The Influence of a Superimposed Alternating Current on the Structure and Porosity of Gold Electrodeposits.

by

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SUMMARY

The structure and porosity of gold electrodeposits produced by conventional direct current plating and by plating with an asymmetric square wave alternating current have been studied. Simple electrolytes free from any addition agents or alloying elements were used as well as proprietary alloy gold solutions. It was found that the porosity determined by a 24 hour sulphur dioxide test was reduced by factors which increased the activity of the gold ions in the electrolyte such as higher temperature and increased concentration of gold salts in the electrolyte.

When applied to simple solutions the use of alternating current was found to reduce porosity, and at the same time the structure of the deposit was modified. The change was particularly noticeable at 20°C when the direct current structure of loose tangled laths became more uniform and compact when alternating current was used. The reverse was true for commercial alloy solutions. Porosity was increased by the use of alternating current and the structure reverted from a solid compact form with direct current to a less uniform and more porous type. This was due to the fact that the alloying element was preferentially removed during the anodic period.

Individual pores were studied using the scanning electron microscope, and two types of porosity were found. Large pores over 0.5uM diameter were usually associated with some form of substrate defect such as embedded particles of polishing compound. Smaller pores which could not be resolved by the scanning electron microscope were detected by the sulphur dioxide porosity test. These pores arise from the failure of adjacent crystals to coalesce during the growth of the electrodeposit and may be termed crystallographic porosit

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1. INTRODUCTION

Electrodeposited gold has been used for many years for its decorative qualities in the finishing of jewellery. More recently it has been applied to the protection of electrical contacts, and 75% of all electrodeposited gold is now used for this purpose. (3) This application is more demanding than that for jewellery and is based on the corrosion resistance of gold and the fact that no oxide film is formed on the surface of the metal. This factor, together with the low resistivity of gold, means that an electrical contact between two gold plated connectors has a very low and constant resistance.

Unfortunately thin gold electrodeposits are almost always porous to some degree, and the pores allow environmental attack on the substrate beneath the gold. All industrial atmospheres contain a few parts per million of hydrogen sulphide and sulphur dioxide, and these small quantities are sufficient to corrode copper which forms the basis of most electrical contacts. The gases attack the copper through the pores in the gold coating and the corrosion product is transported back to the surface of the gold where it spreads to form a thin layer of sulphide. These thin films of corrosion product increase the resistance of a contact and thereby impair its performance.

It is desirable to have a gold electrodeposit with as few pores as possible. One way of achieving this is to use thicker coatings since porosity is known to decrease as thickness increases, but this policy results in coatings which are thicker than those necessary to meet other requirements such as wear resistance. Therefore the porosity of the electrodeposit controls the thickness selected. The gold plated onto an electrical contact forms a significant part of the total cost of the connector, possibly as much as 50-60%. Thus if the quantity of gold required to give adequate protection could be reduced there would be a worthwhile saving in the cost of finished connectors. In order to reduce the amount of gold used, the porosity of the electrodeposit must be reduced. There are two ways of approaching this problem :-

a) New solutions may be developed containing new addition agents or alloying elements.

b) The plating parameters used with existing solutions may be adjusted so as to give optimum values of porosity.

The increased use of gold for the protection of electrical contacts has led to a great increase in research activity on the topic. Originally jewellery was electroplated using alkaline cyanide solutions, but new solutions have been developed based on acid cyanide or other compounds such as gold sulphite. Many of these solutions are claimed to produce low porosity coatings and much research effort is directed to proving it. The situation is confused by the wide variety of porosity tests which are used by different investigators and which preclude direct comparison of results. Different substrate conditions also make comparison very difficult. More recently, independent work has been carried out using a sophisticated pore resistance test to determine the effect of plating variables on porosity. So far, however, little work has been carried out to determine the causes of porosity, although it is known that the condition of the substrate is important. The scope of the previous work is fully described in the following chapter.

