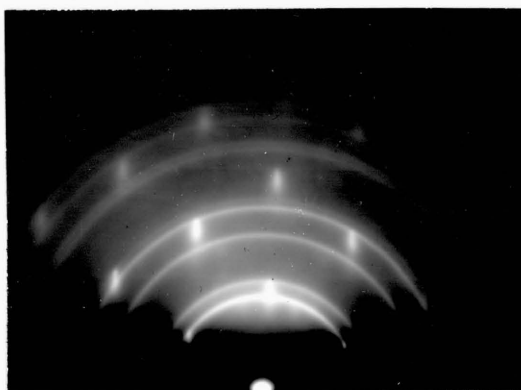
REGION II OF FIG. 64.

Fig.66.

20,400 Å Ni at 600 mA/cm²
on Cu (100), stirred bath
50°C.

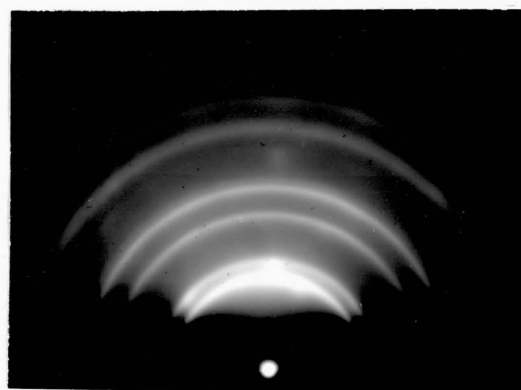


Fig.67.

40,800 Å Ni at 600 mA/cm²
on Cu (100), stirred bath
50°C.

of the diffraction spots towards the shadow edge. The randomly oriented nickel has a mean crystal size larger than 50 Å (as shown by the ring widths) and not more than about 500 Å diameter (as shown by the absence of spottiness of the rings).

3.6. The Structure, Growth and Orientation of Nickel Electrodeposits on an Atomically Smooth Electropolished (110) Face of a Copper Single Crystal Substrate, from the Standard Nickel Sulphamate Solution at 50°C.

In the practical application of plating nickel on to drawn Cu wire for protection against oxidation, the Cu crystals at the surface of the drawn wire are likely to have a (110) plane parallel to the surface or inclined at a small angle to it (cf. the electron diffraction results such as those of Goddard, Harker and Wilman, 1962). The results for deposition on Cu (110) face described below are thus most nearly analogous to this case.

Figs. 7 and 8 show typical electron diffraction patterns illustrating the atomically smooth nature of the electropolished copper (110) face used as substrate.

A wide range of current density was investigated, i.e. from 10 to 600 mA/cm², and deposit thicknesses from 200 to 62,000 Å. The investigation was carried out with both an unstirred and stirred bath.

3.6.1. Nickel Electrodeposits on the Copper (110) Face, from the Sulphamate Bath at 50°C, when the bath is Unstirred.

Fig.68 shows diagrammatically the experimental results on the (110) face of the copper single crystal substrate in the unstirred bath. The whole diagram has been divided into two main regions I and II on the basis of the results obtained. The lines indicate the positions of relatively narrow zones of transition of the deposit structure from one region to that of the neighbouring one. The results within different regions are described below.

Region I; Nickel mainly in a single crystal orientation, with axes parallel to those of the copper crystal, with varying amount of {111} twinning and one-degree (100) orientation.

The region extends up to about 340 mA/cm² for deposit thicknesses studied up to 61,000 Å (cf. Fig.68). Beyond 340 mA/cm², it becomes limited to lower and lower thickness (to the broken line in Fig.68), being only 2000 Å at 600 mA/cm².

In region I, the nickel crystals grow mainly parallel to the substrate copper crystal lattice. In most cases, the parallel growth of the nickel is accompanied by varying amount of {111} twinning and in region I(A) at 10,000 Å and over, with also some nickel in one-degree (100) orientation and some in two-degree orientation. Above

250 mA/cm², the growth of nickel is only parallel to the substrate lattice and with very smooth surface without any additional twinning or other orientations. This part of the region is marked sub-region I(B). The diffraction results corresponding to these sub-regions are discussed below in detail.

Sub-region I(A); Nickel mainly in a single-crystal orientation with axes parallel to those of the copper substrate with a little or much {111} twinning and increasing amount of one-degree (100) orientation after a few thousand angstroms deposit thickness.

Figs. 69 to 73 show typical electron diffraction photographs corresponding to this region in Fig.68. From 10 to 150 mA/cm² very strong {111} twinning is developed together with parallel growth even at a few hundreds angstroms of nickel deposit thickness (see Fig.69).

The diffraction pattern in Fig.69 was obtained when the electron beam was incident along the $\langle 110 \rangle$ direction of the (110) face of the crystal substrate. This gives a centred $\sqrt{2}$ -rectangle spot arrangement with the $\sqrt{2}$ -side vertical. The diffraction spots lying on the plane of incidence have Laue indices of type 220, 440, 660, and so on, showing that the (110) face is parallel to the copper substrate (110) surface or nearly so. The $\langle 111 \rangle$ twinning is concluded by the presence of additional spots, e.g. on the 200 ring position one on each side of, and close to, the 11 o'clock and 1 o'clock positions.

Between 10 and 150 mA/cm² and at above 1,000 Å, a trace of randomly oriented nickel together with the main parallel single-crystal growth and strong {111} twinning is also observed (see Fig.70). Around 10,000 Å, an additional one-degree (100) orientation and a particularly sharply defined two-degree (100) orientation set in (cf. Fig.71) and they become stronger with increasing thickness up to 61,000 Å or more (see Fig.73). From about 150 to 250 mA/cm², the parallel growth of the nickel is accompanied by a little {111} twinning up to about 20,000 Å.

The {111} twinning becomes stronger (as in Fig.70) with increase in deposit thickness. The diffraction patterns from deposits at similar thicknesses up to 150 mA/cm² are nearly the same. At 100 and 200 mA/cm², the deposits of thickness of 61,000 Å yield identical diffraction patterns as shown in Fig.73(a,b,c).

The prominent, sharply defined, two-degree (100) orientation is indicated by a very short arc or spot lying on the 200 and 400 diffraction arcs (of the one-degree (100) arc pattern) where they cross the plane of incidence at heights of 1.4 and 2.8 cm above the undeflected beam spot (cf. Figs. 71 and 73(a)).

Figs. 73(b) and 73(c) were obtained at an azimuth near to the <211> type of direction of the electron beam relative to the Cu (110) surface. They show that at this azimuth a square pattern of hk0 short arcs or spots with

square sides horizontal and vertical is present, associated with these nickel 200 and 400 diffractions.

In Fig.73(b), the main strong spots are in a $\sqrt{8/3}:1$ rectangle pattern (with the $\sqrt{8/3}$ -sides vertical), as is expected at this azimuth from the single-crystal nickel, which is parallel to the copper substrate lattice; and the above square pattern is faint. In Fig.73(c) from another part of the specimen, the square pattern is relatively much stronger.

This particular two-degree (100) orientation is difficult to account for and it appears not to correspond to twinning and repeated twinning of the main parallel growth nickel orientation. Presumably, there must be two of these (100) single crystal orientations associated with the two azimuths of $\langle 211 \rangle$ type relative to the substrate and the parallel nickel.

At 300 mA/cm^2 , a 51,000 Å deposit yields sharp and very elongated diffraction spots - the single crystal spots and the twin spots (see Fig.72). This indicates that the surface is very smooth and parallel to the Cu (110) substrate surface even at 51,000 Å thickness.

Sub-region I(B); Nickel only in a single crystal orientation with axes parallel to those of the copper single crystal.

Fig.74(a,b) shows typical diffraction photographs of this sub-region. Above 250 mA/cm^2 , the nickel seems to

grow only parallel to the copper single crystal lattice and without any twinning or other orientations. The elongation of the diffraction spots normal to the shadow edge is a clear indication of the deposit surface being very smooth and parallel to the (110) substrate surface.

The diffraction pattern in Fig.74(a) shows spots in a centred $\sqrt{2}$ -rectangle arrangement, the $\sqrt{2}$ -side vertical when the electron beam is incident along the $[1\bar{1}0]$ direction of the (110) face; whereas Fig.74(b) is a $\sqrt{8/3}$ -rectangle spot arrangement when the beam is along a $\langle 211 \rangle$ direction of the (110) face.

Starting at about 250 mA/cm^2 , this sub-region becomes limited to lower and lower thicknesses with increasing deposit thickness, cf. Fig.68. Its apex lies at about 50,000 Å corresponding to 340 mA/cm^2 .

Region II; The deposit surface coated with a nickel hydroxide layer, showing the nickel structure after etching.

This region lies on the right of the broken line in Fig.68 above a few thousand angstroms deposit thickness. Here, evolution of gas was observed during electrodeposition. The surface of the deposit was covered with greenish rough deposit, probably nickel hydroxide. The typical diffuse diffraction pattern is shown in Fig.35. After etching away the hydroxide in 5% dil. H_2SO_4 for 15-20 seconds, the underlying surface gave the f.c.cubic nickel pattern. This

region can be further sub-divided into sub-regions II(A) and II(B).

Region II(A); After etching away the hydroxide layer, the deposit surface showing growth of nickel only in a single crystal orientation with axes parallel to those of the copper single-crystal substrate.

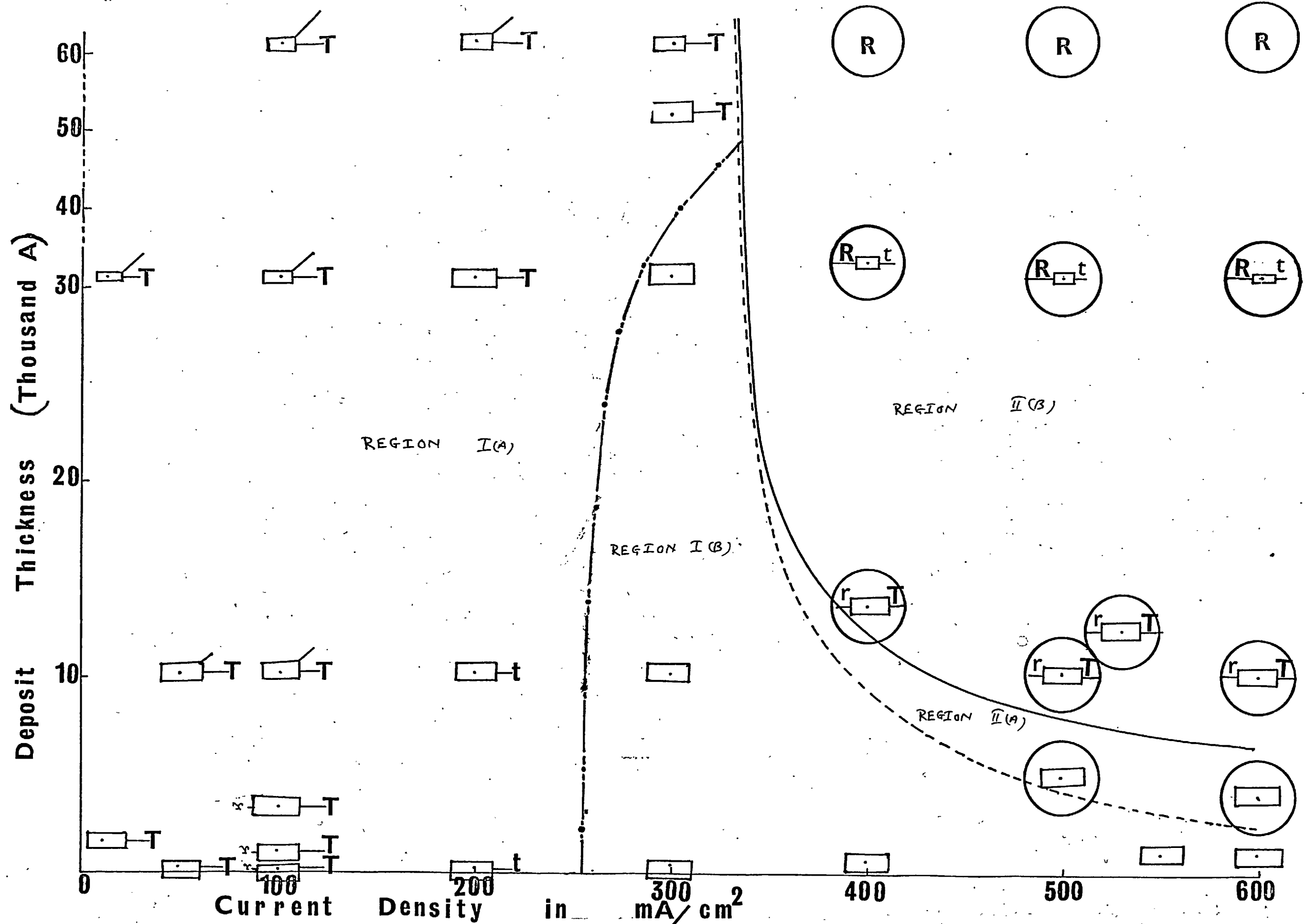
This region is a very narrow strip representing only a few thousand angstroms deposit thickness at 600 mA/cm^2 , with gradual narrowing down to the left, as it curves up to its apex at about 20,000 Å, and in between the broken and continuous line as shown in Fig.68. The deposit surface within this region was covered with nickel hydroxide as already described. The hydroxide-coated surface gave a diffuse pattern as shown in Fig.35. After etching away the hydroxide layer, the underlying surface showed very smooth surfaced parallel single-crystal orientation of the nickel, without any trace of twinning or any other orientation, as shown in Fig.75. The pattern is of centred $\sqrt{2}$ -rectangle type with the $\sqrt{2}$ -side vertical. The elongation of the diffraction spots and the presence of strong Kikuchi bands indicate the high degree of smoothness of the deposit surface on the atomic scale.

Sub-region II(B); After etching away the hydroxide layer the deposit surface showing single crystal nickel parallel to the copper single-crystal substrate, with {111} twinning and increasing amount of randomly oriented crystals.

Typical diffraction photographs corresponding to this region are shown in Figs. 76, 77 and 78. After etching away the hydroxide layer, the metal surface showed parallel single-crystal growth with strong {111} twinning and some random nickel at above 10,000 Å (see Fig. 77). With increase in deposit thickness, the amount of randomly-oriented nickel crystals increases with consequent decrease in parallel growth and {111} twinning. At about 30,000 Å and from 340 mA/cm² or more, the randomly-oriented nickel crystals predominate, with a little single-crystal orientation and {111} twinning (see Fig.76). Beyond 30,000 Å, the remaining small traces of parallel growth and {111} twinning gradually decrease. At about 61,000 Å and beyond 340 mA/cm² the nickel crystals are only randomly oriented (see Fig.78). This sub-region II(B) lies on the right side of the broken line in Fig.68. Starting at about 340 mA/cm², it extends to 600 mA/cm² or beyond.

3.6.2. Nickel Electrodeposits on the Copper (110) face, from the sulphamate bath at 50°C, when the bath was stirred vigorously.

Fig.79 shows diagrammatically the experimental



Fi. 68. Ni on Cu(II)O, Unstirred, 50°C.

For symbols see page 130(A).

REGION I(A) OF FIG. 68.

(Cu (110), unstirred bath, 50°C).

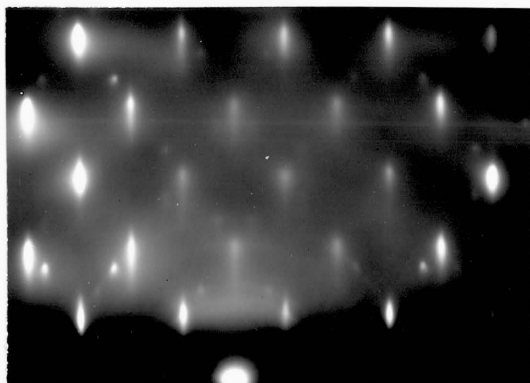


Fig. 69.

200 Å Ni at 100 mA/cm²
on Cu (110), unstirred
bath, 50°C.

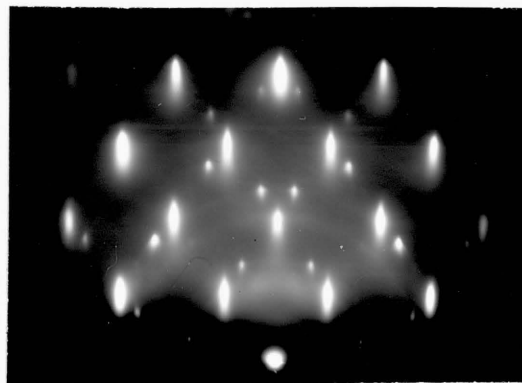


Fig. 70.

1000 Å Ni at 100 mA/cm²
on Cu (110), unstirred
bath, 50°C.



Fig. 71.

10,200 Å Ni at 100 mA/cm²
on Cu (110), unstirred
bath, 50°C.

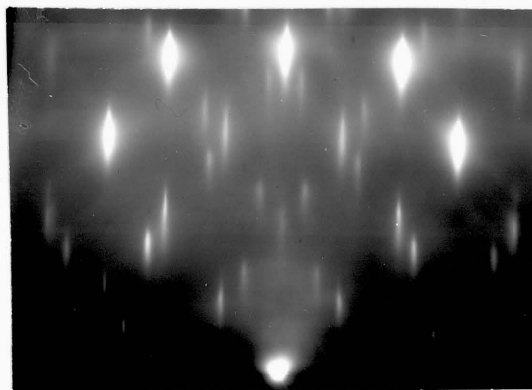
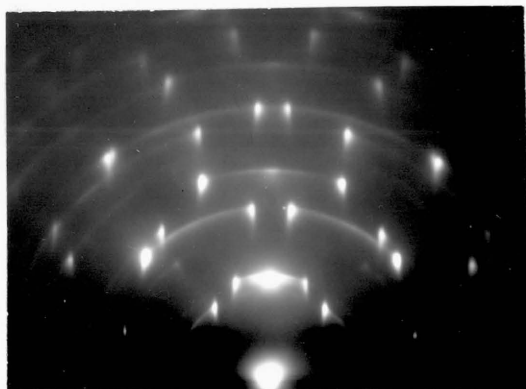


Fig. 72.

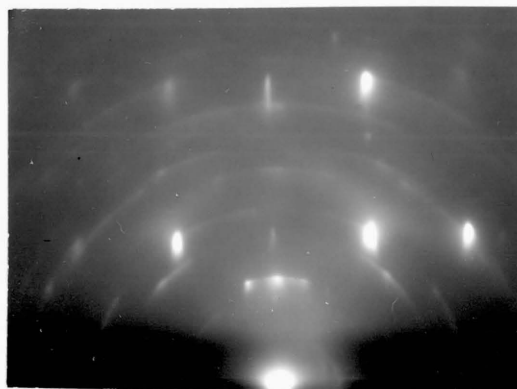
51,000 Å Ni at 300 mA/cm²
on Cu (110), unstirred
bath, 50°C.

REGION I(A) OF FIG. 68.

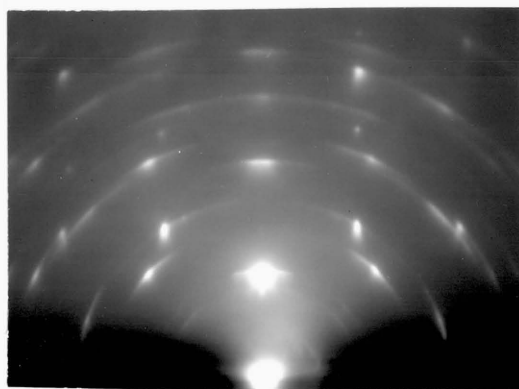
(Cu (110), unstirred bath, 50°C).



(a) Beam along $[1\bar{1}0]$.



(b) Beam along $\langle 211 \rangle$.

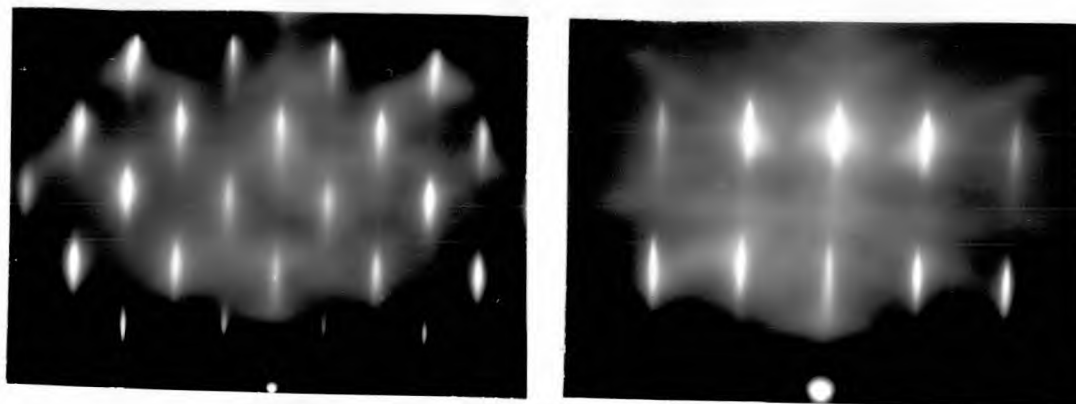


(c) Beam along $\langle 211 \rangle$

Fig. 73. 61,000 Å Ni at 100 mA/cm² on Cu (110), unstirred bath, 50°C.

REGION I(B) OF FIG. 68.

(Cu (110), unstirred bath, 50°C.)



(a)

(b)

Fig.74. 500 Å Ni at 300 mA/cm² on Cu (110), unstirred bath 50°C.

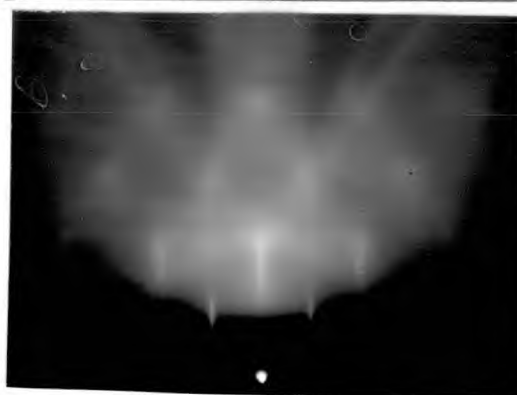
(a) Beam along $\langle 110 \rangle$ (b) Beam along $\langle 211 \rangle$ REGION II(A) OF FIG. 68.

Fig.75. 5,000 Å Ni at 500 mA/cm² on Cu (110), unstirred bath, 50°C.

REGION II(B) OF FIG. 68.

(Cu (110), unstirred bath, 50°C).

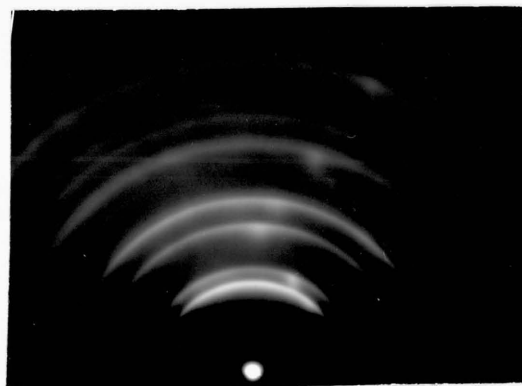


Fig.76. 30,600 Å Ni at 500 mA/cm² on Cu (110), unstirred bath, 50°C.