In the present work, the scanning electron microscope has been used to study the nucleation and growth of gold electrodeposits and the final structure developed in order to assess how pores arise. Attempts have also been made to study individual pores to gain information about their origin. In order to relate the structure of the electrodeposits to their porosity, a simple sulphur dioxide porosity test has been used to give a measure of porosity in terms of pores/cm^2. This work has been carried out on simple solutions prepared in the laboratory and free from any addition agents, and on commercially available pure gold and alloy gold solutions.

Finally, an attempt has been made to reduce the level of porosity of the gold electrodeposits by plating with an asymmetric square wave alternating current. It has been known for some time that the use of periodic reverse and alternating currents can improve the quality of electrodeposits, particularly from cyanide solutions.(25,28,29,31) Benefits claimed were smoother, stress free less porous deposits. A wide variety of frequencies was used for plating, using both commercial and laboratory solutions.

2. LITERATURE SURVEY

2. 1. Introduction

The aim of the programme of research described in this thesis was to study the structure of gold electrodeposits, and to determine the effect of plating with superimposed alternating current on that structure. To do this, the nucleation and growth of the structure has been investigated. The Literature Survey has therefore been extended to cover electrocrystallisation in general, as well as work specific to gold electrodeposits. Similarly, the section on Superimposition of Alternating Currents, deals with metals other than gold. In both cases, it is reasonable to assume that the principles discussed will be applicable to gold plating. However, the electrodeposition of gold will be discussed first. Since porosity is the most important property of gold electrodeposits it will be discussed in more detail than the other properties, as will the methods available for porosity testing.

2. 2. Gold Plating Solutions

Most gold solutions are based on the complex compound gold potassium cyanide $KAu(CN)_2$. Cyanide solutions have many desirable properties such as stability, low metal ion concentration, high polarisation and therefore good macro-throwing power, the ability to dissolve non-metallic films on the substrate thereby enhancing adhesion, and high cathode efficiency. (1)

These solutions were originally used in the alkaline state but this proved to be unsatisfactory for electrical work on printed circuit boards where the alkaline electrolyte tended to attack the plastic laminates of which these boards are constructed. Fortunately it was found that when gold potassium cyanide was dissolved in organic acids, stable solutions resulted. Citric acid and phosphoric acid were both found to be suitable, and many neutral and acidic plating baths were developed which did not attack printed circuit boards. If ammonium citrate or phosphate is used instead of citric or phosphoric acid, well buffered solutions within the pH range 4-6 can be obtained. These solutions retain the advantages of the earlier alkaline baths, and have found widespread use for electrical work.

The various types of cyanide gold plating baths available have been set out by Lee (2) as follows:-

1) Strongly alkaline gold baths, pH 11-12.5
   Based on a solution of $KAu(CN)_2$ in excess free cyanide. Operated at about 70°C. It is not possible to produce a bright deposit more than 1 µM thick with this bath which is most widely used in the jewellery trade.
2) Alkaline gold baths pH 8-10
   Based on $KAu(CN)_2$ dissolved in a mixture of phosphates and/or organic acids. These solutions can be operated at room temperature over a current density range 1-8 amps/ft^2.
   Cathodic current efficiency is high, 85-90%, and bright hard deposits are formed. Silver is often added to enhance the brightness and hardness.
3) Neutral gold baths pH 6-8
   Similar to the weak alkaline baths described above but with a further reduction in pH Used at current densities of 1-3 amps/ft^2., cathode efficiency 90%.
4) Acid gold baths pH3.5-5.5
   Based on $KAu(CN)_2$ dissolved in strongly buffered mixtures of phosphoric and/or citric acid. The temperature range

for the use of these baths is from 50-90°C, and the cathode efficiency increases with increasing pH. Agitation also effects the cathode efficiency, and vigorous agitation is needed if high current densities (up to 25 amps/ft^2) are used. With this type of solution it is possible to plate directly onto copper alloys, steel and other common metals since the complexed gold is not easily displaced by the base metals as occurs if acid chloride solutions are used. Alloying elements may again be added to improve hardness and brightness.

2. 2. 1. Properties of Gold Electrodeposits

Each of the solutions described will produce a deposit of different appearance and properties. Disregarding porosity, which will be discussed later, the most important properties of the gold coatings used on electrical contacts are hardness, wear resistance, ductility, and internal stress. Wear is a difficult property to define, and wear tests usually simulate the conditions o actual service. It can lead to a breakdown of the gold coating and hence an increase in porosity. Many specifications insist that porosity tests are carried out both before and after wear tests. Hardness may be taken as giving an indication of wear resistance although there is no direct relationship between the two. Pure gold deposits are found to be too soft for most applications, and in commercial gold plating solutions the gold deposit is hardened by the co-deposition of an alloying element, the most common being silver, nickel, cobalt and indium. In work on several gold plating solutions, Antler (3) found the hardness values set out below, all the solutions being basically of the acid citrate type.

Alloy Content	Hardness V.P.N.
<0.15%	43-82
0.15% Ni	168-232
0.1% Co	222-234

It must be emphasised again that these hardness figures do not indicate wear resistance. For each alloy deposit and application there is probably an optimum hardness value for maximum wear resistance.

Ductility and internal stress are the remaining major properties. Pure gold deposits are considered to be ductile and have low internal stress. However, when alloying elements are added to improve the wear resistance, cracking of the deposit may result. The ratio of stress : ductility is important, since when a certain critical value is exceeded cracking will occur. In his metallographic examination of thick deposits Antler found that alloy deposits containing 0.1% cobalt or 2.5% cobalt + 1% indium both showed a layered structure with severe internal cracking. Since there was no correlation between the crack pattern and other structural features he suggested that the cracks did not grow up with the deposit. He concluded that the cracks appeared in substantially thick deposits, probably while plating was still in progress, after the internal stress had reached a certain critical value. In the thin deposits (up to 5uM) used for contact purposes there would not be sufficient stress to cause cracking, although such deposits might crack if subjected to any deformation during service. In fact, the present work has shown that cracking can occur in a 5uM deposit of commercial alloy gold, particularly when high current densities are used. This has been confirmed by practical users of the solution concerned.

2. 3. Porosity of Gold Electrodeposits

2. 3. 1. Nature of Porosity

Porosity may be defined as any discontinuity in the gold coating which exposes the basis metal to attack by the atmosphere. The hydrogen sulphide and sulphur dioxide present in industrial atmospheres will attack the copper connector beneath the gold and a film of corrosion product spreads on the surface of the contact causing an increase in the resistance of the contact which is undesirable.

2. 3. 1. 1. Size and Distribution of Pores

Ashurst and Neale (6) used a transmission electron microscope to study porosity, the electron beam passing through the pores but being absorbed by the gold, thus forming an image of the pores. They found the pores to be of irregular shape. The number of pores varied from 0.3/cm^2. in thick deposits tested electrographically to 400/cm^2. in thin deposits examined in the electron microscope. Their results were as follows:-

Gold Thickness, µM	Pore Density / mm^2.	Size of Pores, µM
0.04	1580	95% 0.06-0.2 5% 0.3-0.6
0.13	300	0.02
0.26	21	97.5% 0.02 2.5% 1.5-4.0

These figures illustrate the fall of porosity with increasing thickness which is particularly noticeable in the early stages of plating to which these figures apply. Ashurst and Neale found that at a thickness of 2.5µM the porosity became constant, but other work has not supported this, the porosity continuing to fall off as thickness increased. The average pore sizes and densities quoted above are based on observations of very small areas of electrodeposited gold foil in the electron microscope and must therefore be treated with caution. The results do, however, indicate that the average pore size is very small, about 0.02µM or 200Å in diameter. This diameter applies to coatings 0.26µM thick. In the thicker coatings used commercially these pores might become filled in to some degree, making them very difficult to detect, even using scanning electron microscopy, especially when the low frequency with which these pores occur is considered.