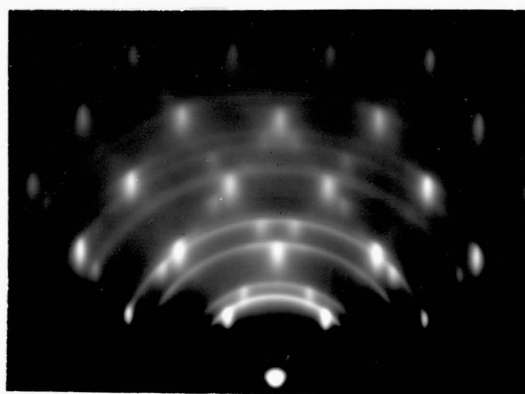


Fig.77
10,200 Å Ni at 600 mA/cm²
on Cu (110), unstirred
bath, 50°C.

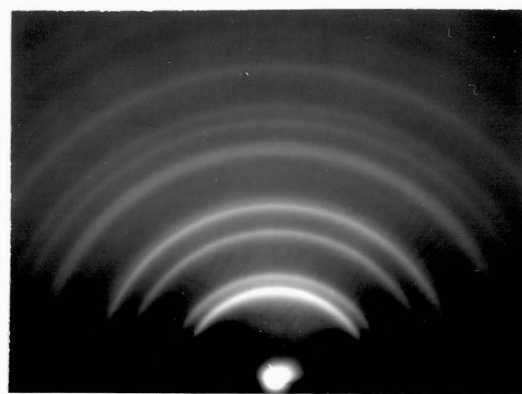


Fig.78.
61,000 Å Ni at 600 mA/cm²
on Cu (110), unstirred
bath, 50°C.

results. The change of the main orientation in the neighbourhood of a certain c.d. divides the whole diagram into two regions I and II as described below.

Region I; Nickel in a single crystal orientation with axes parallel to those of the copper single crystal substrate, with varying amount of $\{111\}$ twinning and one-degree (100) orientation.

Figs. 80 to 84 are representative diffraction patterns corresponding to the region I (cf. Fig.79). Between 150 and 500 mA/cm² the nickel grows in single-crystal orientation parallel to the copper single crystal substrate with little $\{111\}$ twinning. The deposit surface was very smooth, giving rise to much elongation of the diffraction spots at up to about 50,000 Å and within the range of 200 to 500 mA/cm². Above about 45,000 Å, additional one-degree (100) orientation also sets in (see Figs. 79 and 83). This (100) orientation becomes stronger with increase in deposit thickness, where the parallel growth diminishes in amount (see Fig.84). The $\{111\}$ twinning is very faint at around 34,000 Å (see Fig.82), but becomes clearer with some increase in its amount at higher deposit thicknesses (cf. Fig. 83).

At 100 mA/cm², even at 30,600 Å deposit thickness, the one-degree (100) orientation component is very pronounced (with additionally a trace of its octahedral twins present as shown by faint arcs near by the 111 ring)

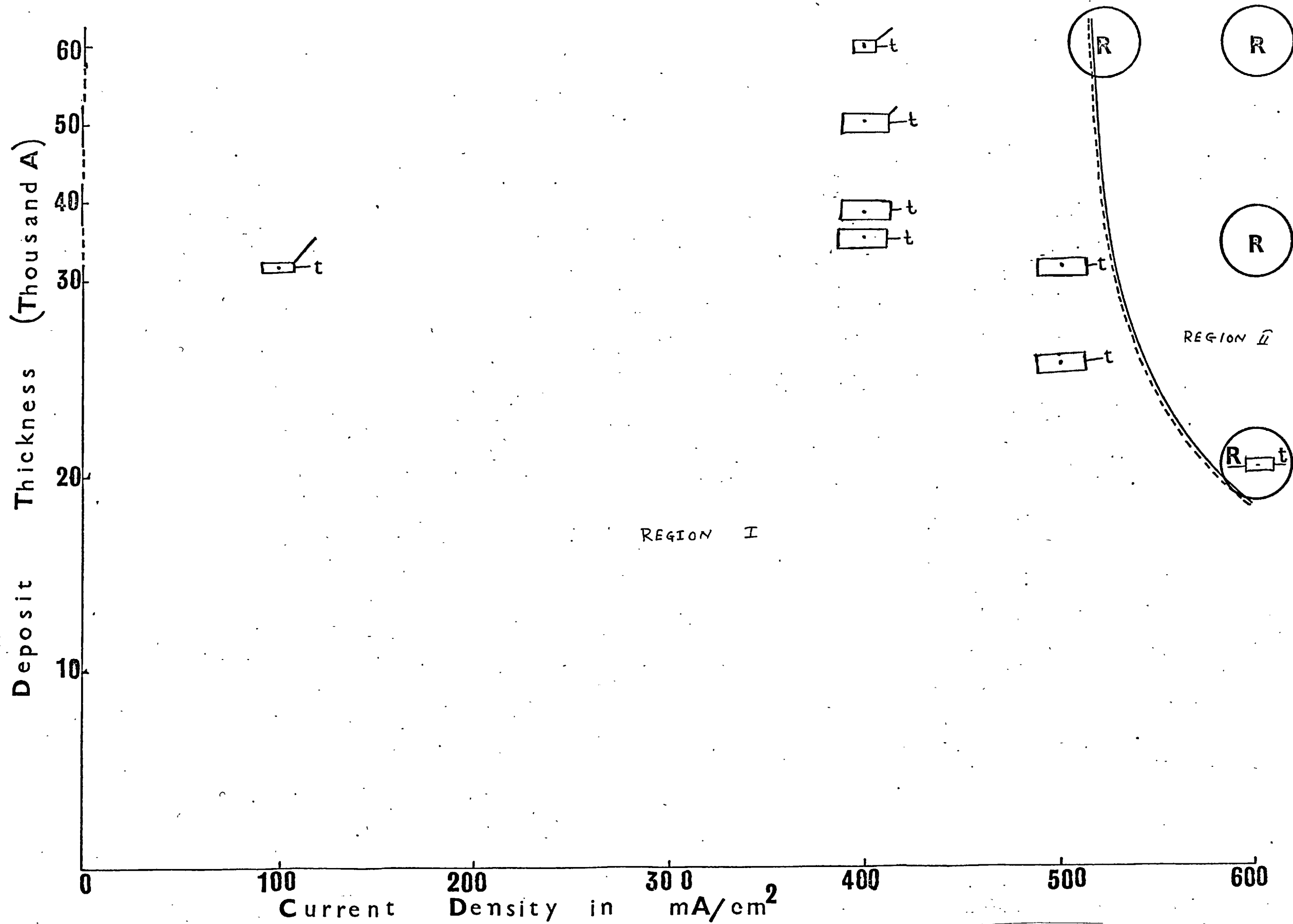
and the parallel single crystal growth is reduced appreciably, and is accompanied by its octahedral twins (see Fig.80(a)). Fig.80(b) shows the optical micrograph of the specimen which yielded the diffraction pattern in Fig.80(a). The optical micrograph shows that the deposit surface was fairly rough.

The comparison of Figs. 68 and 79 shows that the stirring has extended the upper limit of c.d. for region I, from 340 to 520 mA/cm², which is equivalent to about 53% increase in the supply of nickel ions to the solution immediately adjacent to the cathode.

Region II; Nickel deposit surface mostly covered with hydroxide, and showing increasing proportion of random polycrystalline nickel structure.

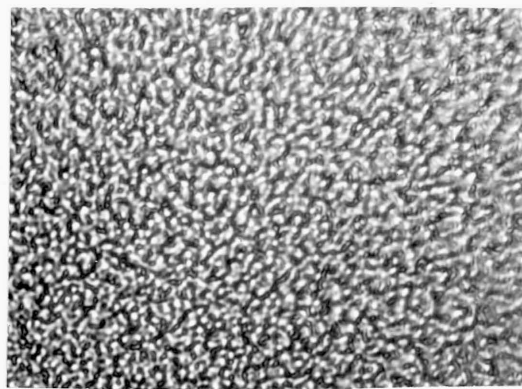
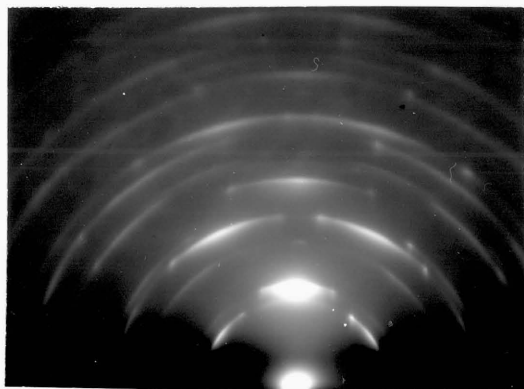
Figs. 85 and 86 show typical diffraction photographs for the region, which starts at about 520 mA/cm² and extends towards higher c.d. (see Fig.79). The evolution of gas observed at c.d. higher than 530 mA/cm² resulted in co-deposition of a hydroxide layer on the electrodeposited nickel in almost all the cases.

The deposit at 600 mA/cm² and 20,400 Å thick with a little hydroxide on it, shows a large proportion of random polycrystalline nickel with less single crystal structure and a trace of {111} twinning of the latter (see Fig.85). Fig.85 shows the centred $\sqrt{2}$ -rectangle diffraction pattern, the $\sqrt{2}$ -side being vertical, when the electron beam was



REGION I OF FIG. 79.

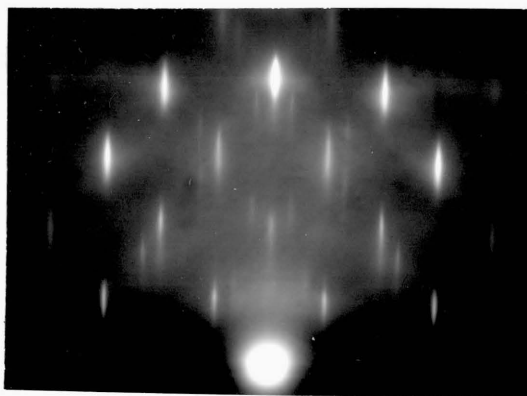
(Cu (110), stirred bath, 50°C).



(a)

(b) Optical micrograph
x 800.

Fig.80. 30,600 Å Ni at 100 mA/cm² on Cu (110), unstirred bath, 50°C.



(a)

(b)

Fig.81. 25,500 Å Ni at 500 mA/cm² on Cu (110), stirred bath, 50°C.

(a) Beam along $\langle 110 \rangle$ (b) Beam along $\langle 211 \rangle$

REGION I OF FIG. 79.
(Cu (110), stirred bath, 50°C).

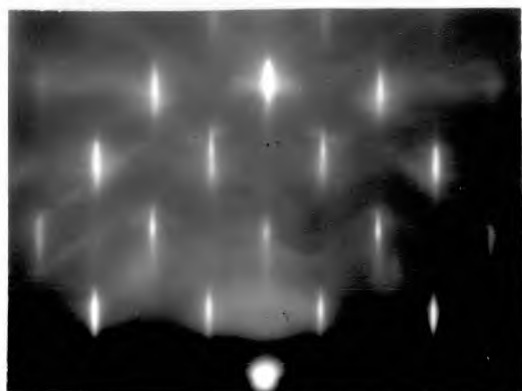


Fig. 82. 34,000 Å Ni at 400 mA/cm² on Cu (110), stirred bath, 50°C.

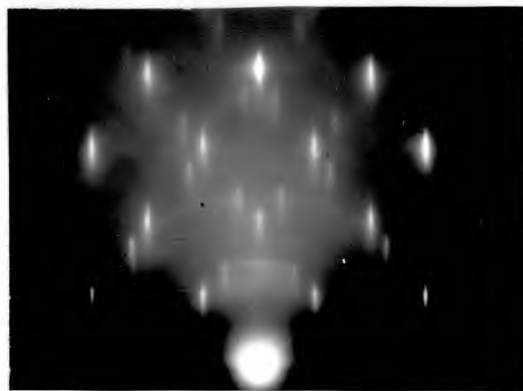


Fig. 83. 49,000 Å Ni at 400 mA/cm² on Cu (110), stirred bath, 50°C.

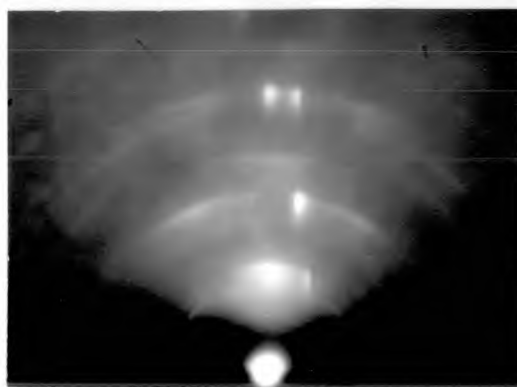


Fig. 84. 61,000 Å Ni at 400 mA/cm² on Cu (110), stirred bath, 50°C.

REGION II OF FIG. 79.

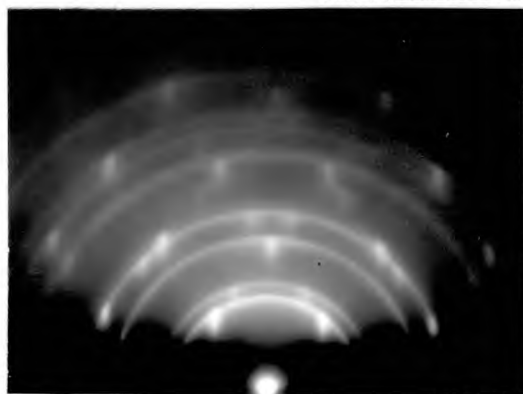


Fig. 85. 20,400 Å Ni at 600 mA/cm² on Cu (110), stirred bath, 50°C.

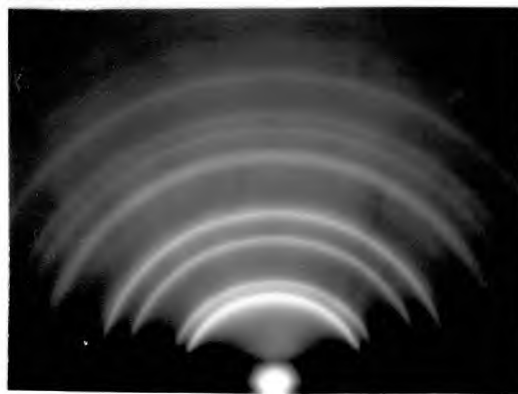


Fig. 86. 61,000 Å Ni at 600 mA/cm² on Cu (110), stirred bath, 50°C.

incident along the $[1\bar{1}0]$ direction of the copper (110) surface. The electrodeposit 30,000 Å thick at 600 mA/cm^2 after etching away the hydroxide shows only random polycrystalline nickel, with the disappearance of the remaining single-crystal structure which was seen at 20,000 Å. The same polycrystalline structure occurs also above 30,000 Å, at 600 mA/cm^2 (see Fig.86).

3.7. The Structure, Growth and Orientation of Nickel Electrodeposits on an Atomically Smooth Electropolished (111) Face of a Copper Single Crystal Substrate, from the Standard Nickel Sulphamate Solution at 50°C.

Figs. 9 and 10 show typical electron diffraction patterns illustrating the atomically smooth nature of the electropolished copper (111) face used as substrate.

The detailed electron diffraction investigation of the structure, growth and orientation of nickel electrodeposits was studied at thicknesses varying from a few hundred angstroms to 61,000 Å, over a wide range of c.d. from 10 to 600 mA/cm^2 . Two sets of results obtained on the unstirred and stirred baths are described below separately.

3.7.1. Nickel electrodeposits on the copper (111) face from the sulphamate bath at 50°C, when the bath was unstirred.

Fig.87 shows diagrammatically the results of the electron diffraction study. The single-crystal growth of nickel deposits parallel to the copper single-crystal substrate does not occur above 25,000 Å even at the lower c.d., unlike the preceding experimental results on the (100). Above 25,000 Å, the experimental results are more analogous to those on the polished polycrystalline copper substrates. The systematic change in the nickel orientation at a certain c.d. divides the diagram (Fig.87) into different regions as discussed below.

Sub-region I(A); Nickel mainly in a single crystal orientation, with axes parallel to those of the copper, with additional {111} twinning, a little randomly orientated nickel, and in some cases some one-degree (100) orientation.

The electron diffraction photographs in Figs. 90 to 94 are typical of the nickel electrodeposits on the (111) face of copper in this region (cf. Fig.87). This region extends up to about 600 mA/cm² or more, but beyond 280 mA/cm² extending up to less and less thickness, 2000 Å, 600 mA/cm².

At 10 mA/cm², 200 Å deposits show very smooth surfaced growth of nickel in single crystal orientations parallel to the copper crystal used as substrate.

The parallel growth is there accompanied by strong $\{111\}$ twinning on the surface (111) plane.

Fig. 90(a) obtained with the beam along the cube-face diagonal direction of the Cu (111) face corresponds to the centred $\sqrt{2}$ -rectangle spot arrangement similar to those in Fig. 6 from the cube-face, but with the rectangle diagonal normal to the shadow edge, together with the mirror symmetrical pattern due to the twin on the surface (111) plane only. Fig. 90(b) was obtained with the beam along a $\langle 211 \rangle$ direction, giving a $\sqrt{8/3}$ -rectangle spot pattern, with the $\sqrt{8/3}$ -side parallel to the shadow edge.

At 10,200 Å, the parallel growth shows strong $\{111\}$ twinning (all four twins) throughout the deposit, a little randomly oriented nickel and some close-packed hexagonal nickel (the only deposit throughout this work to show any, cf. Fig.91).

At above 10 mA/cm², up to about 250 mA/cm², the parallel growth of the nickel, with a little random orientation, is accompanied by very strong $\{111\}$ twinning (on all four octahedral planes) even at a few hundred angstroms deposit thickness (see Fig.92). Below 200 mA/cm², the strong $\{111\}$ twinning persists even up to 10,000 Å or more. At 200 mA/cm², the $\{111\}$ twinning is small in amount at around 10,000 Å. Roughly below 280 mA/cm², an additional one-degree (100) orientation sets in around 1,000 Å and becomes stronger with increasing deposit thickness (see Fig.93).

The nickel deposits follow single-crystal structure to a maximum thickness of about 25,000 Å and 20,000 Å at 10 mA/cm² and 280 mA/cm² respectively. Beyond 280 mA/cm², the parallel growth of nickel, with some additional random orientation, has a little {111} twinning (see Fig.94). Here, the upper limit of the deposit thickness showing single-crystal structure decreases with increase in c.d., and is reduced to about 1,500 Å at 600 mA/cm². The diffraction patterns from the deposits (of the order of a few thousand angstroms thick) between about 250 and 600 mA/cm² are similar to those in Fig. 94.

Sub-region I(B); Nickel mainly in one-degree (100) orientation with varying amount of {111} twinning.

An electron diffraction photograph corresponding to this region is shown in Fig. 95. The one-degree (100) orientation of nickel already developed in the region I(A) is here no longer accompanied by any parallel growth single-crystal orientation. Beyond 25,000 Å only strong one-degree (100) orientation is seen, with varying amount of {111} twinning, or (111) orientation, depending on the c.d. at around 30,000 Å. The arcs indicating either one-degree (111) orientation or most probably {111} twinning are more pronounced towards the lower c.d. side. With further increase in deposit thickness, only very strong (100) orientation exists, together with a trace of its octahedral twins (see Fig.95).

In Fig. 95, which is a diffraction pattern from a thicker deposit (61,000 Å), the two arcs on the 111 ring position, one on each side of, and close to, the plane of incidence, are seen clearly resolved, whereas at 30,000 Å those arcs are not resolved, which gives an impression of one-degree (111) orientation due to coalescing of the two arcs.

Sub-region II(A); Nickel in a single-crystal orientation with axes parallel to those of the copper substrate crystal, with small traces of nickel in one-degree (110) orientation and increasing proportion of random and a little {111} twinning.

Fig. 96 is typical of nickel electrodeposit in this region, which lies below about 19,000 Å and above 280 mA/cm² on the left of the broken line in Fig. 87. The single-crystal growth of nickel parallel to the copper crystal lattice is accompanied by a small amount of {111} twinning, minute traces of one-degree (110) orientation, and much random orientation (see Fig. 96). With increase in deposit thickness the amount of single-crystal structure decreases, whereas that of random nickel increases. This region starts at about 280 mA/cm². After 450 mA/cm², there is a sharp decrease in the upper limit of the deposit thickness in this region as shown by the broken line in Fig. 87.

Sub-region II(B); Nickel crystals in one-degree (110) and (210) orientations.

Figs. 97 and 98 are typical of this region, which starts above 19,000 A and extends between 290 and 410 mA/cm². Here only two orientations, that is one-degree (110) and (210) are developed. The (110) orientation is more pronounced in almost all the cases (see Figs. 97 and 98) except one at 20,000 A and 300 mA/cm².

Region III; Nickel deposit surface covered with hydroxide.

The region III lying on the right hand side of the broken line in Fig.87 is a region where evolution of gas during electrodeposition resulted in co-deposition of hydroxide on the deposit surface. The hydroxide-coated surface showed a diffuse ring pattern (cf. Fig.35). The surface hydroxide was etched away in dil. 5% H₂SO₄ for 15-20 seconds. The underlying metal surface then showed the f.c.cubic nickel structure on examination by electron diffraction. Here, the amount of single-crystal growth of nickel decreases with increase in deposit thickness, but the amount of randomly oriented nickel increases. The complete random polycrystalline state is reached at earlier thicknesses at higher c.d. than at lower c.d. The gradual transition of the structure from one form to the other leads to the three sub-divisions of this region, which are described below separately.

Sub-region III(A); After etching away the hydroxide, nickel in a small amount of single crystal structure showing minute traces of one-degree (110) and (210) orientations but with increasing proportion of random.

Fig. 99 shows a typical pattern from the nickel deposits after etching away the hydroxide layer. In this region (Fig.87) the nickel has partly a single crystal structure up to a maximum of about 16,000 Å, gradually decreasing in amount. This is accompanied with increasing proportion of random nickel plus some one-degree (110) and (210) orientations, as the deposit thickness is increased.

Sub-region III(B); Nickel showing one-degree (110) and (210) orientations after etching away the hydroxide layer.

This is a very narrow sub-region almost triangular in shape between sub-regions III(A) and III(C) (see Fig.87). In this sub-region, the underlying nickel surface after removing the hydroxide layer shows one-degree (110) and (210) orientations, as shown in Fig.100. The (110) orientation is present in larger proportion than (210).

sub-region III(C); Nickel showing only random orientation after etching away the surface hydroxide layer.