Further evidence on the size of the pores has been provided by Leeds.(4) Using the pore resistance test to determine porosity he found that the total pore resistance of a coating of 1 $in.^2$ area and 0.25µM thick deposited from a neutral gold solution was 2.0×10^{-4} $ohms/cm.^2$ If this figure was to be considered as the resistance of one cylindrical pore filled with electrolyte of resistivity 22.4 ohm-cm., then the area of basis metal exposed would be 2.8×10^{-8} $cm.^2$, corresponding to a pore diameter of 2µM. In practice, there would be not one but many pores, probably following tortuous paths rather than cylindrical. Thus the average pore size will again be very small in what is a very thin deposit.

2. 3. 1. 2. Origins of Porosity

The probable causes of porosity may be summarised as follows:- (4)

a) cracking from high internal stress.

b) post plating damage due to wear or mishandling.

c) intrinsic porosity of the electrodeposit itself.

The problems of high stress and wear can be minimised by careful selection of the alloy deposit to be used in relation to the coating thickness required, leaving the intrinsic porosity to be controlled to reduce the overall porosity to an acceptable level. Leeds (4) further analyses intrinsic porosity into two sections:-

1) basis metal effects.
2) electrolyte effects.

2. 3. 2. Effect of Substrate Condition

2. 3. 2. 1. Inclusions

Inclusions, if they are non-metallic and non-conducting, will give rise to pores since no metal is plated onto them. The inclusions may be introduced into the metal during its manufacture, when impurities in the molten metal will be retained and subsequently brought to the surface during rolling, or they may be introduced at a later stage such as the polishing of the substrate immediately prior to plating. It is the second of these mechanisms which is most important, since most metals are polished mechanically before plating. Cathodic cleaning and degreasing treatments which follow polishing will not release inclusions embedded in surface of the cathode. Cooksey and Campbell (5) have produced scanning electron micrographs demonstrating this type of porosity. The micrographs show particles of polishing compound (silicon carbide) protruding uncovered through gold electrodeposits. Ashurst and Neale (6) provided further evidence when they reported a large increase in porosity when they prepared their copper laminate substrate with 240 grade pumice and noted that a treatment such as electropolishing which releases embedded inclusions from the surface brought about a large fall in porosity.

2. 3. 2. 2. Surface Topography

Several authors have studied the effect of surface roughness on porosity. (6,7,8,10) In most cases, however, the rough surfaces were produced by abrasion or mechanical polishing on papers of varying degrees of coarseness. It has been explained earlier that this polishing technique can introduce inclusions into the surface which might themselves cause porosity. Thus an increase in porosity which might be attributed to increased surface roughness may in fact be due to inclusions introduced during the preparation of the rough surface. A further difficulty is that as a given surface becomes rougher, so the actual surface area increases and the effective current density falls as compared with the nominal current density. Some gold plating solutions exhibit changes in porosity as the current density varies (11-15) and so effects attributed to surface roughness could be due to changes in the effective current density.

Obviously, the results from any study of substrate roughness must be interpreted very carefully. The most certain thing that can be said is that for a given weight of gold plated over a given nominal surface area, the coating will be thinner on a rough surface than on a smooth one. It is a general rule that porosity decreases as thickness increases, and so a rough surface would be expected to produce a more porous deposit. This may be the only direct effect of roughness itself, a conclusion reached by Garte (8) who suggested that roughness would amplify the other causes of porosity. The effect of substrate defects and inclusions will be discussed again in section 4. 3. 2.

2. 3. 2. 3. The Metallurgical State of the Substrate Surface.