This sub-region starts at about 420 mA/cm^2 at a thickness of 30,000 Å, and extends to higher thicknesses (cf. Fig.87). At higher c.d. the lower limit of thickness slopes down. In this region the electrodeposits

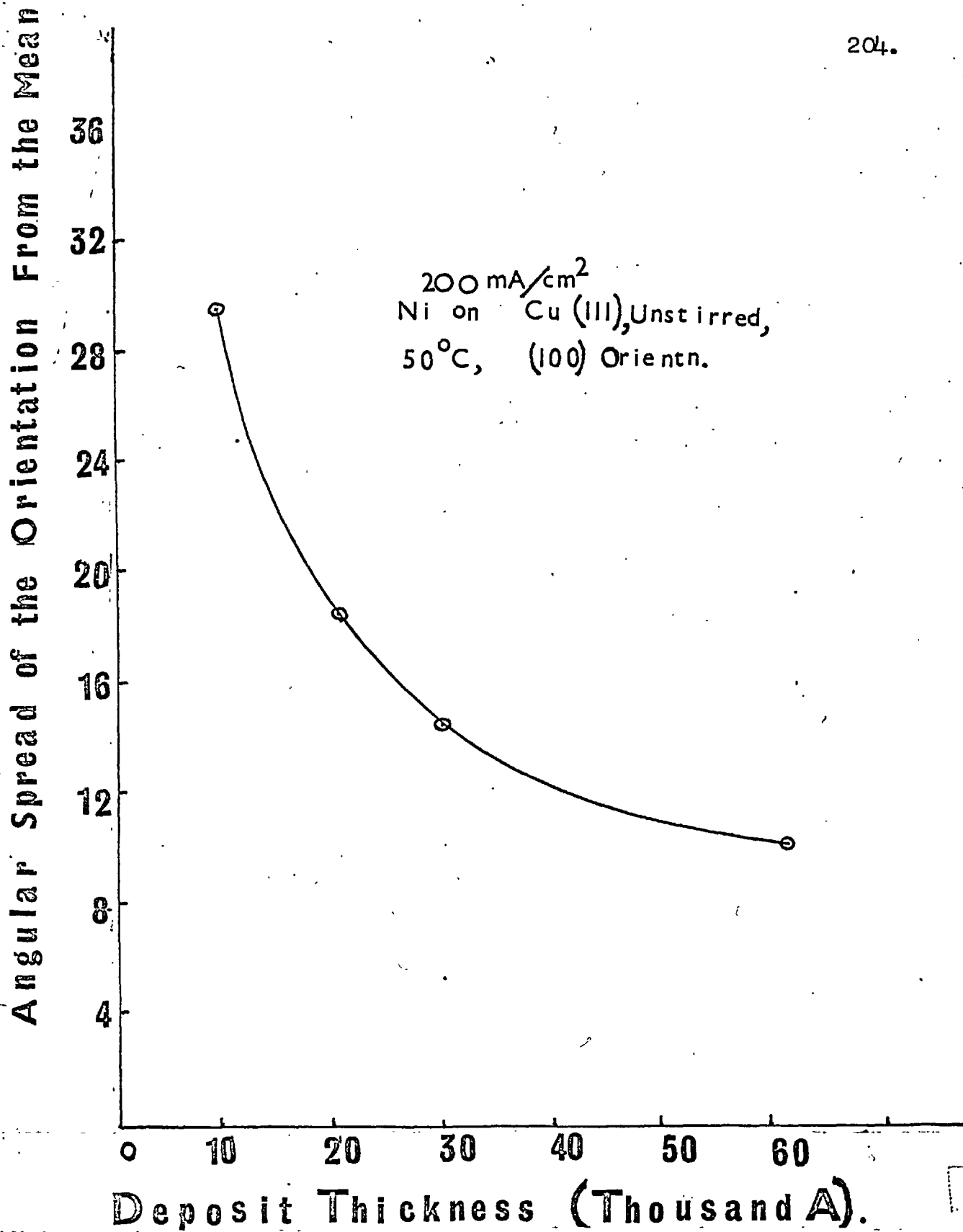


Fig. 88.

Angular Spread of the Orientation From the Mean.

36

32

28

24

20

16

12

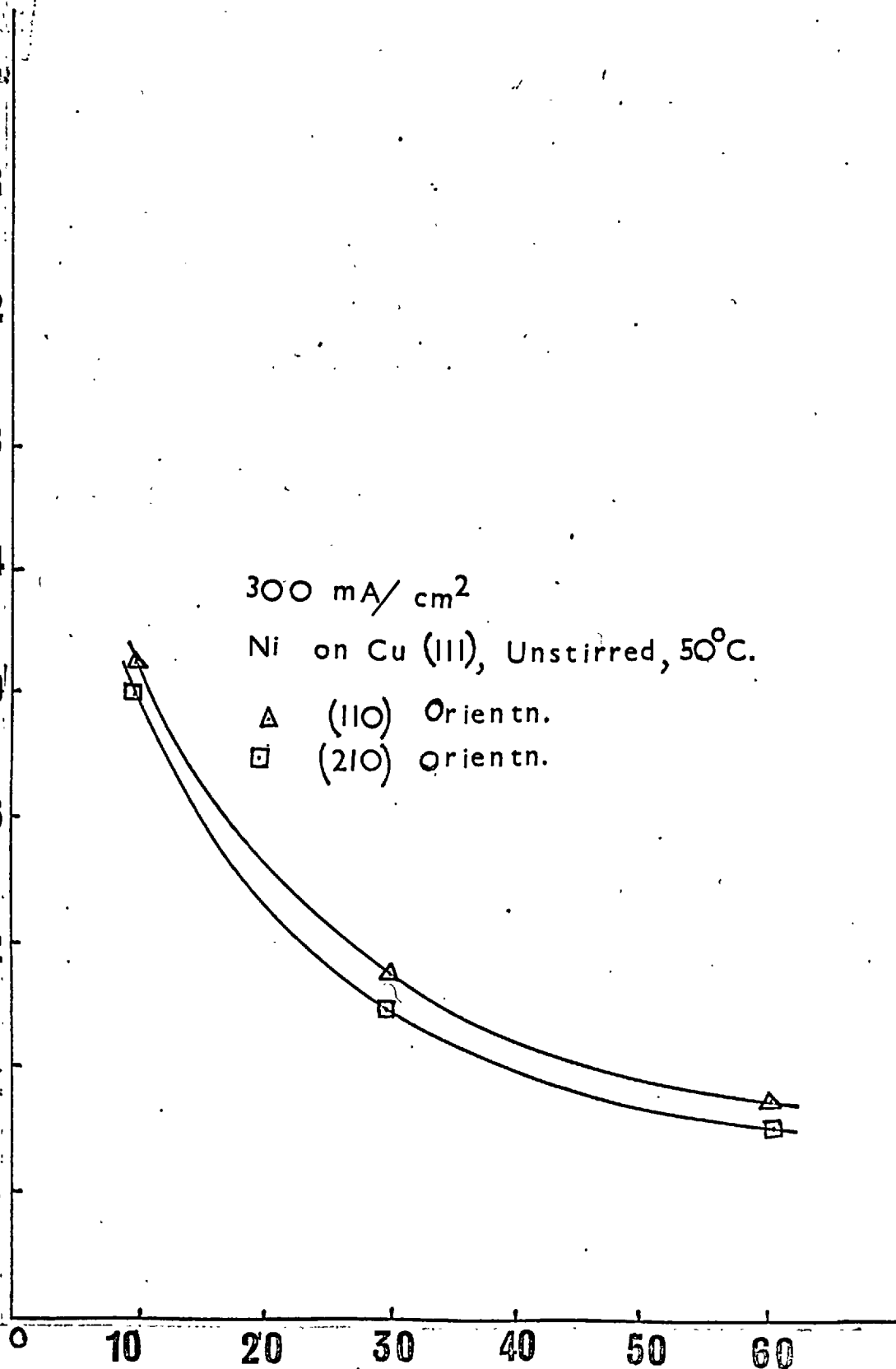
8

4

 300 mA/cm^2 Ni on Cu (III), Unstirred, 50°C . Δ (110) Orientn. $\square$ (210) Orientn.

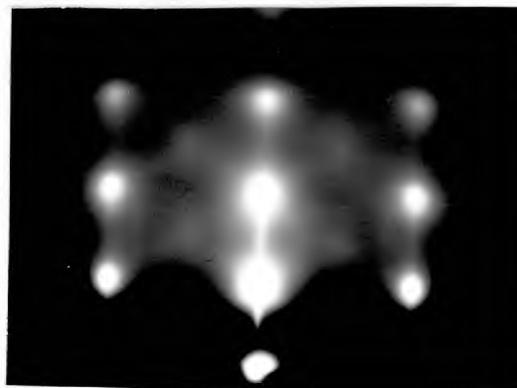
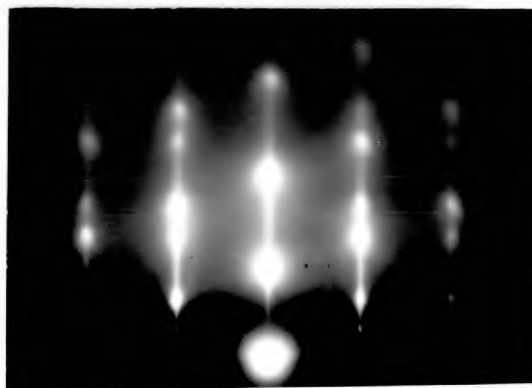
Deposit Thickness (Thousand Å).

Fig. 89



REGION I(A) OF FIG. 87.

(Cu (111), unstirred bath, 50°C)



(a)

(b)

Fig. 90. 200 Å Ni at 10 mA/cm² on Cu (111), unstirred bath, 50°C.

(a) Beam along cube-face diagonal

(b) Beam along $\langle 211 \rangle$

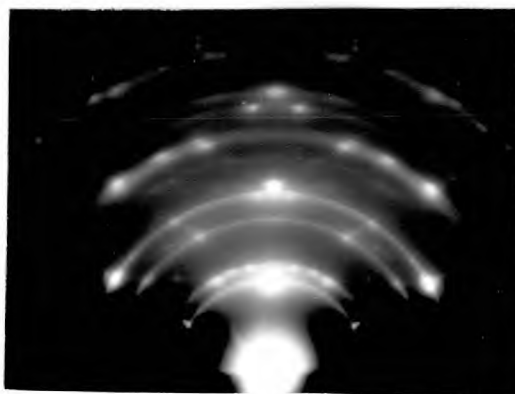
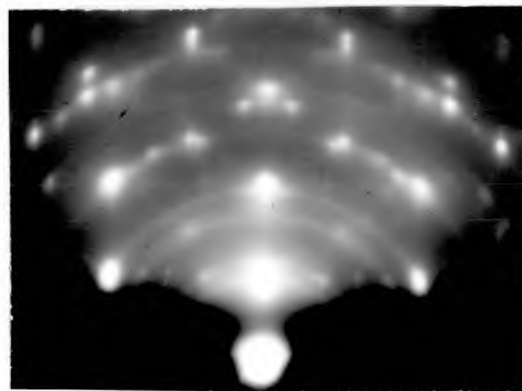
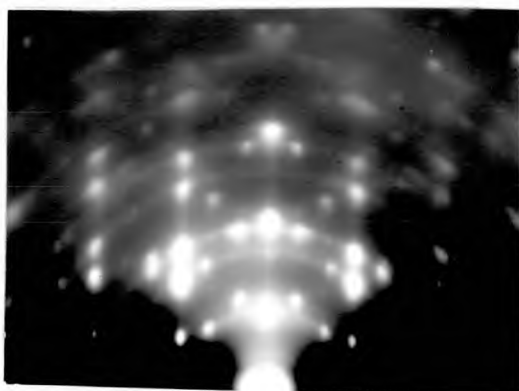


Fig. 91. 10,200 Å Ni at 10 mA/cm² on Cu (111), unstirred bath, 50°C.

REGION I(A) OF FIG. 87.

(Cu (111), unstirred bath, 50°C).

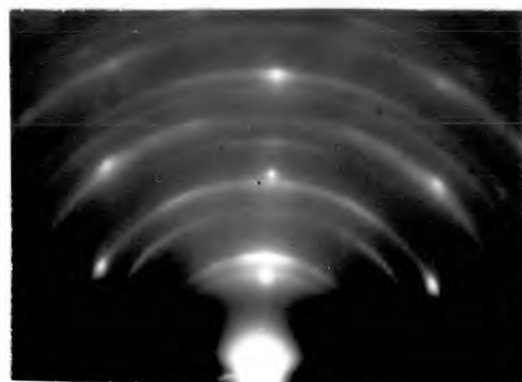
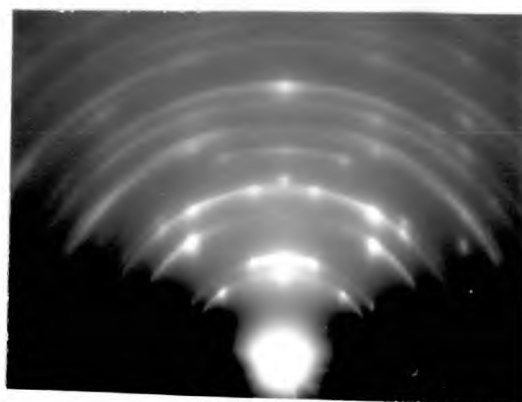


(a)

(b)

Fig. 92. 200 Å Ni at 100 mA/cm² on Cu (111), unstirred bath 50°C.

(a) Beam along cube-face diagonal.

(b) Beam along $\langle 211 \rangle$ 

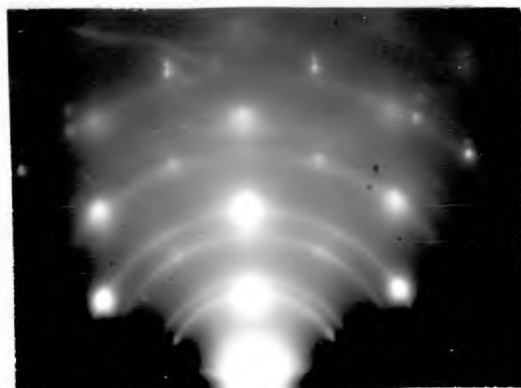
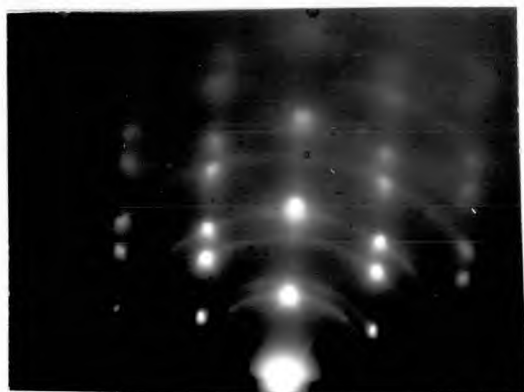
(a)

(b)

Fig. 93. 10,200 Å Ni at 100 mA/cm² on Cu (111), unstirred bath, 50°C.

REGION I(A) OF FIG. 87.

(Cu (111), unstirred bath, 50°C).



(a)

(b)

Fig. 94. 600 Å Ni at 400 mA/cm² on Cu (111), unstirred bath, 50°C.

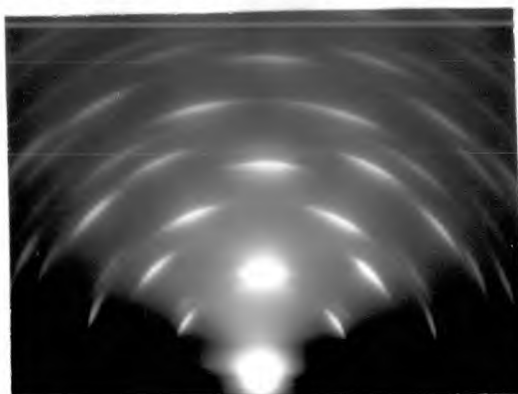
(a) Beam along $\langle 110 \rangle$ (b) Beam along $\langle 211 \rangle$ REGION I(B) OF FIG. 87.

Fig. 95. 61,000 Å Ni at 100 mA/cm² on Cu (111), unstirred bath, 50°C.

REGION II(A) OF FIG. 87.

(Cu (111), unstirred bath, 50°C).

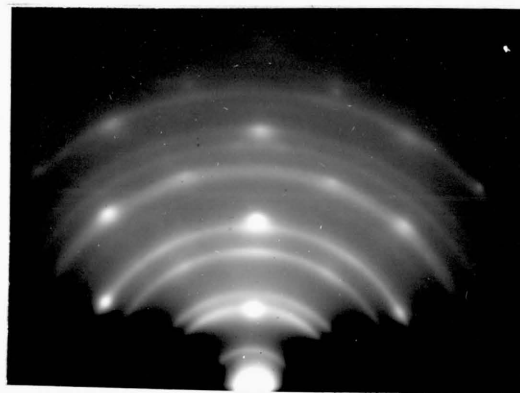


Fig.96. 13,600 Å Ni at 400 mA/cm² on Cu (111),
unstirred bath, 50°C.

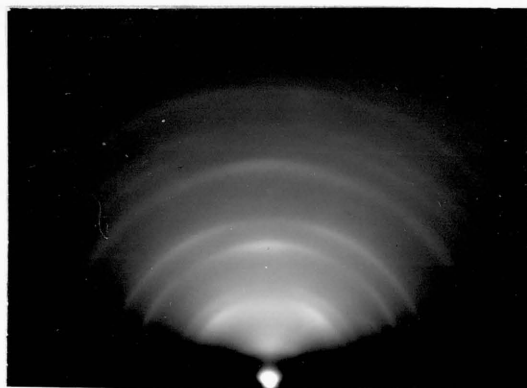
REGION II(B) OF FIG. 87.

Fig.97.

21,300 Å Ni at 400 mA/cm²
on Cu (111), unstirred
bath, 50°C.

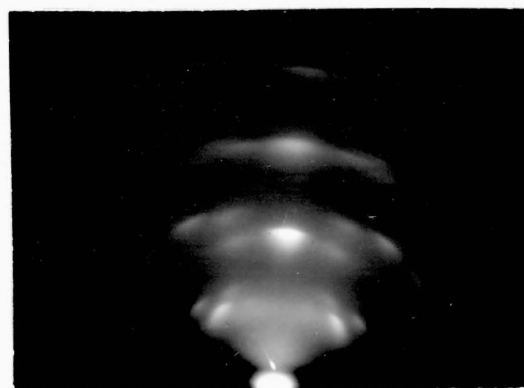


Fig.98.

51,000 Å Ni at 300 mA/cm²
on Cu (111), unstirred
bath, 50°C.

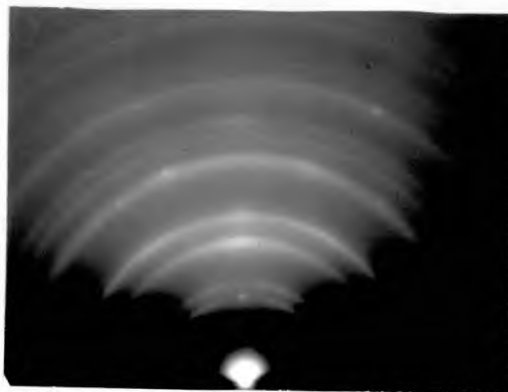
REGION III(A) OF FIG. 87.

Fig.99. 10,200Å Ni at 500 mA/cm^2 on Cu(111), unstirred bath, 50°C

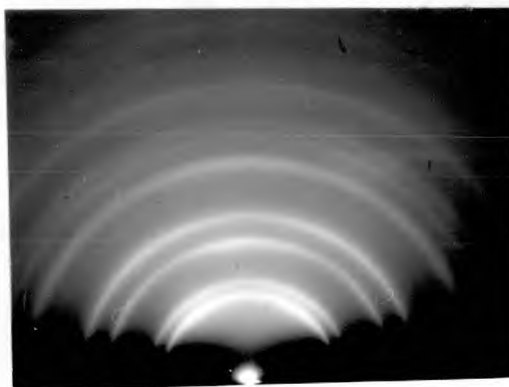
REGION III(B) OF FIG. 87.

Fig.100. 22,400Å Ni at 450 mA/cm^2 on Cu(111), unstirred bath, 50°C

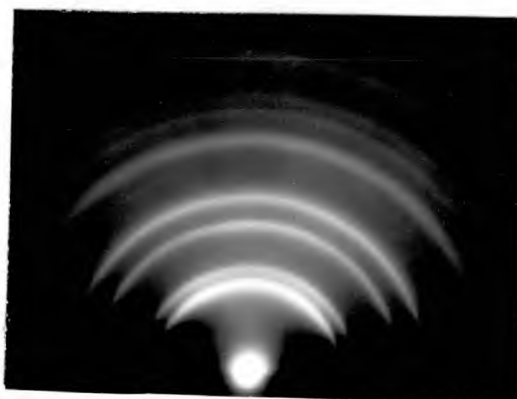
REGION III(C) OF FIG. 87.

Fig.101. 30,600 Å Ni at 500 mA/cm^2 on Cu (111), unstirred bath, 50°C .

investigated up to 61,000 Å all show randomly oriented nickel (see Fig.101)

3.7.2. Nickel deposits on Cu(111) from the sulphamate bath at 50°C when the bath was stirred vigorously.

Fig.102 shows diagrammatically the electron diffraction results on growth and structure of nickel electrodeposits on the (111) face of the copper single crystal substrate. The results clearly divide the whole diagram into two regions I and II as discussed below separately.

Region I; Nickel showing parallel single-crystal growth in decreasing proportion with increase in thickness, and changing to strong one-degree (100) orientation.

Fig.104 shows the typical diffraction photographs of nickel deposits in this region (see Fig.102), which goes up to about 480 mA/cm², whereas in the unstirred bath it was limited to up to 280 mA/cm² only. The trend of the results shows that the parallel growth of the nickel probably cannot go beyond 30,000 Å even at a few mA/cm². The one-degree (100) orientation *must* have started already, though there is no result available below 30,000 Å in this region. At 30,600 Å, the one-degree (100) orientation occurs alone without any additional orientation, except traces of {111} twinning. The arcs on the 200 ring position, from the

(100)-oriented nickel, shows increasing refraction towards the shadow edge with increasing deposit thickness (see Fig. 104).