Clarke and Leeds (9) have shown that for a rolled sheet cathode various 'zones' exist beneath the surface, each 'zone' giving rise to a certain characteristic level of porosity unrelated to that of its neighbours. They determined the porosity index of gold coatings by means of a pore resistance test after etching increasing amounts of gold from the substrate surface prior to plating. They then plotted the porosity index against the depth beneath the original surface to give a 'zone diagram'. Each zone diagram was reproducible for all the metal rolled from one cast of copper, and they attributed the zoning effects to the structural features of the sheet which would have undergone the same mechanical and thermal treatment. Unfortunately, their zone diagrams in many cases extend only to a depth of 10μins., and it has not been determined whether the level of porosity becomes constant at any depth beneath the surface. The fact that their work was carried out on the highly worked outer layers of the sheet may explain the variation in porosity of up to 1000% which they observed.

In contrast to rolled sheet, the reverse side of electroformed copper foil did not show any zone effects, the porosity being independent of the amount of metal removed from the surface by etching in dilute nitric acid. (±5% c.f. ±1000% for sheet) They found this substrate ideal for investigating the effect of plating parameters on porosity, the results of which are described later. The shiny side of the electroformed foil was found to be unsuitable because zone effects were produced, probably due to particles of polishing compound used to clean the stainless steel drum on which the foil is formed becoming trapped in the surface of the foil. There is again no report of how much metal must be removed from the shiny side of the foil to obtain the reproducible level of porosity found on the matt side. The choice of the matt side of the foil is interesting since examination in the scanning electron microscope shows this side to be very rough, but despite this, reproducible results have been obtained.

More recently, Clarke and Chakrabarty (10) have carried out a comprehensive survey of surface conditions and porosity. Surfaces produced by metallurgical polishing and smoothing, mop polishing, chemical polishing, and electropolishing were examined. Annealing at various stages was also investigated. The starting material was again the matt side of electroformed copper foil known to give a reproducible level of porosity. They found that mechanical polishing by mop brought about a high level of porosity, probably due to the large number of inclusions introduced into the substrate surface. When the surface layers of the mop polished substrate were removed by etching, which re-roughened the surface, the porosity fell again and continued to fall as more metal was removed due to the removal of inclusions and worked layers. Metallographic polishing, where the metal is removed by cutting rather than smoothed over, resulted in a reduction in porosity, the effect being more noticeable after annealing. This may be due simply to the smoothing and reduction in area of the substrate.

There is little doubt that electropolishing of the substrate reduces porosity. (6,10) In the case of metals previously polished mechanically, the reduction in porosity is due to the release of particles of polishing compound embedded in the surface. Clarke and Chakrabarty noticed a fall in porosity with increasing polishing time, the fall being attributed to the smoothing of the surface resulting in a thicker and therefore less porous electrodeposit. Similar results were obtained for chemical polishing.

Annealing at any stage tended to reduce the porosity but since annealing the original electroformed foil, and the foil which had been electropolished only with no deformation, also reduced the porosity, it was concluded that stress relief was not the only factor operating and that grain size and recrystallisation were also important.

The grain size of the basis metal is important since the structure of the deposit, and therefore properties such as porosity, is determined by pseudomorphic and epitaxial growth onto the substrate, at least during the early stages of deposition. Epitaxy is the orderly relation between the atomic lattices of the substrate and the deposit at the interface. The difference between the lattice parameters, 2.87Å for gold and 2.55Å for copper, would cause a local stress of 400 tons/in^2. On annealed substrates this stress does not cause porosity and it is difficult to see why the much smaller stresses and strains introduced by mechanical working should give trouble, especially as the rolling of copper would tend to produce a better fit with gold.

The result of pseudomorphism is the copying of grains and micro-irregularities of the substrate by the plated metal, and this is where grain size becomes important. Leeds (4) suggested that there may not be perfect coalescence between adjoining crystals as they grow, but this would imply that a fine grain size increased porosity, which is not the case in practice. The reduction in porosity brought about by annealing, which removes the distorted layers produced by working, also suggests an effect of grain size. However, a fine grained undercoat is found to produce the same reduction in porosity as a coarse grained undercoat (6) suggesting that it is not grain boundaries themselves which cause porosity. Clarke and Chakrabarty conclude that some other 'pore initiator' concentrates at the grain boundaries, such as the micro-crevices present in a worked surface.