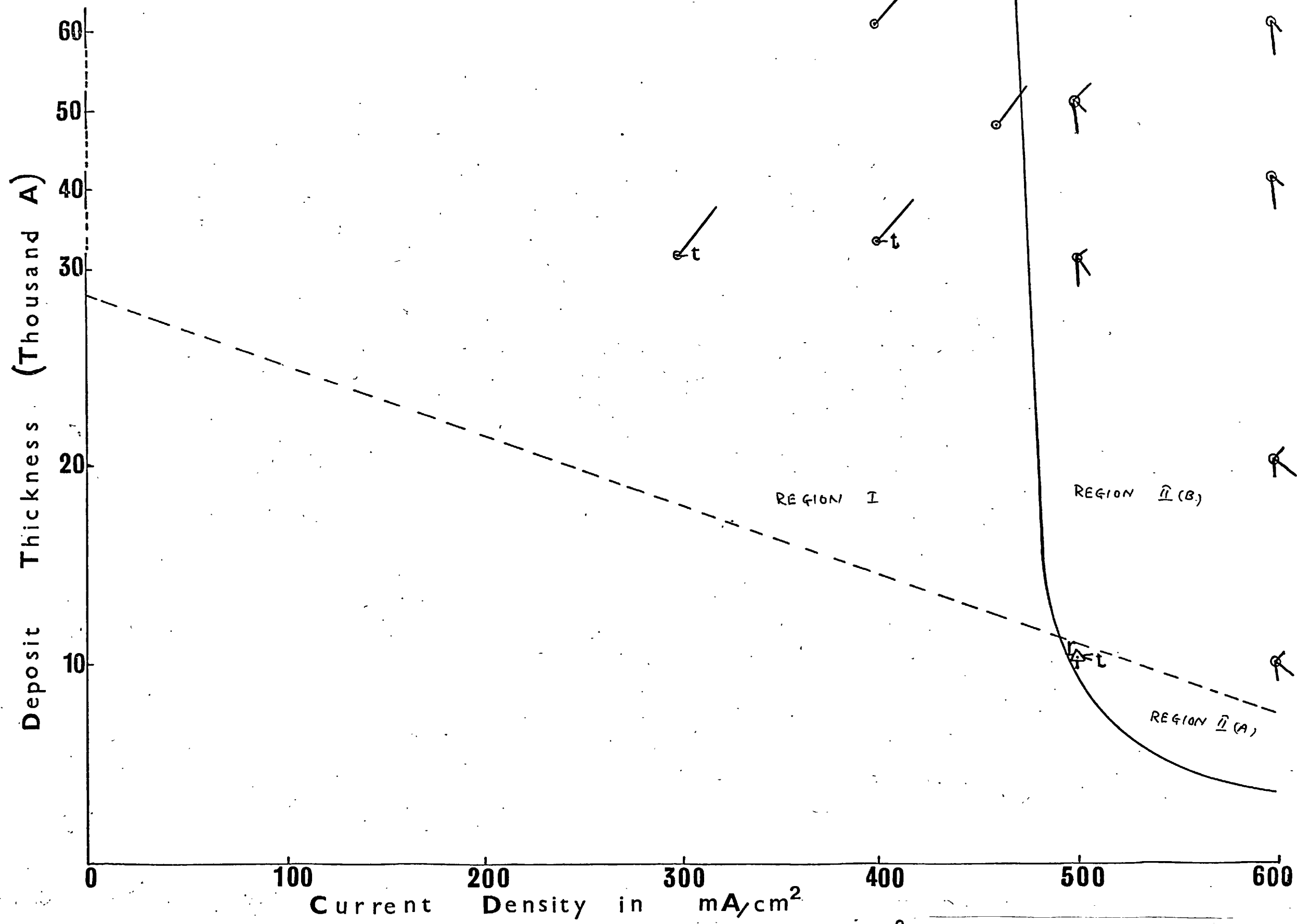
Sub-region II(A); Nickel in parallel growth to the substrate with small amounts of $\{111\}$ twinning, random, and one-degree (110) and (210) respectively.

Fig.105 shows the pattern from a deposit in this region, which is a very small region lying in between 480 and 600 mA/cm² or more, and represents a region of thickness of nearly 5,000 Å (cf. Fig.102). Fig.105 shows that the single-crystal growth of nickel parallel to the substrate crystal is accompanied by some $\{111\}$ twinning, one-degree (110) and (210) orientations and randomly oriented nickel.

Sub-region II(B); Nickel mainly in one-degree (210) and (110) orientations, with additional small amount of one-degree (100) in some cases.

Figs. 106 and 107 show the typical patterns from deposits in this region (cf. Fig.102). Though the present investigation goes up to the 600 mA/cm² and 61,000 Å, this sub-region starts from 480 mA/cm² and presumably extends to c.d. and thickness higher than 600 mA/cm² and 61,000 Å.

At 500 mA/cm², the nickel deposits 30,600 and 61,000 Å thick yield diffraction patterns consisting of one-degree (100), (110) and (210) orientations as shown in fig.106. Similar patterns were obtained at 600 mA/cm² and 10,000 and 20,000 Å.



Ni on Cu (III) , Stirred, 50°C . For symbols see page 130(A).

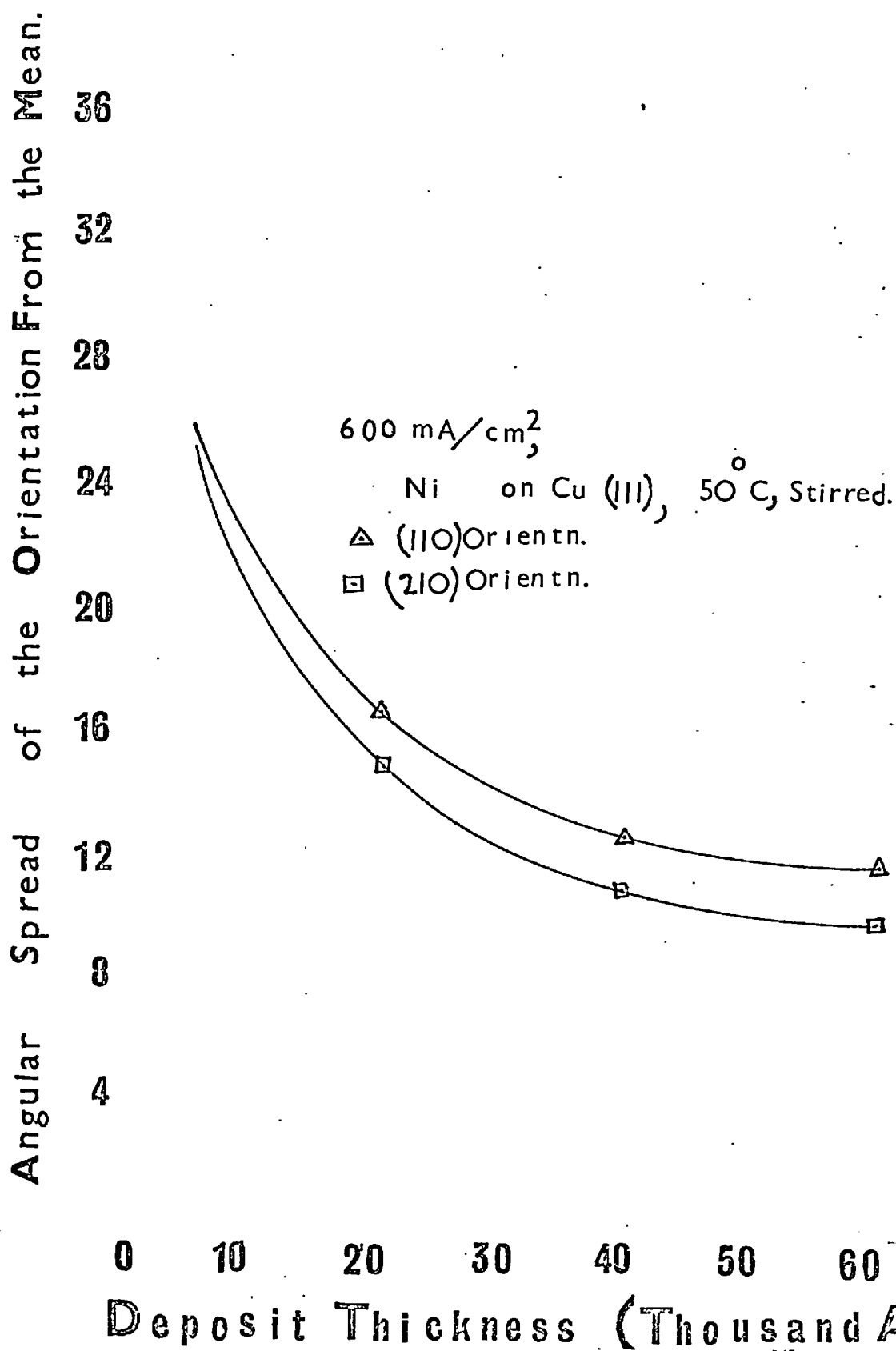


Fig. 103.

REGION I OF FIG. 102.

(Cu(111) stirred bath, 50°C)

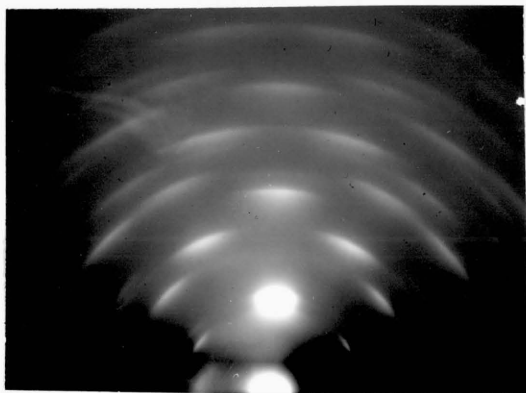


Fig. 104

61,200 Å Ni at 400 mA/cm²
on Cu (111), stirred bath,
50°C.

REGION II(A) OF FIG. 102.

(Cu(111) stirred bath, 50°C)

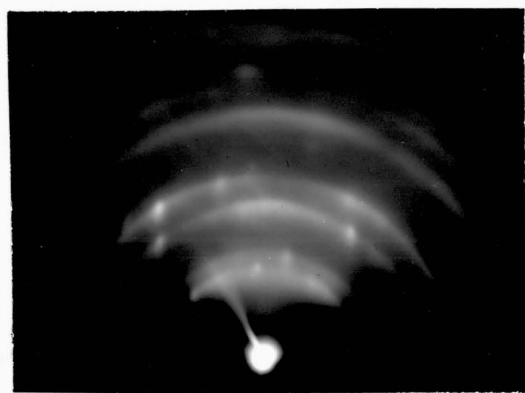


Fig. 105

10,200 Å Ni at 500 mA/cm²
on Cu (111), stirred bath,
50°C.

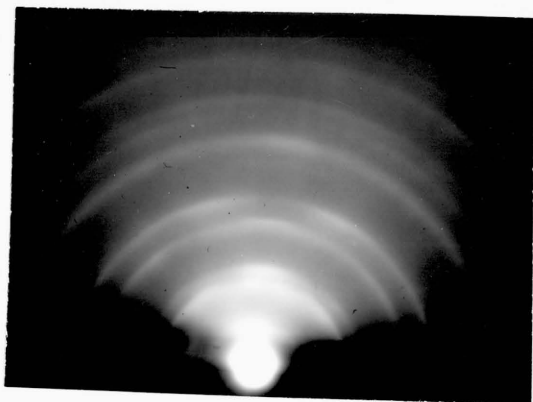
REGION II (B) OF FIG. 102.

Fig. 106

20,400 Å Ni at 600 mA/cm²
on Cu (111), stirred bath
50°C.

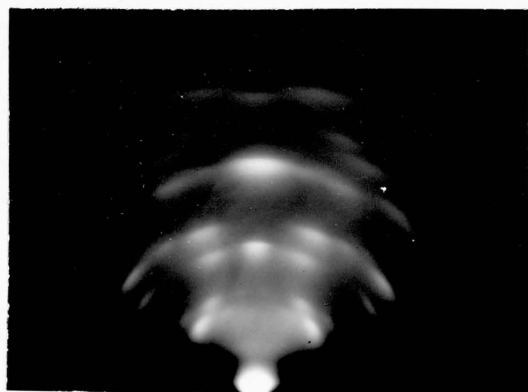


Fig. 107.

61,200 Å Ni at 600 mA/cm²
on Cu (111), stirred bath
50°C.

At 600 mA/cm^2 and above about $30,000 \text{ A}$, the nickel deposit crystals show one-degree (110) and (210) orientations, the (210) being stronger than the (110), as in Fig.107. These results indicate that roughly above 550 mA/cm^2 and $30,000 \text{ A}$, only two orientations, one-degree (110) and (210) occur instead of three ((100), (110) and (210)).

3.8. The structure, growth and orientation of nickel electrodeposits on mechanically polished polycrystalline copper substrates from the standard nickel sulphamate solution at room temperature ($\approx 20^\circ\text{C}$).

3.8(i). Nickel electrodeposits from the sulphamate bath at room temperature ($\approx 20^\circ\text{C}$) when the bath is unstirred.

Fig.108 shows the electron diffraction results on the structure, growth and orientation of nickel electrodeposits under these conditions. On the basis of the results obtained, the whole diagram has been divided into three regions. Each of them is discussed in the subsequent paragraphs. Fig.109 shows the variation of the spread of arcs of one-degree (100) and (210) orientations with deposit thickness. The nature of the curves obtained is analogous to those of the curves at 50°C . (cf. Fig.20).

Region I; Nickel mainly in (100) orientation with and without twinning, or one-degree (111) orientation.

Figs. 110 and 111 are typical photographs showing the results in region I (cf. Fig.108). Extending from 1 to 40 mA/cm², there is mainly one-degree (100) orientation with a trace of {111} twinning, or of one-degree (111), up to 60,000 Å deposit thickness studied. The trace of one-degree (210) orientation is present in a few cases near the boundary of the transition from region I to region II. The small trace of (210) might be attributed to the edge effect where the current density is considered to be higher than the inner part of the deposit surface.

At 10 mA/cm² and 500 Å, the deposit surface regions shows one-degree (100) orientation of the nickel crystal (see Fig.110). With increase in the deposit thickness, the angular spread of the arc showing (100) orientation decreases (cf. Fig.109). At 34,000 Å, the (100)orientation is very strong with some {111} twinning (see Fig.111).

Region II; Nickel in (110) and (210) orientations.

Figs. 112 and 113 show the characteristic diffraction photographs from the deposit in region II (see Fig.108). This region lies mainly between 40 mA/cm² and 90 mA/cm², with some narrowing of the region with increasing thickness. Up to a few thousand angstroms of

deposit thickness, one-degree (110) and (210) orientations are present in almost equal but small amount, in addition to much randomly oriented nickel (see Fig.112). Beyond a deposit thickness of a few thousand angstroms both the orientations become more and more pronounced (see Fig. 108) until at 10,000 Å practically all the nickel is so oriented with a spread of $\pm 25^\circ$ from the mean for the (110) and $\pm 12^\circ$ for the (210) orientation. Above 25,000 Å, the one-degree (110) orientation is nearly equal to, or slightly stronger than the (210), (see Fig.113); but above 40,000 Å, the (210) orientation is very much stronger than (110), even towards the lower c.d. side, i.e. around 50 mA/cm². Starting from about 10,000 Å thickness, the patterns from the (210)- or (110)- oriented nickel show more and more refraction from smooth crystal faces parallel to the substrate, with increasing thickness.

Region III; Nickel deposits showing a surface hydroxide layer.

This is a region (cf Fig.108) where evolution of gases (hydrogen and oxygen) was observed, and the surface of the deposits was coated with a rough greenish deposit, probably nickel hydroxide. This region starts around about 90 mA/cm² and extends to higher c.d.'s. It occurs on the right hand side of the broken line in Fig.108. The hydroxide-coated surface gave a diffuse pattern unlike nickel.

But when the hydroxide was etched in 5% dilute H_2SO_4 for 15-20 seconds, the underlying metallic surface gave a f.c.cubic nickel pattern as discussed below.

Sub-region III(A); Nickel in (110) and (210) orientations below the surface hydroxide.

Fig.114 shows an electron diffraction photograph typical of the nickel electrodeposits in this region (cf. Fig.108). Here, the two orientations (210) and (110) are either equal in amount or probably (110) orientation is slightly more in proportion than (210) (see Fig.114). This region extends roughly up to 30,000 Å at 100 mA/cm².

Sub-region III(B); Nickel showing random orientation below the hydroxide layer.

Fig.115, showing only a ring pattern, indicated that the nickel crystals are randomly oriented. At 100 mA/cm², this region starts above 30,000 Å (see Fig.108).

7.8(ii). Nickel electrodeposits from sulphamate bath at room temperature ($\approx 20^\circ\text{C}$), when the bath is stirred vigorously.

Fig.116 shows diagrammatically the structure, growth and orientation of nickel electrodeposits under these conditions. The results are grouped into three main regions, as for the unstirred bath. The stirring has increased the upper limits of c.d. for both regions I and II by nearly 50% and 20% respectively.

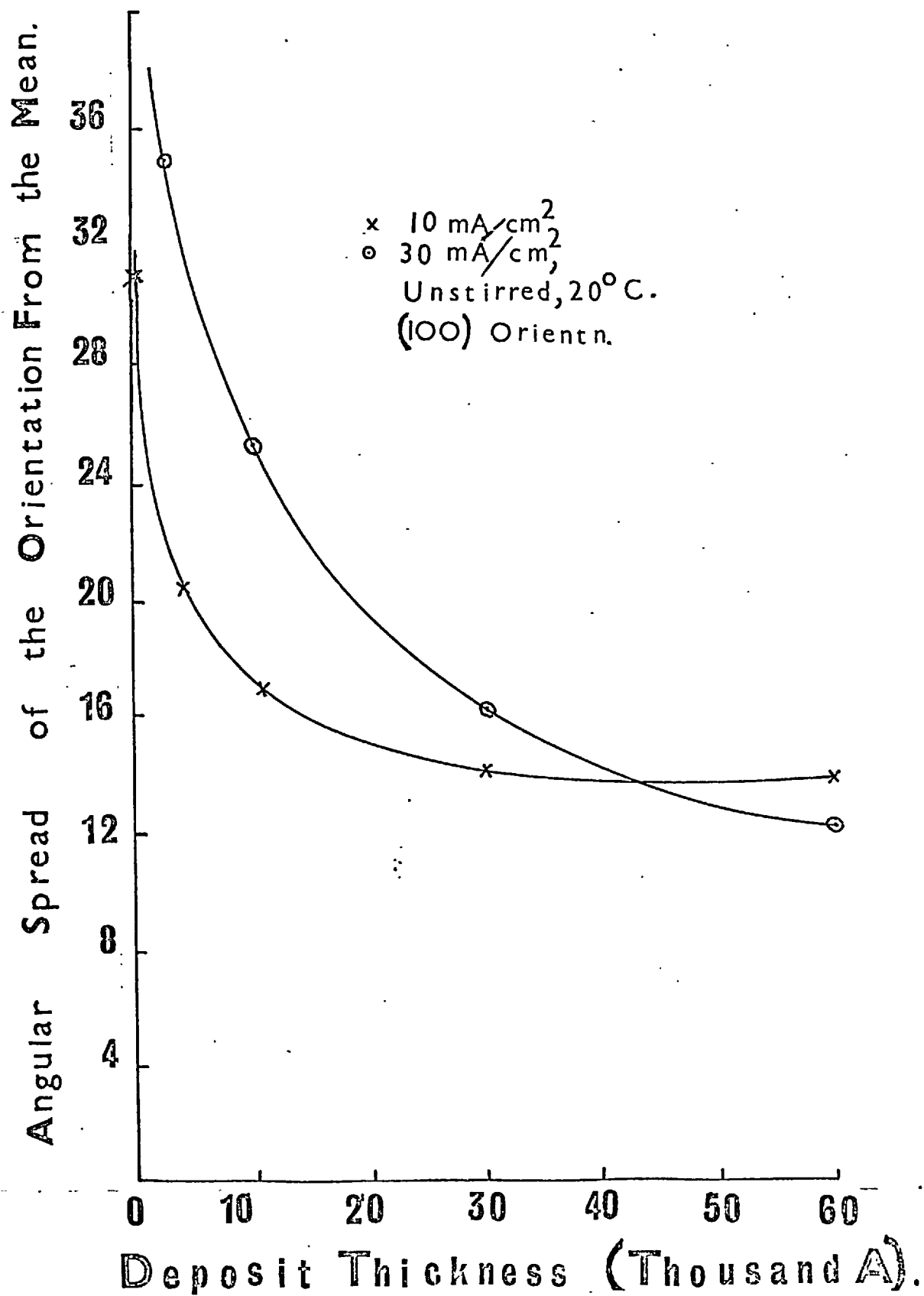


Fig. 109. (a).

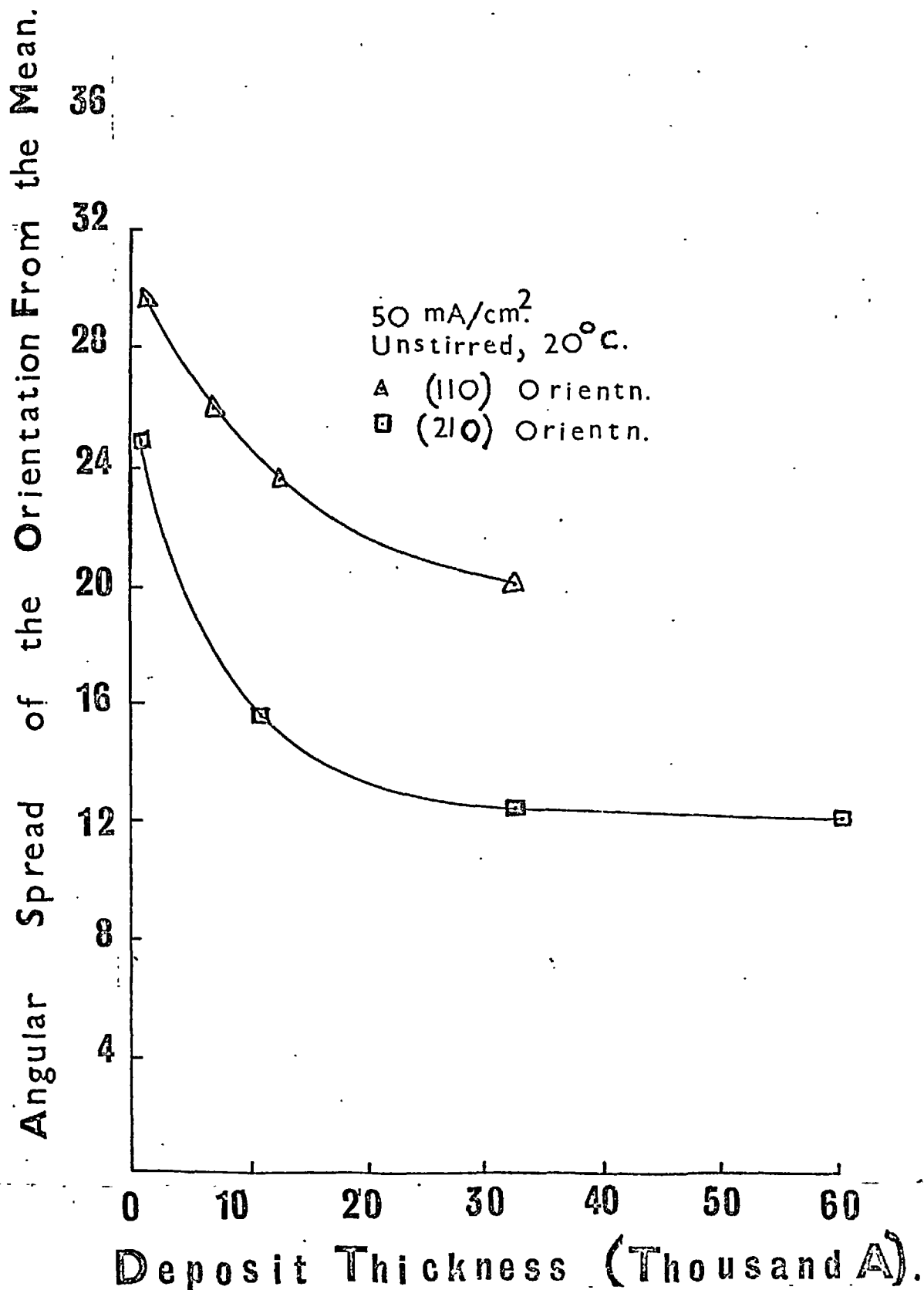


Fig. 109 (b)

REGION I OF FIG. 108.

(Polished polycrystalline Cu, unstirred bath, 20°C).

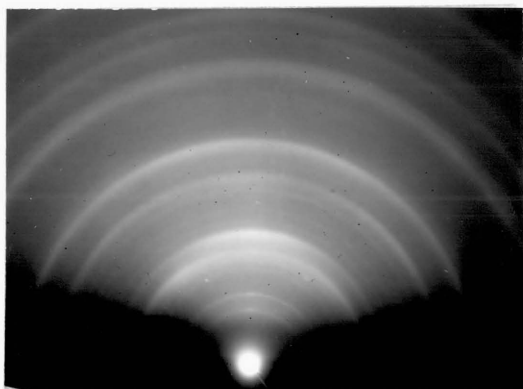


Fig. 110

570 Å Ni at 10 mA/cm²
on polished polycrystalline
Cu, unstirred bath, 20°C.

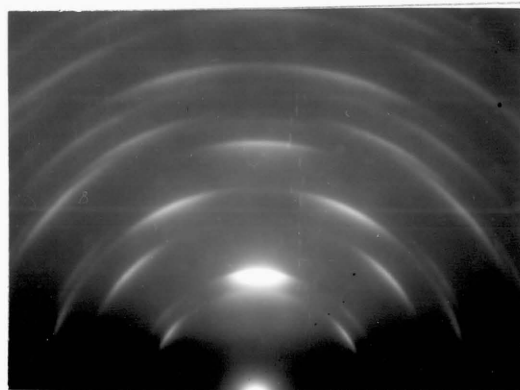


Fig. 111

34,000 Å Ni at 10 mA/cm²
on polished polycrystalline
Cu, unstirred bath, 20°C.

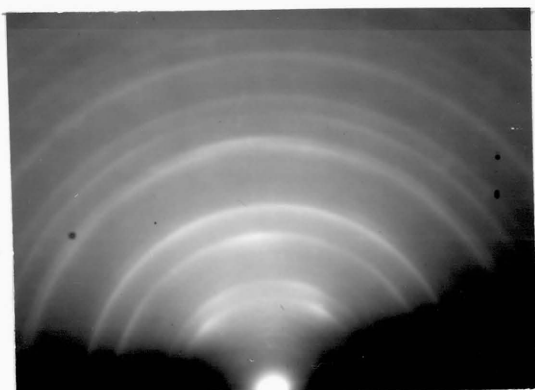
REGION II OF FIG. 108.

Fig. 112

675 Å Ni at 75 mA/cm² on
polished polycrystalline
Cu, unstirred bath, 20°C.

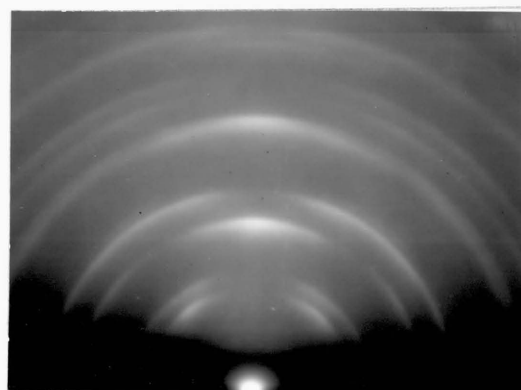


Fig. 113

32,000 Å Ni at 50 mA/cm² on
polished polycrystalline
Cu, unstirred bath, 20°C.

REGION III(A) OF FIG. 108.

(Polycrystalline Cu, unstirred bath, 20°C)

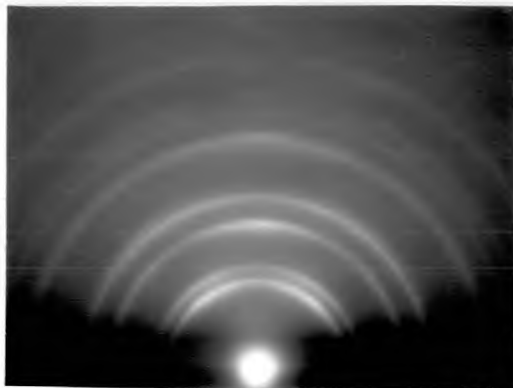


Fig.114.

20,700 Å Ni at 100 mA/cm² on polished polycrystalline Cu,
unstirred bath, 20°C.

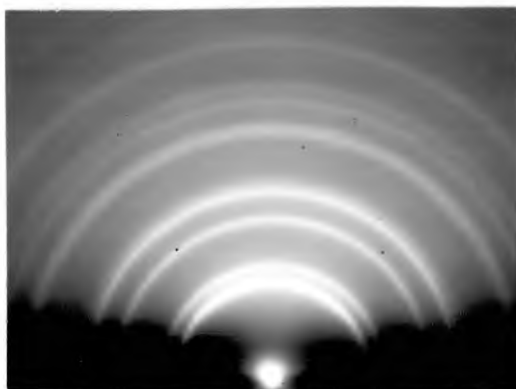
REGION III(B) OF FIG. 108.

Fig.115.

50,800 Å Ni at 75 mA/cm² on polished polycrystalline Cu,
unstirred bath, 20°C.

Region I: Nickel mainly in (100) orientation with small or much {111} twinning.

Fig.117 is an electron diffraction pattern of the characteristic structure of nickel electrodeposits in region I (cf. Fig.116). The approximate demarcation separating region I from II is around 60 mA/cm^2 . In region I, the deposit surface is very bright in most cases. It shows one-degree (100) orientation with trace of {111} twinning. However, near the boundary region of region II, a trace of some one-degree (210) is also observed, together with the main (100) orientation. That the trace of (210) orientation along with the strong (100), arises due to the higher c.d. near the edges of the specimen is supported by the presence of strong (210) orientation in the adjoining region II.

Region II; Nickel in (110) and (210) orientations.

Figs. 118 and 119 show how the nickel crystals are oriented in the electrodeposits within this region. One-degree (210) orientation always accompanies (110) (cf. Figs. 118 and 119). With increasing deposit thicknesses, (210) orientation becomes more prominent, and the diffraction arcs show some refraction normal to the shadow edge, indicating relatively smooth faces parallel to the substrate. At about $51,000 \text{ A}$, the (110) orientation becomes almost negligible in amount compared to the strong (210) orientation (see Fig.119).

Region III; Nickel deposits showing a surface hydroxide layer.

The broken line in Fig.116 separates region II from III at about 110 mA/cm^2 . During electrodeposition above 110 mA/cm^2 , there was evolution of gases leading to co-deposition of nickel hydroxide with the nickel. The hydroxide was removed by etching it away in 5% dilute H_2SO_4 for 15-20 seconds. The underlying metallic surface showed the characteristic nickel diffraction pattern, as described in the following two sub-regions.

Sub-region III(A); Nickel in (110) and (210) orientations below the surface hydroxide.

Fig.120 shows the typical structure of nickel electrodeposits in this region (cf. Fig.116). Though the pattern shows clear rings, due to nickel deposit mostly polycrystalline, still there are very faint traces of one-degree (110) and (210) orientations (see Fig.120). These faint traces are less prominent with increasing deposit thickness.

Sub-region III(B); Nickel in random orientation below the surface hydroxide.

Fig.121 shows the typical electron diffraction pattern of the electrodeposit in sub-region III(B) (cf. Fig. 116). At 120 mA/cm^2 this region starts beyond 17,000 Å. The ring pattern obtained from all the deposits in this region shows that the nickel crystals are randomly oriented.

REGION I OF FIG. 116.

(Polished polycrystalline Cu, stirred bath, 20°C).

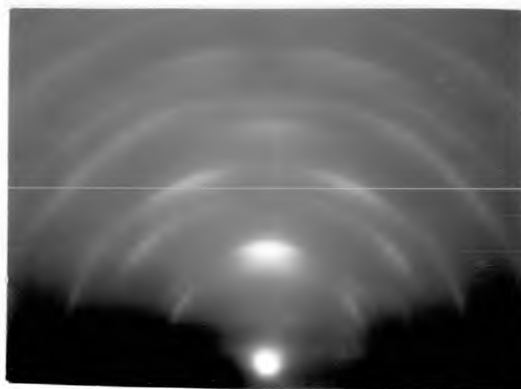


Fig.117

32,400 Å Ni at 50 mA/cm² on polished polycrystalline Cu, stirred bath, 20°C.

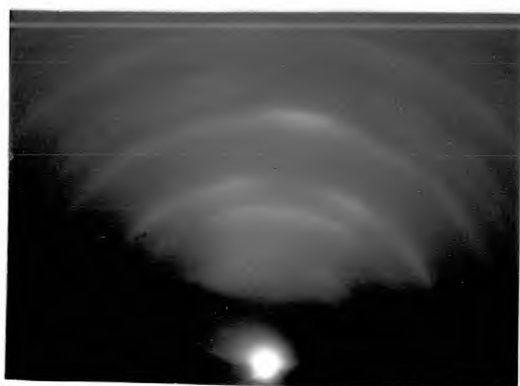
REGION II OF FIG. 116.

Fig.118.

10,200 Å Ni at 75 mA/cm²
on polished
polycrystalline Cu,
stirred bath, 20°C.

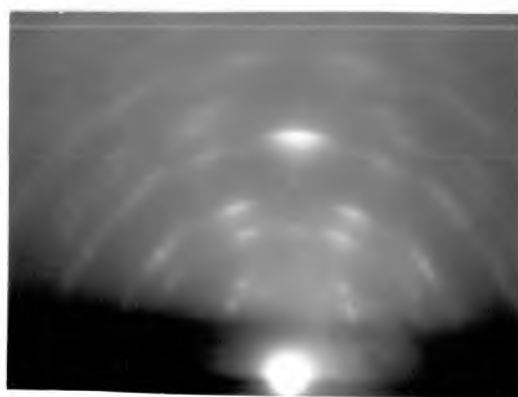


Fig.119.

50,600 Å Ni at 100 mA/cm²
on polished
polycrystalline Cu,
stirred bath, 20°C.

REGION III(A) OF FIG. 116.

(Polished polycrystalline Cu, stirred bath, 20°C).

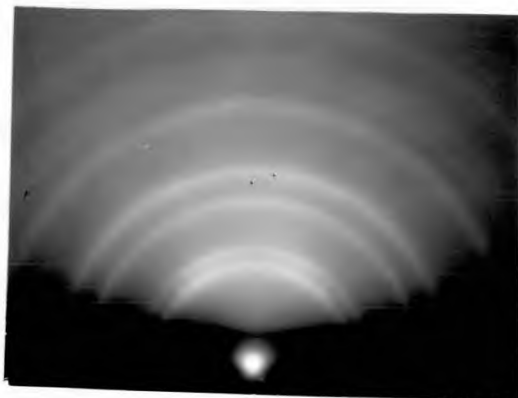


Fig.120.

400 Å Ni at 150 mA/cm² on polished polycrystalline Cu,
stirred bath, 20°C.

REGION III(B) OF FIG. 116.

Fig.121.

31,500 Å Ni at 130 mA/cm² on polished polycrystalline Cu,
stirred bath, 20°C.

3.9. The Structure, Growth and Orientation of Nickel Electrodeposits on an Atomically Smooth Electropolished (100) Face of Copper Single Crystal Substrate, from Standard Nickel Sulphamate Solution at Room Temperature ($\approx 20^{\circ}\text{C}$), with the Bath Unstirred.

Fig.122 shows diagrammatically the experimental results. The present electron diffraction study of nickel electrodeposits on the (100) face of the copper single crystal at room temperature extends up to 140 mA/cm^2 . The results are comparable to those at 50°C , but it appears that the upper limit of c.d. giving smooth parallel single-crystal growth has been reduced to around 105 mA/cm^2 instead of the 250 mA/cm^2 observed at 50°C . Above 105 mA/cm^2 the deposit surfaces are covered with greenish rough deposits of hydroxide and with the underlying nickel showing an increasing amount of random orientation with increasing thickness or c.d. The whole diagram has been divided into two regions.

Region I; Nickel in parallel single crystal growth to the copper single crystal substrate.

Fig.123 shows a typical electron diffraction result corresponding to this region, which extends mainly up to 105 mA/cm^2 . Beyond 105 mA/cm^2 the upper limit of deposit thickness giving only single crystal structure decreases with c.d. The nickel deposits up to 105 mA/cm^2 always show

parallel single crystal growth without anything additional (see Fig.123). The other deposits in this region yield diffraction patterns similar to Fig.123. The elongation of the diffraction spots indicates that the surface is highly smooth on the atomic scale. The deposits appear uniform, bright and shiny.

The general nature of the different regions is almost the same as observed at 50°C. But the boundary separating this region of parallel growth from that giving surface hydroxide has shifted roughly to 105 mA/cm² at room temperature ($\approx$ 20°C) instead of the 250 mA/cm² observed at 50°C.

Region II; Nickel deposit showing a surface hydroxide layer.

This region roughly starts at 105 mA/cm² and extends towards higher c.d. During electrodeposition, evolution of gases and formation of bubbles were observed near and on the cathode surface. There was a greenish rough deposit of nickel hydroxide on most of the deposit surface. Near the edge region some black deposit was also observed. The hydroxide layer covering the metal surface was removed by etching in 5% dil. H₂SO₄ for 10 secs. The underlying metal surface showed f.c.cubic nickel. The results are discussed below with reference to the typical diffraction photographs.

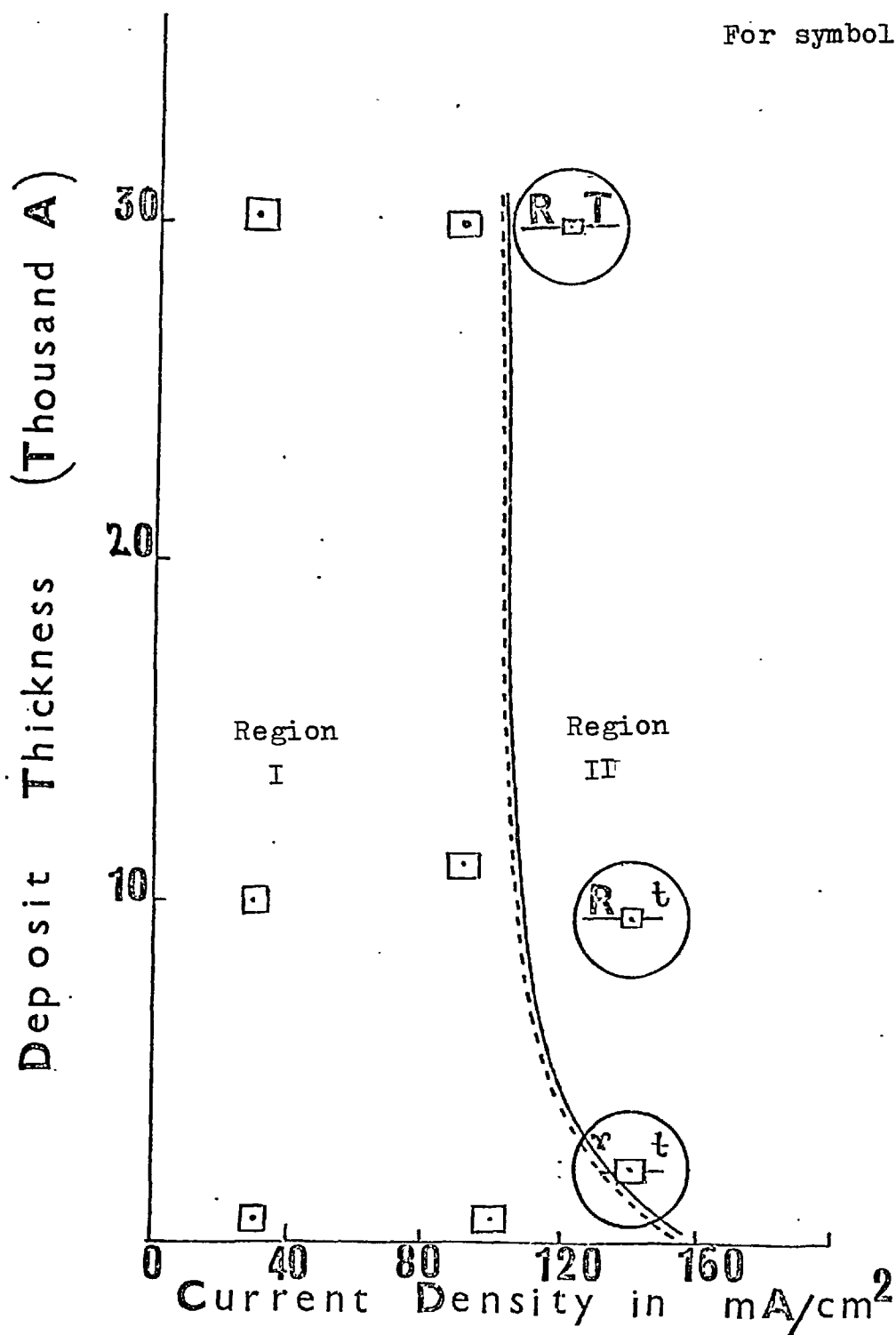
Region II ; Below the hydroxide layer, the nickel in parallel growth and with varying amount of $\{111\}$ twinning and random orientation.

Figs. 124 and 125 show typical electron diffraction photographs. At 140 mA/cm^2 , the deposits of thickness of 2,000 Å, show mainly parallel single crystal growth with very minute traces of $\{111\}$ twinning and random nickel (see Fig.124). On further increase in deposit thickness the random nickel becomes more pronounced, whereas the parallel growth is less represented. At about 9,500 Å, the central part of the deposit surface is mainly randomly oriented with small traces of parallel growth and $\{111\}$ twinning. The other part of the same surface shows only randomly oriented nickel. At 120 mA/cm^2 , 30,000 Å deposits also show nearly the same structure as obtained at 140 mA/cm^2 and 9,500 Å thickness, but the amount of random nickel is rather more (see Fig.125).

3.10. The Structure, Growth and Orientation of Nickel Electrodeposits on an Atomically Smooth Electropolished (110) Face of a Copper Single-Crystal Substrate, from the Standard Nickel Sulphamate Solution at Room Temperature ($\approx 20^\circ\text{C}$) with the Bath Unstirred.

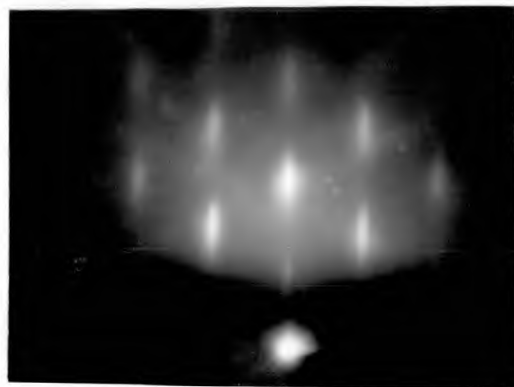
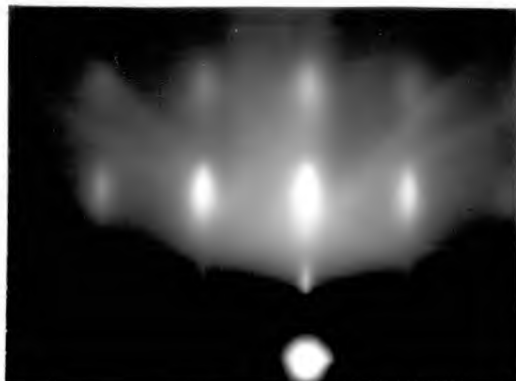
Fig.126 shows diagrammatically the experimental results. The electron diffraction study was limited to between 1 mA/cm^2 and 140 mA/cm^2 , and without stirring the

For symbols see page I30(A).

Fig. 122. Ni on Cu (100), unstirred, 20°C .

REGION I OF FIG. 122.

(Cu (100) unstirred bath, 20°C).



(a)

(b)

Fig.123. 11,200 Å Ni at 90 mA/cm², Cu (100), unstirred bath, 20°C.

(a) Beam along cube edge.

(b) Beam along cube face diagonal

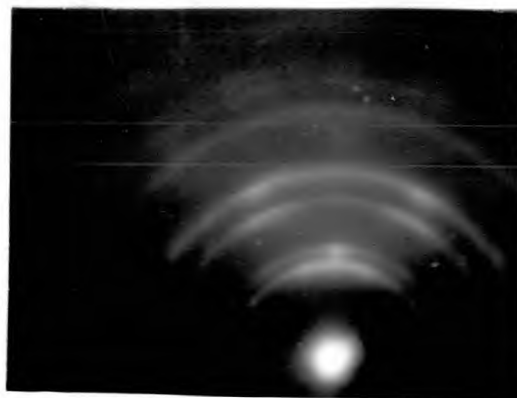
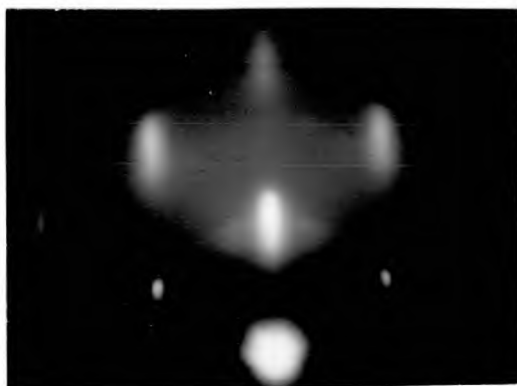
REGION II OF FIG. 122.

Fig.124.

2400 Å Ni at 140 mA/cm²
on Cu (100), unstirred bath
20°C.

Fig.125.

30,000 Å Ni at 120 mA/cm²
on Cu (100), unstirred bath
20°C.

bath. The general trend of the results is similar to that on the (110) face of copper at 50°C , with the difference that the region of smooth parallel single-crystal growth without the formation of a nickel hydroxide layer on the deposit surface is limited to below about 120 mA/cm^2 instead of up to 340 mA/cm^2 at 50°C . The whole diagram (Fig.126) has been divided into two main regions taking into consideration the change of structure across a narrow transition region.

Region I; Nickel mainly in parallel single-crystal growth to the copper single-crystal substrate with varying amount of $\{111\}$ twinning and one-degree (100) orientation.

Figs. 127 and 128 show typical electron diffraction photographs from the nickel deposits corresponding to this region (cf. Fig.126). This region extends from 0 to 120 mA/cm^2 .

The nickel grows mainly parallel to the substrate crystal. However, the parallel growth is accompanied by varying amount of octahedral twinning at different stages of c.d. and deposit thickness. At 1 mA/cm^2 and at 450 A, the nickel deposit shows some random orientation in addition to single-crystal structure and $\{111\}$ twinning. At about 5,400 A, one-degree (100) orientation is developed and there is a decrease in the amount of parallel growth. At 30 mA/cm^2 , the parallel growth with strong $\{111\}$ twinning continues from 400 A to 30,000 A deposit thickness.

At 100 mA/cm^2 , the deposits show very smooth epitaxially parallel growth up to $30,000 \text{ \AA}$. Only a little $\{111\}$ twinning is observed at 500 and $30,000 \text{ \AA}$ deposit thicknesses (see Fig.127), whereas at $10,000 \text{ \AA}$ there is no $\{111\}$ twinning (see Fig.128). The elongation of the diffraction spots shows the degree of smoothness of the deposit surface.

Region II; Nickel deposit showing surface hydroxide layer.