2. 3. 2. 4. Undercoats

The importance of the substrate surface condition has led to the use of undercoats, mostly nickel, copper, or silver, in an attempt to reduce porosity, Ashurst and Neale (6) investigated the use of bright nickel, Watts nickel and copper. The porosity of 1-2.5µM gold deposits was reduced to $\frac{1}{10}$ by a nickel undercoat 1.3µM thick, bright and Watts nickel being equally effective. The beneficial effect of the undercoat decreased as the gold thickness rose above 2,5µM, so that at 5µM porosity was about the same as with no undercoat. Bright copper also reduced the porosity, but thicker layers were necessary than with nickel.

Leeds (4) considers that the following factors are important where undercoats are concerned:-

a) Inclusions in the surface must be covered and any pseudomorphic effects minimised. The undercoat must give a uniform, smooth, fine grained, and unworked surface.

b) A less corrodible intermediate layer should be used.

c) The undercoat will be effective only if it has lower porosity than the gold itself would have if plated directly onto the surface, for pores in the topcoat tend to be continuations of those in the undercoat.

Undercoats are often used in practice, particularly in America, to enable a thinner gold plate to be used to give the desired protection.

2. 4. Porosity Testing

Many tests are available for the porosity testing of gold electrodeposits. They may be divided into four basic types of test, electrographic, liquid corrosion, gaseous corrosion, and electrochemical, each of which will be described in a separate section.

2. 4. 1. Electrographic Tests

This type of test has been fully described by Noonan.(16) The specimen under test is made the anode and placed in intimate contact with a printing medium which is impregnated with a suitable electrolyte. The cathode completes the circuit and may also act as a bearing surface to which pressure is applied to force electrolyte into the various openings. When the voltage is applied and the current flows substrate atoms ionise and move into the printing medium where they react chemically with the electrolyte or other reagent to form identifiable reaction products. The amount of metal transfer necessary to produce identifiable pores is found to be less than 100 micrograms/cm^2.

In practice the test specimen is usually flat and sandwiched between two aluminium electrodes. The printing medium can be photographic papers cleared of silver salts, and the electrolyte must be a non-interfering substance which reacts with the indicating reagent. Pressures of 500-2000p.s.i. are used and the current allowed to flow for 1-2 minutes. The print is then developed by immersion in an indicating reagent which reacts with the substrate ions contained in the electrolyte to form a precipitate which marks the site of the pore. In some cases one solution can act as electrolyte and indicator, such as sodium sulphite for a copper substrate, though Noonan reports that better prints are obtained when separate electrolytes and indicators are used.

The disadvantages of electrographic testing are that as described it can be used only on flat surfaces, and on these the pressure applied may cause damage to the gold plate and therefore a false high reading of porosity. That this does in fact happen has been shown by the numerical results of Ashurst and Neale (6) obtained by repeated electrographic testing and transmission electron microscopy, and by the scanning electron micrographs of Cooksey and Campbell (5) which illustrate cracks in a gold coating after electrographic testing.

A further disadvantage of the electrographic test is that the porosity is determined by pore counting. This takes no account of the size and distribution of the pores, large pores being counted in exactly the same way as very small pores. To overcome this problem Garte (17) proposed a test in which the porosity was determined quantitively by dissolving the spots and analysing colourimetrically for basis metal. A visual record can be obtained before the spots are dissolved or alternatively by making two prints, since Garte asserts that there should be little difference between the two, although other work has suggested enlarging of the pores and the introduction of new pores by the pressure applied during the test. Nevertheless, Garte's method does give a quantitive indication of porosity which may be taken as a measure of the amount of corrosion products, and therefore corrosion rate, rather than the number of pores present.

To enable the electrographic test to be used for curved surfaces, Bedette and Chiarancelli (18) suggested using a gel in place of conventional papers. They claimed that this method was simpler to use and accurate since the gel entered the pores. Appropriate electrolytes and reagents are added to the gel and a record is provided by photographing the component after electrolysis. As an alternative to gelatin, plaster of paris may be used, though the plaster cast of the component must be split in half after the test to reveal the pore sites.

Despite the disadvantages of spot counting, electrographic techniques are widely used in industry for quality control purposes since the test can be carried out very easily and quickly and it gives a permanent record of porosity.

2. 4. 2. Gas Tests.

Gas tests are the other type which is often used commercially to assess porosity. Again they involve pore counting and take no account of the size and distribution of the pores. The basis of the test is to expose the plated article to a gaseous atmosphere which is corrosive to the substrate but not to gold. The substrate is then attacked by the gas and the corrosion product is transported back through the pores to the surface of the gold where it marks the pore site. Porosity levels are assessed by counting and are normally quoted as the number of pores in a certain area. Since the pores are to be counted it is essential that the gas used for the test should not be too wet, otherwise spreading of the corrosion product will result. On coatings of high porosity this leads to merging of the marked pores making counting impossible.

In commercial practice (19) gas tests usually involve exposure of the gold plated component to atmospheres containing 1% by volume of either sulphur dioxide or hydrogen sulphide. The latter may be generated within a desiccator by the action of sulphuric acid on sodium sulphide or introduced in a bell jar. The test consists of exposing the component for a minimum of 24 hours in each atmosphere. A longer test has been devised by the Post Office, where an atmosphere containing 20 p.p.m. of oxides of sulphur is used. This atmosphere is produced by burning coal gas enriched with carbon disulphide. Water sprays are also used in this test, the component being exposed to the water and gas for 8 hours, then to air for 16 hours. The cycle is repeated for 60 days.

The length of some of the tests described is a serious disadvantage, and Leeds and Clarke have proposed a faster alternative using a much more corrosive atmosphere of 10% sulphur dioxide. (20) This gas is generated by mixing together sodium thiosulphate and 50% sulphuric acid in a closed vessel such as a desiccator. The required 10% sulphur dioxide is generated within minutes of the start of the test and maintained there by a buffering action of the reactants throughout the 24 hours of the test. This removes the disadvantage of some tests where a fixed volume of gas is introduced which may be lost by leakage. An advantage of the 10% sulphur dioxide test is that the humidity of the gas can be controlled by varying the amount of acid in the reaction mixture without greatly effecting the sulphur dioxide concentration, enabling the pores to be marked very clearly. Leeds and Clarke have used their gas test to confirm the results obtained from their pore resistance test and have found good agreement between the two.

2. 4. 3. Liquid Tests.

Liquid tests are accelerated corrosion tests and are used in America for quality control purposes. Salt spray tests are often used but their effectiveness in marking pore sites depends to a certain degree on the substrate beneath the gold coating, nickel for example being particularly resistant to corrosion in a salt spray.

Liquid tests can be made quantitive. (21) The test then measures the relative amount of exposed substrate surface. While this does not indicate the number of pores it is acceptable because the role of the electrodeposit is to protect the substrate from environmental attack.

Frant (21) has developed a test suitable for gold on copper, a solution of ammonia and ammonium persulphate being used to attack the copper. The amount of copper dissolved is proportional to the amount of copper substrate exposed, the contact time, and the agitation rate. Since the rate of attack is determined by the rate of transport of reagent into and corrosion product out of the pores it is not possible to measure directly the area of copper exposed. In the test described by Frant, the plated components are placed in a solution of 25mls. of concentrated ammonia and 25 mls. of 1M ammonium persulphate solution. The flask is then placed onto a reciprocating shaker and left for 30 minutes, after which the concentration of copper is determined by spectrophotometry and porosity described in parts per million of copper. The difficulties arising with the test are that the degree of agitation is very important and must be standardised, and that specimens of low porosity may require a much longer period of exposure than 30 minutes. It is also essential that any unplated areas are stopped off very carefully, otherwise the copper dissolved from such areas will be far in excess of that removed through the pores.