This region lies above 120 mA/cm^2 . The electrodeposition is accompanied by evolution of gas and formation of bubbles around the cathode. The evolution of gas increases with increase in current density. The deposit surface was coated with a greenish rough deposit mainly, but near the edges black deposits were also observed. The hydroxide layer was etched away in 5% dil. H_2SO_4 . The underlying metal surface showed the nickel pattern as discussed below.

Region II ; Below the hydroxide layer, nickel in parallel single-crystal growth with varying amount of $\{111\}$ twinning and random orientation.

Figs. 129 and 130 show typical electron diffraction results on nickel deposits above 120 mA/cm^2 . This region starts around 120 mA/cm^2 but no upper limit has been determined.

The nickel electrodeposits grow parallel to

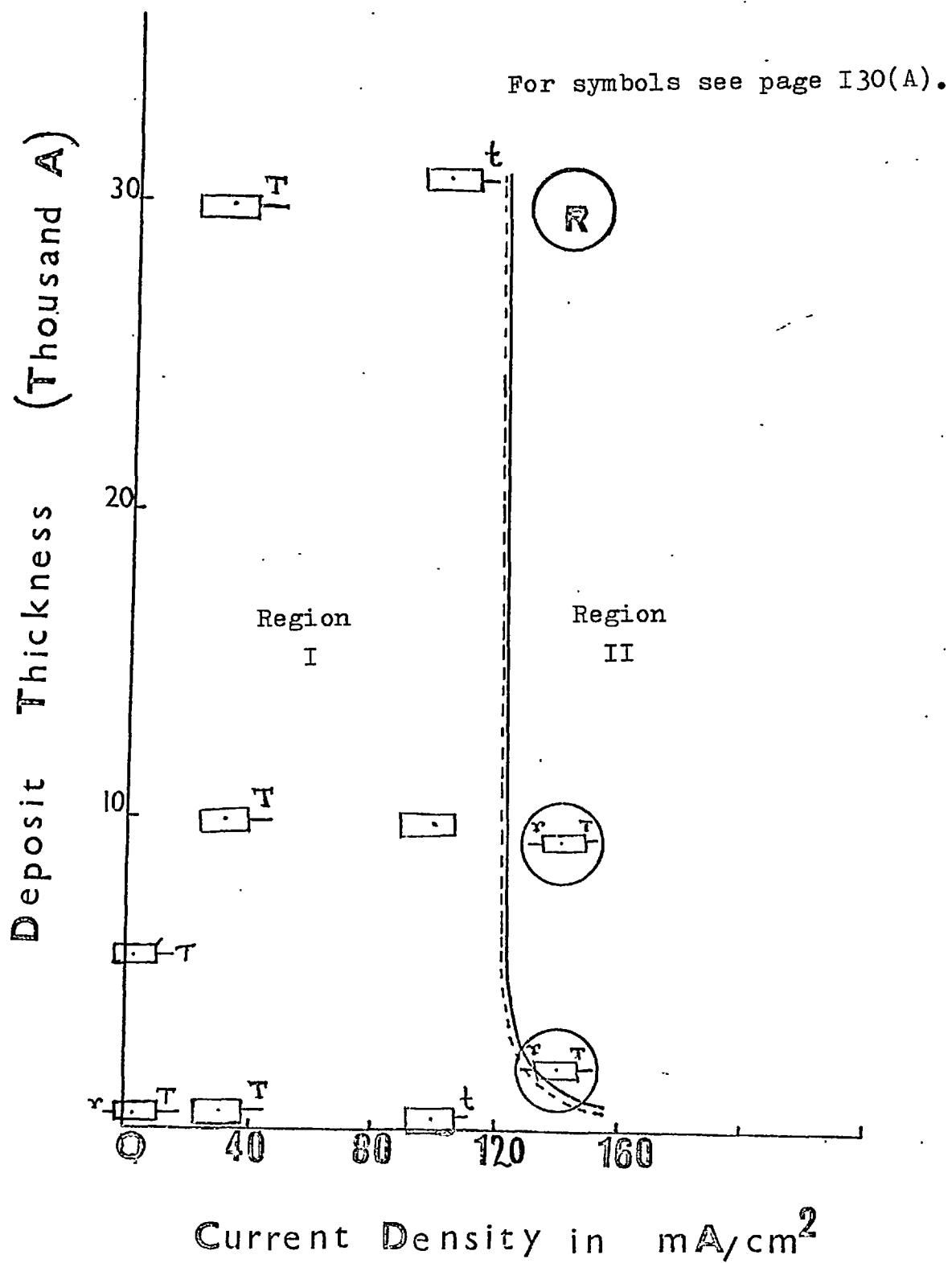


Fig. 126. Ni on Cu (110), unstirred, 20° C.

REGION I OF FIG. 126.

(Cu (110), unstirred bath, 20°C).

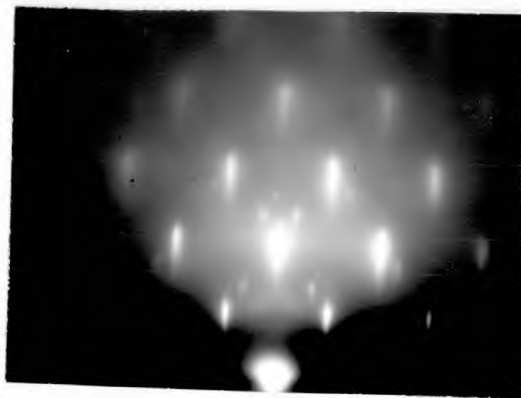


Fig.127.

500 Å Ni at 100 mA/cm² on
electropolished Cu (110),
unstirred bath, 20°C.

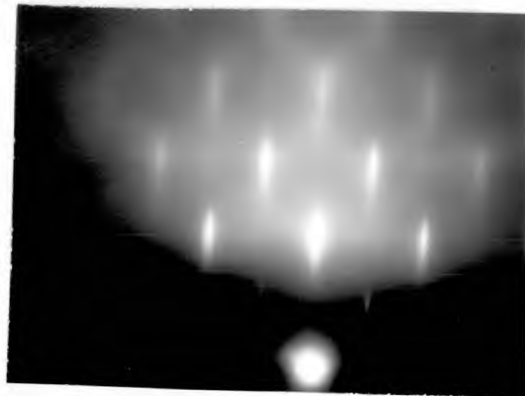


Fig.128.

10,200 Å Ni at 100 mA/cm²
on Cu (110), unstirred
bath, 20°C.

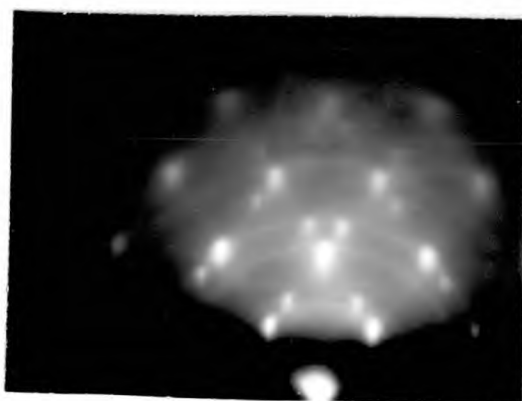
REGION II OF FIG. 126.

Fig.129.

2,000 Å Ni at 140 mA/cm²
on Cu (110), unstirred
bath, 20°C.

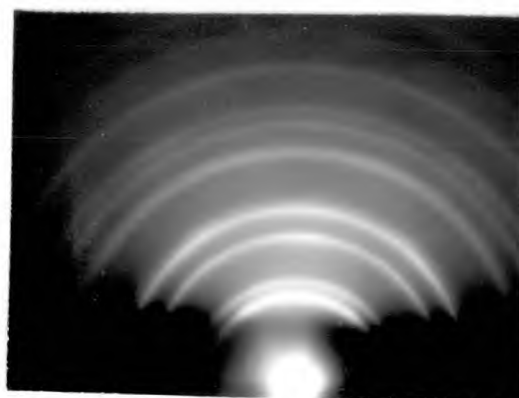


Fig.130.

28,500 Å Ni at 140 mA/cm²
on Cu (110), unstirred
bath, 20°C.

the substrate copper lattice, together with random orientation and $\{111\}$ twinning. The $\{111\}$ twinning is strong even up to 10,000 Å (see Fig.129) at 140 mA/cm². The random orientation gradually increases with deposit thickness with decrease in parallel growth. At 28,500 Å the nickel deposit becomes completely random polycrystalline, with a small trace of one-degree (110) orientation (see Fig.130).

3.11. The Structure, Growth and Orientation of Nickel Electrodeposits on an Atomically-Smooth Electropolished (111) Face of a Copper Single-Crystal substrate, from the Standard Nickel Sulphamate Solution at Room Temperature ($\approx 20^{\circ}\text{C}$), with the Bath Unstirred.

Fig.131 shows diagrammatically the results of the electron diffraction study of the surface structure of the nickel electrodeposits at various thicknesses (0 to 30,000 Å) and c.d. (0 to 140 mA/cm²). The general nature of the diagram is similar to that of Fig.87, which shows the surface structure of the nickel electrodeposits on a Cu (111) face at 50°C. In the present case (i.e. at 20°C), the upper limits of thickness and c.d., defining a region where there is a particular type of the deposit surface structure, are reduced to lower values. The systematic transition of results from one type of structure to the other at about a certain c.d. divides the whole diagram into regions as discussed below.

Sub-region I(A); Nickel mainly in a single-crystal orientation with axes parallel to those of the copper substrate, and with {111} twinning, a little random and in some cases one-degree (100) orientation.

Fig.132 shows a typical electron diffraction photograph from the deposits in this region (cf. Fig.131).

This region extends up to about 140 mA/cm^2 or more. Beyond about 40 mA/cm^2 , this region is confined to lower and lower thicknesses and lies between 0 and 1,000 Å at 140 mA/cm^2 . At 10 mA/cm^2 , the upper limit of this region is about 6,000 Å, but decreases with increase in c.d.

In this region, the crystals in the nickel electro-deposits grow epitaxially parallel to the substrate surface, with other orientations also present, e.g. twinning and some random nickel. At 10 mA/cm^2 , a deposit thickness of 500 Å is mainly a single-crystal orientation with strong

{111} twinning and randomly oriented nickel. Between 30 and 140 mA/cm^2 , the deposits of thickness of the order of 600 Å show single-crystal orientation in parallel growth to the substrate, together with a little {111} twinning and small random (see Fig.132).

At all c.d. (0 to 140 mA/cm^2), the amount of single crystal orientation decreases with increase in thickness, whereas the twinning and random orientation become stronger. The single-crystal growth persists to a higher deposit thickness at lower c.d. than that at higher c.d.

Below 50 mA/cm^2 , the deposits thicker than $4,000 \text{ \AA}$ show some one-degree (100) orientation at their surface, in addition to parallel growth, with some $\{111\}$ twinning and random orientation.

Sub-region I(B); Nickel mainly in one-degree (100) orientation with varying amount of one-degree (111) orientation or $\{111\}$ twinning.

A typical electron diffraction photograph from the deposit surface in this region (cf. Fig.131) is shown in Fig.133. The nickel deposits do not show any single-crystal structure in epitaxial growth on the substrate. Around $8,000 \text{ \AA}$ and up to 40 mA/cm^2 , the deposit surface shows one-degree (100) with a little $\{111\}$ twinning or (111) oriented nickel crystals. The amount of (111) orientation or $\{111\}$ twinning decreases with increase in deposit thickness whereas that of (100) increases. Finally, only strong (100) orientation remains (see Fig.133), causing a drawing out of the diffraction arcs towards the shadow edge due to strong refraction at atomically highly smooth faces parallel to the substrate surface. This region extends from 0 to 40 mA/cm^2 above about $6,000 \text{ \AA}$.

Sub-region II(A); Nickel in single-crystal orientation with axes in parallel growth to those of the copper single-crystal, with small traces of one-degree (110), increasing proportion of random and {111} twinning.

A typical electron diffraction photograph corresponding to this region in Fig.134 shows that the nickel crystals in the deposit surface are oriented parallel to the substrate lattice with some {111} twinning and random nickel in addition to a little one-degree (110) orientation. This region starts at about a point (80 mA/cm² and 6,500 Å) where the regions I(A), I(B) and II(B) meet, and extends up to 140 mA/cm² or more. At 140 mA/cm² it represents about 800 Å thickness in between I(A) and II(B).

Sub-region II(B); Nickel crystals in one-degree (110) and (210) orientations.

Fig.135 shows the typical surface structure related to this region (cf. Fig.131). In this region the single-crystal orientation of the nickel in the deposit surface region no longer exists. Only one-degree (110) and (210) orientations occur. At about 10,000 Å, the (210) and (110) orientations are nearly equal, but in thicker deposits (e.g. 30,000 Å) (110) orientation is more pronounced than (210) towards lower c.d. (80 mA/cm²), whereas (210) is very much stronger than (110) near the higher c.d (100 mA/cm²). Above 9,000 Å this region lies between 40 and 120 mA/cm². Below 9,000 Å, it becomes narrower and extends to 140 mA/cm²

Region III; Nickel deposit surface covered with nickel hydroxide.

This region, lying on the right hand side of the broken curve in Fig.131 (above about 120 mA/cm^2) is a region where evolution of gas during electrodeposition resulted in co-deposition of nickel hydroxide on the deposit surface. The hydroxide-coated surface showed diffuse haloes (see Fig. 35). The surface hydroxide was etched away in 5% dilute H_2SO_4 for 15-20 seconds. The underlying metal surface had f.c.cubic nickel structure on examination by electron diffraction as discussed below.

Sub-region III(A); Nickel showing one-degree (110) and (210) orientations after etching away the hydroxide layer.

This sub-region sets in at about 120 mA/cm^2 (at above 6,000 Å) and continues up to 140 mA/cm^2 or more. The typical electron diffraction pattern from the deposit surface in this sub-region after etching away the hydroxide layer is shown in Fig.136. Here both one-degree (110) and (210) orientations occur simultaneously in almost equal proportions. Their prominence decreases with increase in the deposit thickness. The upper limit of this region extends up to about 15,000 Å at 140 mA/cm^2 .

Sub-region III(B); Nickel showing only random orientation after etching away the hydroxide.

This region starts above 120 mA/cm^2 , but at higher deposit thicknesses than sub-region III(A). The lower limit of the deposit thickness above which this region sets in, decreases with increasing c.d., e.g. at 120 mA/cm^2 and 140 mA/cm^2 , the minimum deposit thicknesses giving rise to the occurrence of this region are about 20,000 and 15,000 Å respectively. The electron diffraction pattern from the deposit surface in this region is shown in Fig.137, and indicates that the nickel in the deposit surface is randomly oriented polycrystalline.

For symbols see page I30(A).

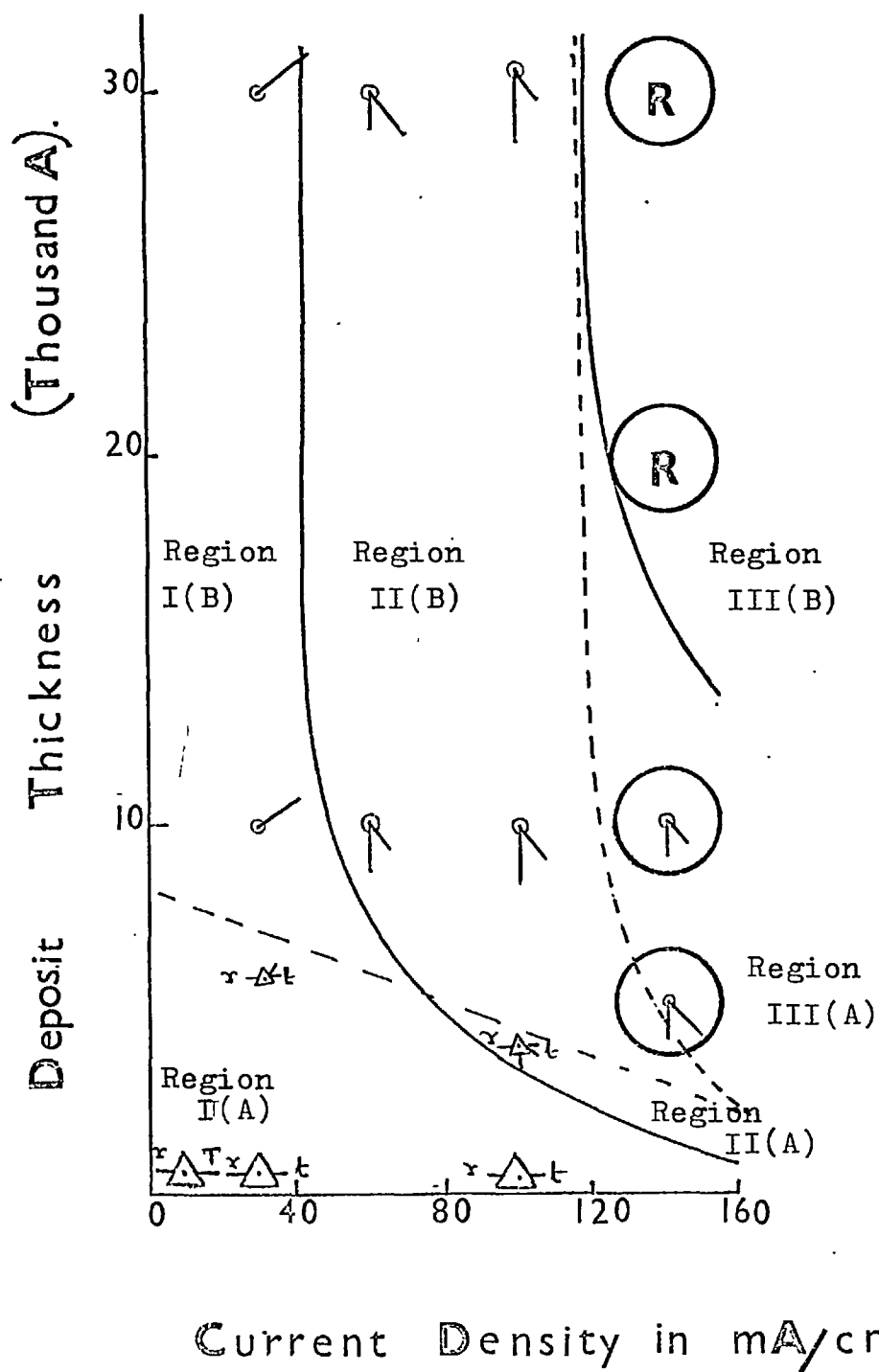


Fig.131. Ni on Cu(II), unstirred, 20°C.

(Cu (111), unstirred bath, 20°C)

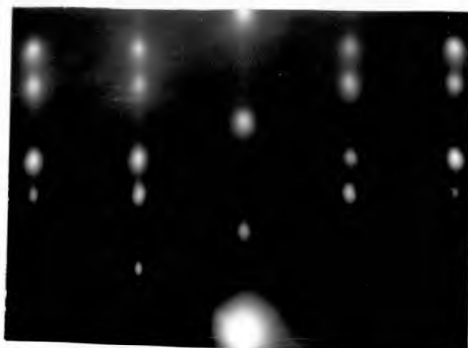


Fig.132.

600 Å Ni at 30 mA/cm² on
Cu (111), unstirred bath,
20°C.

SUB-REGION I(B) OF FIG. 131.

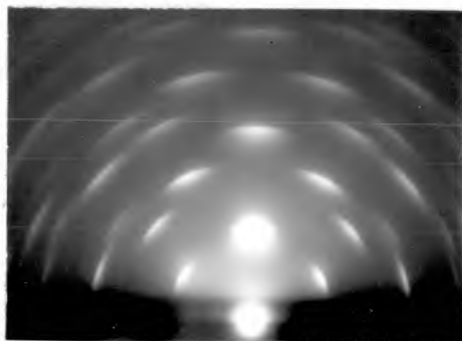


Fig.133.

30,000 Å Ni at 30 mA/cm² on
Cu (111), unstirred bath,
50°C.

SUB-REGION II(A) OF FIG. 131.

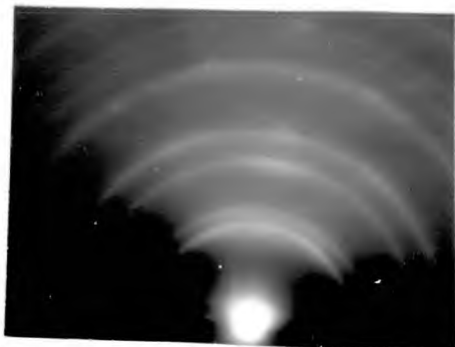


Fig.134.

3,600 Å Ni at 100 mA/cm² on
Cu (111), unstirred bath,
50°C.

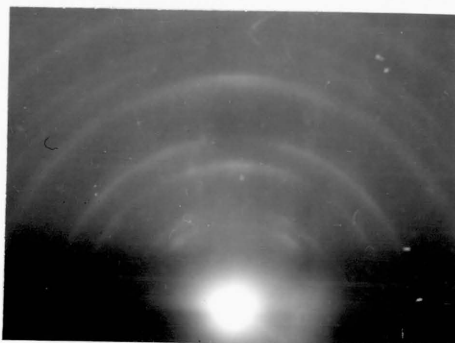
SUB-REGION II(B) OF FIG. 131.

Fig.135.

10,400 Å Ni at 100 mA/cm^2 ,
on Cu (111), unstirred bath,
 50°C .

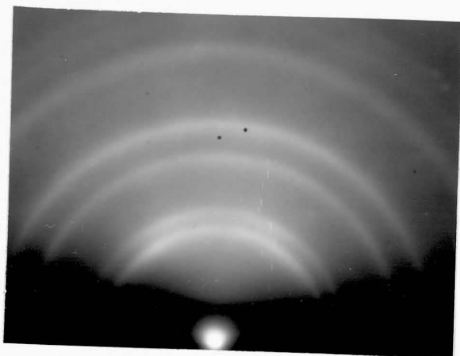
SUB-REGION III(A) OF FIG. 131.

Fig.136.

9,500 Å Ni at 140 mA/cm^2 ,
on Cu (111), unstirred bath,
 50°C .

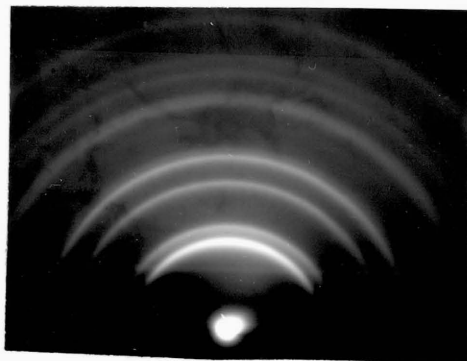
SUB-REGION III(B) OF FIG. 131.

Fig.137.

20,400 Å Ni at 140 mA/cm^2 ,
on Cu (111), unstirred bath,
 50°C .

4. DISCUSSION.

4.1. The Epitaxial Orientation of the Initial Thin Deposits ($\leq 1,000$ Å).

The nickel deposits in the present case are always face-centred-cubic (except ^{for a trace} in one deposit for some reason). The initial thin nickel deposits ($\leq 1,000$ Å) are mainly epitaxially oriented (single-crystal on copper single-crystal substrates) both at 20°C and 50°C.

On the Cu (100), (110) and (111) substrates (cf. Figs. 54, 68, 87, 122, 126, 131), the cube-axes of the nickel are parallel to those of the single-crystal substrate. However, at low c.d. (in a range of c.d. depending on the bath temperature), on Cu (110), in some cases varying amounts of $\{111\}$ twinning occurred, and on the Cu (111) face, twinning with also a small amount of random polycrystalline nickel was observed.

On polycrystalline copper (cf. Figs. 18 and 108), the thin nickel deposits show a corresponding wide range of orientation of the substrate, that is, the growth of the nickel is also epitaxial on the polycrystalline copper.

Nickel and copper are both face-centred-cubic metals, and have closely similar lattice spacings. The lattice misfit of Ni ($a = 3.528$ Å) on Cu ($a = 3.6153$ Å) is small, only - 2.59%. Because of the smallness of the lattice misfit, the parallel single-crystal lattice orientation is

the one which gives the closest atomic fitting and therefore occurs.

Although the nickel lattice is smaller than that of copper and therefore under tension, no rotational "directed" disorientation was observed like that which Kumar (1955) found in copper on Ag (100) and (110) faces (see Section 1). On the other hand, as noted above, twinning occurred apparently attributable to the misfit stresses, and a small proportion of random nickel occurred, perhaps nucleated in the misfitting regions of the nickel nuclei as they grew larger and contacted neighbouring nuclei.

The results using the stirred bath (cf. Figs. 38, 64, 79, 102 and 116) show that the stirring does not affect the development of epitaxy of the nickel on copper.

The parallel epitaxial orientation of nickel on copper in the present experiments is the same as that found (using other nickel baths) by other investigators at a few limited conditions of c.d. and thickness, e.g. Wood (1931), Finch and Sun (1936), Cochrane (1936), Thirsk (1939), ^{Clark, Pish, and} Weeg (1944), Finch, Wilman and Yang (1947), Leidheiser and Gwathmey (1951), Finch and Layton (1951), Lawless and Garmon (1963), Reddy and Wilman (1965), Lawless (1967).

On the Cu (100) face, in epitaxial thin nickel deposits, the twinning is surprisingly absent except at very high current densities (cf. Figs. 54 and 122), unlike on the

Cu (110) and (111) faces. At present it is not clear why there is absence of twinning on this face. It is not apparently connected with any special difference in the degree of perfection in the layerwise growth because the electron diffraction pattern shows highly smooth surface on the atomic scale. The interesting observation was made in the present experiments that on the Cu (110) face (cf. Fig.68), although in thin deposits the epitaxial nickel was accompanied by twinning, the twinning decreased as the c.d. increased, and finally became absent above 250 mA/cm^2 (with unstirred bath at 50°C). This suggests that an annealing process is occurring at the higher c.d., when the rate of arrival of energy at the cathode surface, in the deposit formation, becomes larger. It was observed in some cases that the temperature of the cathode and the solution rose by 10°C or more during 1 minute of deposition.

Regarding the rise in temperature of the cathode in the solution during electrolysis Wilman (1955a) supported by other observations, (Murbach and Wilman, 1953, Hunter and Fowle, 1954, and Wilman, 1955b) concluded that a very thin surface region of the cathode may attain an effective temperature of several hundred $^\circ\text{C}$ due to the net energy set free when the ions are neutralised there.

On the Cu (111) face (cf. Fig.87), epitaxially oriented thin nickel deposits at 50°C and above 25 mA/cm^2

are always accompanied by either a large or small amount of $\{111\}$ twinning and a small amount of random polycrystalline nickel. In this case, also, the degree of twinning decreases with increase in c.d., like that on the Cu (110) face, with the difference that the twinning is present at all c.d. up to 600 mA/cm^2 or more (decreasing as the c.d. increases). It is noteworthy that at 10 mA/cm^2 a nickel deposit about 200 Å thick (cf. Fig. 91) shows twinning only on the surface (111) plane. This is as found by Setty and Wilman (1955) for Ag on Ag (111), and corresponds to the two alternative nearly equivalent epitaxial orientations on the copper (111) face.

4.2. The Effect of Current Density and Deposit Thickness on the Degree of Twinning in the Nickel Deposits.

Nickel on the Copper (100) face.

The present experimental results on the nickel electrodeposits on the Cu (100) face (cf. Fig.54) are noteworthy, in that they show no initial twinning associated with the epitaxial misfit. The relation of the later twinning to the c.d. and the deposit thickness therefore corresponds to the growth of nickel on the Ni (100) face and is analogous to that of Ag on the Ag (100) face (cf. Setty and Wilman, 1955; Sundaram, 1966); and Cu on the Cu (100) face (cf. Cusminsky, 1965). In all these cases, at any c.d. the twinning occurs above a certain critical thickness which decreases with increase in the c.d., under particular bath conditions. The twinning occurring at a particular c.d. increases in amount with the increase in the deposit thickness until the deposit structure becomes random polycrystalline.

At 20°C with an unstirred bath (cf. Fig.122) the pure single-crystal epitaxial parallel growth of the nickel deposits on Cu (100) without any other orientation, is found to be accompanied by a varying amount of twinning above about 105 mA/cm² (or more in the case of thinner deposits <10,000Å). The relation of this c.d. to that found by Cusminsky (1965) for Cu on Cu (100) is discussed in section 4.7.

In the present experiments, the development of twinning at 50°C with an unstirred bath (cf. Fig.54) is similar to that at 20°C , except that the c.d. above which the twinning for deposits of 30,000 Å or more takes place is higher than at 20°C . The effect of using the stirred bath at 50°C (cf. Fig.64) is to increase still further this critical c.d.

Wilman (1955), Setty and Wilman (1955), Matthews, Mutucumarana and Wilman (1960) concluded that if twinning is nucleated during the growth process (with a certain probability) its growth is likely to be promoted as a result of the "outward growth" tendency which increases with increase in c.d. The twin growth, once initiated, becomes finally strongly represented; because of being favourable to more rapid outward growth receiving more deposited ions by diffusion.

Concerning the initiation of twinning, the faster the cations are deposited (the higher the c.d.) the higher the probability of some atoms not reaching the minimum potential energy sites of the growing deposit crystal nuclei, before being overlaid and hemmed in by further deposited atoms. Thus, an alternative set of potential troughs can be adopted^b for growth. The sites in the twin lattice constitute such an alternative set, and thus the deposit grows partly in twin orientation relative to the initial growth.

Perhaps, above a certain rate of deposition there would result such twinning and stacking faults in the sequence of the $\{111\}$ sheets of atoms in the lattice which initiate twinned growth (Setty and Wilman, 1955). At low c.d. the atoms being deposited will be most free from disturbances caused by deposition of other atoms in neighbouring positions, and they reach the positions of the lowest potential energy, continuing the atomic lattice of the substrate crystal. When the rate of deposition of atoms reaches a high enough value, however, many atoms are being deposited at any instant in any given locality and a proportion of them evidently do not reach the positions of lowest potential energy before being overlaid and built-in in positions which correspond to the formation of a $\{111\}$ twin.

When several neighbouring atoms have formed such a twin nucleus, there is little probability of the atoms in this becoming rearranged into the lowest energy positions, thus the twin nuclei grows further, and must themselves tend to be further twinned as growth proceeds. The higher the c.d. or the deposit thickness the more also is the outward growth of projecting parts favoured, leading to a rougher surface, as was indeed observed from the decreasing elongation of the diffraction spots, and by the optical micrographs. This factor may then favour repeated twinning of the twins, leading to random polycrystalline structure

at higher c.d. or thicker deposits in conjunction with the disorientating effects associated with stresses at the junctions of the twins as they grow together in contact with each other.

In the present experiments (cf. Fig.122) at 20°C with an unstirred bath, the c.d. above which twinning is observed in relatively thick deposits on the Cu (100) face, is about 105 mA/cm² (increasing ^{with decrease in} deposit thickness below 10,000 Å). Although this value of the critical c.d. is much higher than the 13 and 28 mA/cm² found by Setty and Wilman, 1955 and Sundaram, 1966 for Ag on Ag (100), and the 15 mA/cm² found by Cusminsky, 1965 for Cu on Cu (100), the rate of deposition of Ni atoms/site/sec. is comparable (see section 4.7).

The c.d. above which the twinning mainly occurs is the same as that above which the codeposition of hydroxide is observed on the nickel deposit surface, with vigorous evolution of gas during electrodeposition (not observed by previous workers). This suggests a further possible origin of twinning, probably the excessive accumulation or evolution of hydrogen ions or atoms on the cathode disturbs the lattice formation (cf. Finch, Wilman and Yang, 1947) leading to twinning. With further increase in deposit thickness (which increases the c.d. at the projecting parts) or c.d., there is increase in gas evolution and so in the degree of twinning which further gives place to random polycrystalline structure.

The co-deposition of hydroxide also may increase the effective c.d. and thereby decrease the substrate influence and the mobility of the deposited ions or atoms on the substrate. These effects might also be responsible for the occurrence of the twinning in the region where hydroxide is co-deposited.

Nickel on the Copper (110) face.

In the present experiments, the development of twinning occurs even in the first thin epitaxial nickel layers and continues in the further deposition. There is thus no similarity with the results of Setty and Wilman, 1955, Sundaram, 1966 (Ag on Ag (110)), and Gusminsky, 1965 (Cu on Cu (110)).

At 20°C with unstirred bath (cf Fig.126), the nickel deposits on Cu (110) show epitaxial parallel growth together with a varying amount of twinning at nearly all c.d. (from 10 to 140 mA/cm²) and thickness 500 to 30,000 Å). There is no region of pure single-crystal epitaxial growth of nickel on Cu (110) even at lower c.d. and deposit thickness. This is unlike the results on nickel deposits on Cu (100). At 100 mA/cm² the twinning is only a little in thin deposits (<500 Å). It is completely absent at 10,000 Å and then appears at 30,000 Å. On the other hand, the twinning is strongly present at nearly all thicknesses at c.d. on either side of 100 mA/cm² (i.e. <or> 100 mA/cm²).

The presence of twinning at all c.d. even in thin deposits can be attributed to the lattice misfit between Ni and Cu (cf. Section 4.1). It is in agreement with the observations of Kumar (1955) of twinning in Cu on Ag (110).

At 50°C with an unstirred bath, the twinning in the nickel deposit on Cu (110) is present at all thicknesses from 200 to 60,000 Å in region I(A) (cf. Fig.68). At 200 mA/cm², though the twinning is small in amount up to 10,000 Å or more, it becomes strong above 20,000 Å. This is probably due to the outward growth tendency leading to roughening of the deposit surface and hence rise in effective c.d. locally. The absence of twinning in the regions I(B) and II(A) can be attributed to the annealing effect due to the higher rate of liberation of energy during deposition at the higher c.d. (see Section 4.1).

In region II(B) (cf. Fig.68), the occurrence of twinning around 10,000 Å and more, in spite of the probable annealing effect during electrodeposition at higher c.d., can be argued to be due to two reasons. Firstly, vigorous evolution of gas during electrolysis and consequent deposition of hydroxide may lead to disturbance in the lattice formation, and to the mobility of atoms or ions on the cathode surface. Besides this, there would be more rapid roughening of the cathode due to preferential deposition on the projections of the cathode surface with increasing

thickness. This results in outward growth, and hence growth on twins may be promoted. Though the electrodeposition is occurring at higher c.d., the release of energy might be insufficient to cause adequate annealing effect to make the twinning completely absent. Around 30,000 A (from 340 to 600 mA/cm² or more), the single-crystal and twin spots are comparable in intensity but less prominent; the randomly-oriented nickel being developed to a large extent.

Nickel on the Copper (111) face.

At 20°C with an unstirred bath (cf. Fig.131), the epitaxial parallel single-crystal growth occurs and the {111} twinning is present in varying amount together with some random polycrystalline nickel in the nickel deposits on Cu (111), up to about 3,000 A at 10 mA/cm². The upper limit of deposit thickness, up to which epitaxial parallel single-crystal growth together with twinning occurs, but is then followed by random or one-degree orientation, decreases with increase in c.d. and tends to about 2,000 A at 140 mA/cm².

At 50°C with an unstirred bath (cf. Fig.87) at 10 mA/cm², the 200 A nickel deposits show twinning on the surface (111) plane only. But thicker deposits (about 10,000 A) have strong twinning on all the (111) planes. The presence of strong twinning in between 30 and 250 mA/cm², and its presence in small amount between 250 and 600 mA/cm²

in the initial thin deposits, have already been explained in section 4.1.

The twinning is present with the epitaxial single crystal growth up to a maximum thickness 25,000 Å at 10 mA/cm². The upper limit of the deposit thickness up to which the twinning occurs together with parallel single-crystal growth decreases approximately linearly with increasing c.d. At 600 mA/cm², it reduces to about 14,000 Å. At higher c.d. (> 280 mA/cm²) in thicker Ni deposits, though the amount of twinning is comparable to that of the single-crystal orientation, both of them gradually become less prominent than the increasing proportion of the random polycrystalline.

The small amount of twinning persists (at both 20°C and 50°C) in regions I(B) (cf. Figs. 131 and 87) where the epitaxial single-crystal growth of nickel has disappeared, giving place to the one-degree (100) orientation. The presence of this type of twinning with one-degree (100) orientation is similar to that observed in the nickel deposits on the polished polycrystalline copper.

Nickel on the polycrystalline copper.

The {111} twinning is also observed in small amount in the deposits on polycrystalline copper, especially when the bath is unstirred. Both at 20 and 50°C with unstirred bath, (cf. Figs. 108 and 18) it is found to occur slightly above about 6,000 Å in the region of cube-face orientation.

(at 20°C between 0 and 40 mA/cm²; and at 50°C between 30 and 270 mA/cm²). Initially, the arcs (mainly on the 111 ring position) characteristic of {111} twinning are not clearly resolved. But at 30,000 Å or above, the arcs are more clearly resolved (cf. Figs. 28, 111, 117)

With the stirred bath, both at 20 and 50°C, (cf. Figs. 116 and 38) the twinning is seen only in a few cases. Thus it can be concluded that stirring reduces the growth of twinning.

4.3. The Effect Of Current Density and Deposit Thickness on the Development of the Preferred One-Degree Orientations of "Lateral" and "Outward" Growth Types.

4.3.1. Nickel deposits on polished polycrystalline copper.

The mechanically polished copper surfaces used in the present experiments were composed of small crystals of copper in nearly random orientations and had relatively smooth though usually slightly undulating surfaces with some shallow abrasion grooves. The crystal surfaces were thus irregular in form and the atomic groupings would correspond to small crystal nuclei, adsorbing strongly the atoms of the first layers of the deposit. These thin deposits, apparently consisted of epitaxially oriented nickel crystals in orientations parallel to those of the individual copper substrate crystals and therefore likewise in nearly random disposition. As the deposit thickness increases, however, the bath conditions promote the more rapid growth of those crystals having certain definite orientations characteristic of these conditions (Finch and Sun, 1936; Finch and Layton, 1951; Finch, Wilnan and Yang, 1947).

4.3.1.(a). Development of one-degree (100) orientation in Ni on polycrystalline copper.

There will be a tendency for those crystal nuclei having the most densely-populated planes of atoms parallel to the substrate to grow side-ways more rapidly than others if deposition conditions favouring lateral growth are used. The lateral extension of these planes enables them to receive more incident metal ions than the other lattice planes, and in the further deposition, the deposit crystals will soon be oriented for the most part with these most densely packed lattice planes parallel to the cathode surface. Nickel is an unusual case in which the lateral type of growth results in the formation of a plane of slightly less than maximum possible atomic packing (i.e. $\{100\}$ instead of $\{111\}$) parallel to the substrate (cf. Finch and Layton, 1951).

In the present experiments, there is a very close relationship between the current efficiency and the development of the (100) orientation. At 20 and 50°C, the current efficiency is 100% up to about 40 and 270 mA/cm² respectively on the polished polycrystalline copper with the unstirred bath. The cube-face orientation also at 20 and 50°C is developed on polycrystalline copper only up to 40 and 270 mA/cm² respectively. Thus it is evident that 100% current efficiency or nearly so is essential for the

development of smooth and bright nickel deposits with cube-face orientation in the conditions stated above.

The angular spread of the arcs from their mean positions corresponding to the (100) orientation decreases with the increase in the deposit thickness at a particular c.d. The variation of the angular spread of the arc, on the 200 ring in the plane of incidence with the increase in deposit thickness, is shown in Figs.20 and 109. As regards the magnitude of the angular spread of the arc, great accuracy was not attempted and thus it is arbitrarily defined. The intensity of the arc is maximum in the middle and falls off rapidly along the arc, on either side of the plane of incidence. Though the angular spread of the arc is arbitrarily defined as extending to the point where the intensity is negligible relative to the maximum, there is a general trend of decrease in the angular spread of the arc with the increase in deposit thickness, in all the cases.

The angular spread of the arc decreases up to a certain deposit thickness and then acquires nearly a constant value. The decrease is seen to be more rapid at lower c.d. (e.g. at 1 and 10 mA/cm²) than at higher c.d. (e.g. at 50, 100 and 240 mA/cm²). The flattened off part of the curve (for the thicker deposits) is at a level which rises with increase in c.d. (cf. Figs.20 a to e). The

decrease in the angular spread is clearly associated with the layerwise growth and development of crystal faces, as in the case of vapour deposition (cf. Evans and Wilman, 1952; Dutta and Wilman, 1970). It appears that the ions arrive at the crystal surface and evidently migrate to the edges and are retained there, so extending the face. The faces having the ions incident normally thus receive a larger number of ions per unit area of the face, and grow laterally most rapidly, so that these crystals soon preponderate. At higher c.d., the nucleation of a new layer on the existing surface layer has a higher probability than at low c.d., thus fewer atoms arrive at the edge and hence the lateral growth of a crystal face is less rapid, and the preferred orientation is less rapidly developed.

In the present experiments, under conditions of lateral growth, atomically smooth cube faces were indicated by the electron diffraction study (cf. Fig. 28), although optical microscopy and electron microscopy had not given any clear indication.

The angular spread of the 200 arc, corresponding to (100) orientation obtained with the stirred bath, is comparatively less than that with the unstirred bath, other conditions remaining unchanged. (cf. Figs. 20 (a to e)). Though the stirring does not alter very much the magnitude of the angular spread, it does alter a little.

At 20°C (cf. Fig. 109), the nature of the curve is similar to that at 50°C (cf. Figs. 20 a-e), but at 20°C, the minimum value of the angular spread shown by the flattened off part, at 10 and 50 mA/cm², is higher than at 50°C.

The effects of both the stirring and the rise in bath temperature are in the sense expected, that is, they reduce the tendency of deposition on projections. There is also some indication that for a constant deposit thickness the angular spread increases with increase in c.d., up to a certain c.d. and then becomes almost constant (see Fig.21).

4.3.1.(b) Development of one-degree (110) and (210) orientations in Ni on polycrystalline copper.

The development of one-degree (110) and (210) orientations on polished polycrystalline copper is characteristic of outward growth, that is of the region where the current efficiency is less than 100%. The conditions which tend to promote outward growth are stated in section 1.3.2.1(a). Under these conditions, the deposition on random-crystalline substrates will take place to a greater extent on the projecting parts of the cathode surface. The initial randomly disposed crystal nuclei of the deposit will grow outward more rapidly if they have the most densely populated lattice row perpendicular to the

substrate, and this will lead to preferential deposition, and growth of, crystals in such an orientation.

The one-degree (110) and (210) orientations occur at relatively high c.d. They occur in a narrow region between the regions of cube-face orientation and random orientation (cf. Figs. 18, 38, 108, and 116).

The form of the loci separating the lateral growth region from that of outward growth is roughly similar to the curve of D_d against the c.d., plotted by Matthews, Mutucumarana and Wilman (1961) from the data of Ibl and Trumpler (1952) in the case of Cu electrodeposits from 0.1 M CuSO_4 . D_d is the deposit thickness at the arbitrary stage of deposit roughness corresponding to the first visible dimming of the cathode.

In the present experiments, like the (100) orientation, the angular spread of the arcs from the mean positions showing (110) and (210) orientations also decreases with increasing deposit thickness (at any particular c.d.) and finally acquires almost a constant value. In thicker deposits, the arc on the 220 ring in the plane of incidence shows more refraction towards the shadow edge. This indicates that very smooth (110) faces were developed parallel to the substrate. The decrease in the angular spread in the case of (110) and (210) orientations is less rapid than that of (100) (cf. Figs. 20(f), 89, 103, 109(b)).

The angular spread of the arcs shown is smaller with the stirred bath than with the unstirred, in the case of the (100) lateral growth type of orientation (see Fig 20), but the development of the (110) or (210) outward growth orientation is changed by vigorous stirring to lateral growth (100) orientat^{where}.

At relatively high c.d. (cf. Figs. 18, 38, 108 & 116) / the co-deposition of hydroxide occurs, the underlying metal deposit surface shows (110) and (210) orientations in nearly equal proportions, but in thicker deposits only random polycrystalline structure is seen. The appearance of (210) orientation is much more pronounced when the deposition is carried out at a high c.d. and especially at room temperature as Banerjee and Goswami (1955) also found.

4.3.2. Development of preferred one-degree orientations in nickel deposits on the Cu (100) face.

At 50°C with the unstirred bath (cf. Fig. 54) there is an indication of the presence of a narrow outward-growth region (between 250 and 320 mA/cm² at about 30,000 A or more) where small traces of one-degree (110) orientation are obtained. The position of this region is comparable to some extent with that found on polycrystalline copper substrates.

4.3.3. Development of one-degree orientations in nickel deposits on the Cu (110) face.

It is particularly interesting to note that one-degree (100) orientation is developed in nickel deposits on the Cu (110) face (cf. Fig. 68). At 50°C with the unstirred bath, the nickel deposits above 8,000 Å and below 200 mA/cm² show the beginning of the development of one-degree (100) orientation. This becomes stronger with increase in deposit thickness. Even at 200 mA/cm² in thick deposits ($\approx 60,000$ Å) one-degree (100) orientation is strongly developed together with the single-crystal structure (cf. Fig. 68). The one-degree (100) orientation appears to have developed from the small amount of random nickel which is seen to occur (due to misfit effects) together with the epitaxial single crystal nickel deposits even a few thousand Angstroms thick. Once this one-degree (100) orientation sets in, there is preferential deposition and so it becomes stronger with increasing thickness.

4.3.4. Development of one-degree oriented nickel in deposits on the Cu (111) face.

The development of the preferred one-degree orientations of lateral and outward growth types at 20 and 50°C (cf. Figs. 87, 102 & 131) are noteworthy. There are regions of lateral ($\{100\}$) and outward ($\{110\}$ and $\{210\}$) growths analogous to those with the polished polycrystalline

copper substrate (cf. Fig. 18). In this case also, it can be concluded that a small amount of randomly-oriented nickel, present with the epitaxial single-crystal nickel deposit, gives rise to the development of one-degree $\{100\}$, $\{110\}$ and $\{210\}$ orientations, depending on the bath conditions. These orientations become stronger (with the shortening of the arcs) with the increase in deposit thickness.

4.4. The Co-deposition of Nickel Hydroxide at the Higher Current Densities and its Relation to Current Efficiency.

At certain current densities higher than a certain value (at a given temperature and deposit thickness) vigorous evolution of gas was observed during electrodeposition of the nickel, and the nickel deposit surface was covered with a greenish rough deposit whose lattice constant corresponded approximately to that of $\text{Ni}(\text{OH})_2$

The appearance of hydroxide, at 20°C with an unstirred bath, on nickel deposits on polycrystalline copper and on Cu (100), (110) and (111) substrates occurs at about 80, 105, 120 and 115 mA/cm^2 respectively, corresponding to 30,000 Å of the nickel deposit (cf. Figs. 108, 122, 126 and 171). At 50°C , the onset of hydroxide co-deposition shifts to higher c.d., i.e. 315, 250, 340 and 410, corresponding to the same deposit thickness and for the same sequence of the substrate nature as above (cf. Figs. 18, 54, 68 and 87).

With the stirred bath at 50°C , the co-deposition of the nickel hydroxide on polycrystalline copper substrates starts at about $450 \text{ mA}/\text{cm}^2$, corresponding to deposit thickness of 30,000 Å (cf. Fig. 38). However, under the same bath conditions, on Cu (100) and (111) substrates, no hydroxide co-deposition is observed even up to $600 \text{ mA}/\text{cm}^2$ and 60,000 Å deposit thickness (cf. Figs. 64 and 102), whereas on Cu (110)

face the $\text{Ni}(\text{OH})_2$ co-deposition begins to appear above 540 mA/cm^2 under similar conditions (cf. Fig.79).

It is considered (e.g. Macnaughton, Gardam and Hammond, 1933; Glasstone, 1942; Finch, Wilman and Yang, 1947; Gray, 1953) that the co-deposition of hydroxide at high c.d. is due to the removal of hydrogen ions by deposition at the cathode (and evolution of hydrogen) making the electrolyte near the cathode region impoverished in hydrogen ions (increase in pH), i.e. more alkaline, leading to the precipitation of $\text{Ni}(\text{OH})_2$ on the nickel deposit. A similar case of hydroxide co-deposition was observed by Reddy (1958), Reddy and Wilman (1959 and 1963), i.e. deposition of $\text{Fe}(\text{OH})_2$ along with Fe. (cf. Banerjee and Goswami, 1955).

The co-deposition of a substance along with the metal being electrodeposited causes (1) a decrease of the substrate area available for electrodeposition, i.e. an increase in effective c.d.; (2) a decrease of the mobility of the deposit atoms or ions on the substrate surface before they become incorporated in the lattice; and (3) a diminution of the substrate influence which tends to initiate epitaxial growth, i.e. a decrease of the value of the critical thickness up to which the deposit grows epitaxially.

Though the c.d. at which the $\text{Ni}(\text{OH})_2$ co-deposition sets in is found to vary with the copper substrate nature, it does not appear to follow any regular sequence, e.g. in relation to the atomic density of the surface plane.

Comparing Figs. 18, 108 and 16, it is clear that the hydroxide co-deposition starts in the c.d. region where the current efficiency falls a little below 100%. This co-deposition of nickel hydroxide causes an instability in the nature of the electrodeposition, because by reducing the surface area on which the metal can be deposited, it causes the c.d. effectively to be increased, which further increases the co-deposition.

Co-deposition of hydroxide at high c.d. can be avoided by increasing the bath temperature and/or the degree of agitation.

4.5. The Effect of Bath Temperature.

The qualitative aspects of the present results are in agreement with the observations and the conclusions of the previous workers, e.g. Glasstone (1942), Finch and Layton (1951), Finch, Wilman and Yang (1947), Setty and Wilman (1955), Kumar (1955), and Reddy (1958). The results now, however, provide new quantitative information.

They also observed that the structure of an electrodeposit prepared at a high bath temperature and at a particular c.d. is the structure that is observed to occur at a lower c.d. when the electrodeposition is carried out at room temperature. Increase in temperature, therefore, has the same effect on electrodeposit structure as a decrease in c.d. In other words the maximum critical c.d. for epitaxial growth to continue or for the co-deposition of hydroxide to occur to any given thickness increases with an increase in bath temperature.

An increase in temperature is known to affect not only the diffusion of cations to the solution near the cathode, but also the mobility of the deposit atoms on the substrate surface. The effect of temperature on electrodeposit structure is, however, mainly explained in terms of the influence of temperature on the rate of cation supply to the cathode (Finch and Layton, 1951). At room temperature, above a certain c.d., the rate of diffusion fails to keep

pace with the rate of deposition, resulting in a depletion of cations in the regions near the cathode, which leads to an outward growth tendency and/or co-deposition of hydroxide.

Increase in bath temperature increases the diffusion of the cations to the cathode surface and thereby reduces the outward growth tendency at any given c.d. Studies of the electrodeposit structure have not been linked with measurements on the diffusion rates. The latter may not, therefore, be solely responsible for the effect of temperature on the structure. It is likely that other consequences of temperature increase also play some part in affecting the structure and growth of electrodeposits. As an example, the mobility of the deposit atoms or ions on the surface of the growing deposit, which is also a function of temperature, might affect the deposit structure, but this is likely to be only a minor effect.

At first sight the deposit structure appears to correspond to an increase of the mobility of the ions or deposited atoms at the surface of the growing crystals at increased temperature, so that practically all the deposited atoms reach sites of the lowest potential energy and on a single-crystal substrate the crystal growth is followed without twinning to higher c.d. (Setty and Wilman, 1955). A rise of bath temperature, however, increased the rate of diffusion and dissociation of the ions. Possibly also there may be a reduction of the number of water molecules

surrounding the cations and carried by them (Bockris and Razumney, 1967).

Due to the rise in temperature, the adsorbed molecules, colloidal material and foreign ions present on the cathode surface may acquire a more rapidly varying dynamic nature, allowing more opportunity of the access of the metal ions to the cathode surface and also assist their greater mobility over it. This will tend to promote lateral growth of the deposit crystals up to higher c.d. A low temperature or the evolution of hydrogen causes the deposit to be oriented with a less densely-packed lattice plane parallel to the substrate.

Comparing Figs. 108 and 18, it is found that region I in Fig.108, where nickel deposits on polycrystalline copper are mainly in cube-face orientation, extends only up to 40 mA/cm^2 when the electrodeposition is carried out at 20°C , whereas an analogous region II in Fig.18 extends to 270 mA/cm^2 when the electrodeposition is carried out at 50°C . The increase in the upper limit of c.d. giving mainly (100) orientation, (lateral growth) caused by increase in temperature, is due to the increase in the rate of arrival of metal ions at the cathode. This is due to increase in both the speed of the ions and that of the undissociated molecules diffusing towards the cathode region, when the ion concentration tends to be impoverished by deposition.

The rise in temperature from 20°C to 50°C causes an extension of the upper limit of c.d. by 19% per °C if a linear relation holds. This is concluded to correspond to a 19% increase in the supply of cations near the cathode surface per °C rise in temperature.

Identical quantitative increases in the supply of cations per degree Centigrade rise in temperature were also found for the lateral growth region when the electrodeposition was carried out in the stirred electrolyte, the other conditions remaining the same (cf. Figs. 116 and 38).

At lower bath temperatures and at high c.d. the ion concentration near the cathode may be reduced to such an extent that deposition of hydrogen and other cations occurs, or metallic hydroxides or basic compounds are precipitated (Macnaughton, Gordan and Hammond^m, 1933), and interfere with the mobility of the metal ions on or near the cathode surface.

The increase in temperature from 20°C to 50°C also pushes up to higher c.d. the stage of the onset of vigorous gas evolution and nickel hydroxide deposition on the nickel deposit surface. In the case of nickel on polycrystalline copper substrates, both with unstirred and stirred baths, the c.d. at the onset of vigorous gas evolution (for 30,000 A deposits), and the consequent deposition of nickel hydroxide, is pushed to higher c.d. by about 10% per degree Centigrade rise in temperature from the

value at 20°C. Under similar conditions, on Cu (100), (110) and (111) faces, the c.d. at which the vigorous evolution of gas occurs with co-deposition of nickel hydroxide, is found to increase by 5, 6 and 8 per cent per °C respectively, above the value at 20°C. That is, the supply of cations in the cathode region is increased by 5, 6 and 8 per cent per degree centigrade rise in temperature.

4.6. The Effect of Vigorous Stirring of the Bath or of the Rotation of the Cathode.

At bath temperature 50°C , comparing the results on polycrystalline copper substrates (cf. Figs. 18 and 38) it is found that the upper limit of c.d. for deposits thicker than 10,000 Å in region II of mainly strong (100) orientation (lateral type of growth) is raised from 270 to 410 mA/cm^2 due to vigorous stirring of the bath. This extension is by about 52%. The current density at which hydroxide deposition occurs (the lower limit of region IV, Figs. 18 and 38) is also pushed up, from 310 to about 450 mA/cm^2 , that is by about 45% when the electrolyte is vigorously stirred during electrodeposition.

At 20°C bath temperature, the other conditions remaining the same, the upper limit of the region of lateral type of growth and the c.d. for hydroxide deposition are similarly raised by about 50 and 40 per cent respectively due to vigorous stirring of the bath (cf. Figs. 108 and 116).

These extensions are in agreement with the conclusions of Finch and Sun (1936), Finch and Layton (1951), and Finch, Wilman and Yang (1947). They concluded that in order to promote lateral type of crystal growth, there should not be undue impoverishment of ionic concentration of the electrolyte in the cathode region, that is the rate of supply of ions to the cathode region by diffusion and migration

is not less than or very much less than the rate of deposition of ions on the cathode. They also concluded that the stirring of the bath during electrodeposition is one of the main factors which tend to favour the lateral type of growth and preferred orientation.

In the present results the effect of vigorous stirring is very marked and is defined quantitatively. The extension of the upper limits of the c.d. for the lateral-growth regions both at 50° and 20°C (cf. Figs. 18, 38, 108, 116) by stirring the electrolyte during electrodeposition can be explained in the light of the conclusions of Finch and his co-workers mentioned above. Since stirring favours lateral growth, this indicates that the stirring increases the degree of maintenance of the supply of ions to the electrolyte in the vicinity of the cathode surface and thus promotes lateral growth up to higher c.d.

The supply of ions near the cathode region can take place in two ways, e.g. by diffusion and convection. Glasstone (1942) suggested that if the electrolyte is agitated in any manner, the effective thickness of the diffusion layer is diminished. The decrease in the thickness of the diffusion layer depends not only on the rate of agitation, but also on the type of device employed for stirring the solution. Agar (1947) quoted Levich's mathematical relation between the thickness of the diffusion layer and the speed of stirring, indicating that the

thickness of the diffusion layer decreases with the increase of the speed of stirring the electrolyte.

The general conclusion of Glasstone (1942), Levich (1942, 1944), Agar (1947) and Vetter (1967) that stirring the electrolyte decreases the thickness of the diffusion layer around the cathode surface implies a consequent increase in the rate of supply of cations near the cathode surface. While it would be difficult to calculate the rate of increase in the cation supply, the above observations in the present results provide a direct estimate that the increase in rate of cation supply was of the order of 50%. Similarly the c.d. for hydroxide deposition also represents a definite degree of depletion of the cation supply, and is pushed toward high c.d. by about 40 - 45%.

Also, in the case of nickel deposition on copper (100), (110) and (111) faces used as substrate at 50°C, the stirring extends the upper limits of all the regions to higher c.d. (cf. Figs. 54, 68 and 87). The upper limit of c.d. giving epitaxial parallel growth of nickel without co-deposition of nickel hydroxide on Cu (100), (110) and (111) faces is extended by >140, 60, and >43 per cent respectively. The percentage increase in c.d. at which hydroxide is deposited is thus on (100) face more than twice as large as that on the (110) face.

If the results on the polycrystalline substrates are compared with the current efficiency results, it is found that the nickel crystals grow with (100) orientation so long as the current efficiency is 100%. In the stirred bath, 100% efficiency is maintained up to higher c.d., thus extending the region of cube face orientation up to higher c.d. Therefore, to obtain smooth, bright and non-porous deposits, (i.e. at 100% current efficiency) up to the highest c.d. possible, the maintenance of an efficient circulation of the electrolyte is of critical importance.

The Effect of the Rotation of the Cathode.

The present results (see (1.3.2.1(c))) suggest that the orientations of the electrodeposited crystals on the rotated cathode (bath unstirred or on stationary cathode with bath stirred) fall into two categories according to whether (i) the crystal orientation changed to the most densely packed type, or (ii) the crystal orientation was unaffected.

The nickel electrodeposits from the sulphamate bath at 50°C on polycrystalline copper shown in Table 1 have been obtained under three conditions, that is, with the stationary and rotating cathode in the unstirred bath, and with the stationary cathode in the stirred bath. If the rotation of the cathode causes a marked increase in the current efficiency of the metal deposition, then the deposit crystals may change from the type of orientation

characteristic of the prevailing^{bath}/conditions on a stationary cathode to the most densely packed plane as orientation plane, provided that the non-appearance of the latter in the deposit crystals on a stationary cathode is entirely due to a lower current efficiency.

From Table 1, comparing the structure of the nickel electrodeposits on the stationary cathode with those on a cathode rotated at 1200 r.p.m., it is found that the rotation of the cathode promotes lateral growth up to higher c.d., which depends on an increase in the cation concentration near the cathode, leading to an increase in current efficiency of deposition. The crystal orientation does not show any change either by stirring the electrolyte or by rotating the cathode if the c.d. is lying within that range where current efficiency is 100%. As an example, the deposit at 240 mA/cm^2 always shows one-degree (100) orientation without being affected by rotation of the cathode or stirring of the bath.

With the unstirred bath at higher c.d. ($> 270 \text{ mA/cm}^2$) at 50°C , the nickel crystals show outward growth orientation, i.e. mainly (110) orientation with or without (210). This orientation at high c.d. agrees with the previous observed conditions for outward growth (Finch and Sun, 1956; Finch and Layton, 1951; Finch, Wilman and Yang, 1947; Matthews, Mutucumarana and Wilman, 1961; Naybour, 1968;

Diggie, Despic and Bockris, 1969).

At 300 mA/cm^2 and 10,000 and 15,000 A (see Table 1) the change of orientation of the nickel deposit from (110) with the bath unstirred - outward growth —, to (100) — lateral growth - when rotating the cathode, is in agreement with the conclusions of Burgers and Quanjel (1942), Finch, Wilman and Yang (1947), Wyllie (1948), and Finch and Layton (1951). The rotation of the cathode (like stirring) increases the supply of cations in the region near the cathode. This reduces the degree of impoverishment of cation concentration of the solution in the cathode region and thus favours lateral growth.

Similarly, in the present work, at 400 mA/cm^2 on a stationary cathode (bath unstirred) vigorous gas evolution and co-deposition of nickel hydroxide on the surface of nickel deposits 22,000 A thick was observed. On the other hand, no co-deposited nickel hydroxide was observed and the deposit showed lateral growth orientation if the cathode was rotated or the bath was stirred during electrodeposition, other conditions remaining the same (see Table 1).

In some cases (see Table 1), the presence of a small amount of some additional orientations, e.g. (210), (110), etc. with the main orientation, might be due to the non-uniformity of the c.d. all over the cathode surface (cf. 3.3), i.e. higher c.d. near the edge of the cathode.

Nernst (1904) first postulated a relation between the current efficiency and the rotation of the cathode. In terms of the theory of the diffusion layer (see section I) the actual concentrations of the deposited cations at the cathode surface are controlled by two factors, that is, the rate of removing them by deposition (thus the c.d.) and the rate of replenishment through this diffusion layer. Under outward growth conditions replenishment is inferior to the rate of removal, at the beginning of the deposition, and these two rates do not become equal until the cation concentration falls near the cathode to a value at which equilibrium is reached. The concentrations of the various deposited cations at this cathode surface are therefore more or less decreased, and this is called the phenomenon of "Concentration polarisation".

Glasstone (1942) concluded that the thickness of the diffusion layer (δ) is reduced if the electrolyte is agitated. Levich (1942, 1944) concluded (see 1.3.2.1(d)) that approximately, for a circular disc rotating about its axis:

$$\delta = \frac{0.022}{\sqrt{R}}$$

where R is the number of revolutions per second.

Thus at 1200 r.p.m., $R = 20$ revs/sec., and δ is about one-fourth of its value on a stationary cathode. Correspondingly, the cation concentration at the cathode is much increased.

The observed changes in the crystal orientation, due to either the rotation of the cathode or stirring, are thus associated with an increase in the supply of cations near the cathode surface. This reduces the outward growth tendency and increases the lateral growth tendency. At still higher c.d. it may increase the current efficiency of deposition, if this is less than 100%, and may cause avoidance of oxide or hydroxide co-deposition.

4.7. The Dependence of the Nickel Electrodeposit Structure on the Crystallographic Form of the Substrate.

In the present experiments, although there is parallel single-crystal growth of the nickel on the Cu (100) face, up to large thickness and c.d., there is no purely single-crystal growth of the nickel on the Cu (110) and (111) faces at low c.d. and deposit thickness, like the one observed by Setty and Wilman (1955) (Ag on Ag (100), (110) and (111)), Cusninsky (1965) (Cu on Cu (100), (110), and Sundaram (1966) (Ag on Ag (100), (110) using nitrate bath). The reason for the absence of initial twinning of nickel on Cu (100) is at present not known, though the strong preference for cube faces to be developed on the nickel may suggest a greater stability of lateral growth of the initial nuclei in this case.

The epitaxial misfit of -2.59% in the case of nickel on copper seems to be responsible for the occurrence of the appreciable amount of twinning in the nickel on the Cu (110) and (111) faces together with the single-crystal structure even at low c.d. ($\approx 10 \text{ mA/cm}^2$) and deposit thickness ($\approx 200 \text{ \AA}$) both at 20 and 50°C . Kumar (1955) also observed twinning at low c.d. and deposit thickness in the electrodeposits of Ag on Cu single-crystal and Cu on Ag single-crystal. He concluded that the presence of twinning was due to the epitaxial misfit between Cu and Ag. Other

investigators quoted above in this section used the same metal as substrate and deposit, so no epitaxial misfit came into play, and they observed no initial twinning of the continued single-crystal growth.

On the other hand, it is interesting to note that no twinning or trace of any other orientation except parallel single-crystal growth is observed in the nickel deposits on the Cu (100) face up to a certain c.d. and the deposit thickness (depending on the bath conditions) in spite of the same epitaxial misfit being present between Ni and Cu on Cu (100) as it is on the Cu (110) and (111) faces. That is, there is a region of pure single-crystal epitaxial growth at low c.d. and deposit thickness below the twinning sets in. The c.d. at 20° and 50°C above which the twinning, in the surfaces of deposits 20,000 Å thick or more, occurs is about 105 mA/cm² and 250 mA/cm² respectively. The change from the single-crystal epitaxial growth above this c.d. into a region where twinning accompanied the epitaxial growth is similar to what was observed by Setty and Wilman, 1955, Gushinsky, 1965, and Sundaram, 1966. This c.d. at 20°C for the (100) face, according to their observations was about 13, 25 (Ag on Ag (100)) and 15 mA/cm² (Cu on Cu (100)) respectively, which are very much lower than the present value of 105 mA/cm² at 20°C. The current efficiency, however, is about 28%, i.e. only about 29.4 mA/cm² was carried by the nickel ions.

The number of atoms per site per second deposited at the above c.d. values is thus calculated to be about 80, 140 and 90 respectively in the above cases. But in the present experiments, it comes to about 70 only. This comparison shows that the number of atoms/site/sec. above which twinning occurs is less in the present case than for Ag on Ag (100) from AgNO_3 solution. The deposition of the gaseous ions at the cathode probably contributes in the present case to cause twinning of the Ni at a lower number of atoms/site/sec. than would have been the case in the absence of gas evolution.

5. GENERAL CONCLUSIONS.

From the present detailed and systematic studies of the structure, growth and orientation of the nickel electrodeposits in relation to current density, deposit thickness, substrate nature, temperature, stirring of the bath, and rotation of the cathode; the main conclusions arrived at are as follows.

1. The present work appears to be the first systematic study by electron diffraction of the nickel deposit structure from the sulphamate bath. The nickel deposits are consistently face-centred cubic. Though Sathyanarayana and Rana Char (1957) and Saleen, Brook and Cuthbertson (1967) studied briefly the structure of nickel electrodeposits from the sulphamate bath, their studies were confined to morphological aspects only.

2. The initial thin deposits are mainly epitaxially oriented on the copper substrates (polycrystalline and single crystal). On the other hand, the presence of $\{111\}$ twinning even in thin nickel deposits on Cu (110), and twinning with some random nickel on Cu (111) is evidently due to the epitaxial misfit of nickel (-2.59%) on copper. In spite of this epitaxial misfit, the absence of twinning on Cu (100) up to relatively higher c.d. (depending on the bath conditions) is particularly

interesting. The development of twinning and its amount at different stages of c.d. and deposit thickness depends on the crystallographic form of the substrate, other conditions remaining unchanged.

3. At relatively high c.d. (up to a certain thickness) the nickel deposits show an absence of twinning on Cu (110), and the decreasing amount of twinning on Cu (111) as the c.d. is increased. This suggests that there is an annealing effect during electrodeposition at high c.d.

4. The amount of twinning increases with increase in the nickel deposit thickness, and sometimes also with the increase in c.d. in the case of thicker deposits ($> 30,000$ A).

5. The evolution of gas and co-deposition of hydroxide play an important role in the growth of nickel deposits as they lead to more random disposition of the deposit structure. The larger the evolution of gas, the quicker is the change to random orientation as the deposit thickness increases.

6. The correlation between 100% current efficiency and the development of cube-face orientation (lateral growth) is of much importance from the practical point of view. In order to have bright, smooth and non-porous nickel deposits with cube-face orientation (lateral

growth), 100% current efficiency must be maintained. The (110) and (210) orientations (outward growth) occur in the region where the current efficiency is appreciably below 100%. The conditions of outward growth with certain modifications can be utilised in order to prepare metal powder for use in powder metallurgy.

7. The observed improvement brought about by vigorous stirring of the bath, in promoting lateral growth up to high c.d. on polycrystalline copper, and epitaxially parallel growth on Cu single-crystals is also of much practical use. The vigorous stirring increases the supply of cations in the cathode region. It also reduces the degree of twinning at almost all c.d. and deposit thickness, and makes the deposit surface smoother. The stage of the onset of gas evolution and hydroxide co-deposition also shifts to higher c.d.

8. The rotation of the cathode during electro-deposition has a similar effect on the deposit structure to that of stirring the bath.

9. An increase in bath temperature also increases the supply of cations in the vicinity of the cathode. The lateral or single-crystal growth is followed up to higher c.d. and deposit thickness, and the onset of gas evolution, co-deposition of hydroxide, and the development of random nickel are delayed to higher c.d.

10. Even with the stirred bath and high temperature, undue increase in c.d. beyond a certain value is not desirable. As soon as co-deposition of hydroxide occurs, an unstable condition is set up, because the c.d. rises and the co-deposit thus increases. The rate of deposition of nickel is thus decreased rather than increased further.

11. The nature of the crystal growth involves prominent development of particular crystallographic faces, mainly cube faces in the lateral growth region. The deposition is thus by layerwise build up of the atoms or ions, and presumably involves some surface mobilities of the adsorbed cations. The crystal growth process accounts for the observed development of preferred crystal orientation as the deposits grow thicker.

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