A development of the liquid test has been described by Tweed.(22) The test employs exactly the same solution as Frant, but makes use of ultrasonic agitation. A considerable saving in time results, only 4 minutes being required as opposed to 30 minutes with mechanical agitation and two days with none. Tweed attributes this reduction to the rapid replenishment of the solution at the corrosion sites due to the removal of surface tension effects which normally block pores. The amount of copper dissolved is determined colourimetrically by comparison with standards containing between 10 and 500 p.p.m. of copper. He suggests that the major part of the basis metal is removed from pits formed after some undermining of the plated layer. The basis metal is dissolved more rapidly after the formation of these pits, and hence the time taken is shorter. No clear evidence is offered for the existence of these pits except that the pores 'open up' if the test is overrun.

2. 4. 4. Electrochemical Tests.

Schome and Evans (23) developed a porosity test which measured the corrosion occurring at the pores in a coating under conditions such that the corrosion rate was controlled by the anodic corrosion of the basis metal. Erhard (1) adapted the test for gold electrodeposits to give a simple anodic dissolution test which assigns a numerical value to porosity which is related to the area of copper exposed at the base of the pores. When gold is made the anode in a sulphuric acid solution at voltages below the oxygen evolution potential, the current which flows is very small. When copper is made the anode under similar conditions, the anodic current density is relatively high. The current density increases with increased voltage until the anode reaction products are formed faster than they can diffuse away. The anode current density is then limited by the rate of diffusion and becomes independent of voltage until oxygen is evolved to disrupt the anodic film. Erhard's test is to measure the current density under steady state conditions and to compare the value to those obtained from specially prepared samples with known areas of copper exposed. He claimed to detect pores with an area of the order of 10^{-6} $ins.^2$

Clarke and Britton (24) developed a test in which the current passed by the coated metal was largely controlled by the resistance of an electrolyte filling the pore channels. If a metal carrying a coating of another metal cathodic to it is immersed in an electrolyte, a current flows between the coating and the basis metal. The potential measured by a Luggin capillary placed against the surface is determined by the initial potential and polarisation characteristics of the two metals, and by the resistance of the electrolyte filling the pore channels.

If a small current is passed through the electrolyte from the coated panel to a separate cathode, then the potential observed will be displaced by an amount V.

If the applied current is i, r is the resistance of the electrolyte, and E is the displacement of the potential of the basis metal from polarisation, then :-

$$V = E + ir$$

If the solution and displacement of potential are such that the coating metal remains inactive, the current passes largely via the exposed substrate and pores.

If the panel has area A and the applied current density calculated on the whole anode surface is I, the total current is equal to the sum of the currents through the pore channels.

$$AI = \sum i = \sum \frac{V - E}{r}$$

When the pores are considered as parallel sided this becomes

$$AI = V - E \sum \frac{1}{r}$$

if the average pore resistance per unit area of coating is R

we have $\frac{1}{R} = \frac{1}{A} \sum \frac{1}{r}$

and $V = E + IR$

$$\frac{dV}{dI} = R + \frac{dE}{dI}$$

If $\frac{dE}{dI} \lll R$, meaning that the polarisation of the basis metal changes little with current density increases, and if R is not affected by the passage of current, the plot of V, the measured displacement of potential against I, the applied current density should be a straight line whose slope is governed by the mean resistance per unit area of the electrolyte filled pores reaching the basis metal. Hence the slope $\frac{dV}{dI}$ may be used as a measure of porosity, a high $\frac{dV}{dI}$ value meaning a low porosity in the coating.

The conditions required for the test are :-

1. the coating shall pass a current negligible compared to the pores
2. there must be no local attack on the coating
3. polarisation of the basis metal must be insensitive to changes in current density.
4. the electrolyte contained in the pores shall be affected by the passage of current in such a way that its resistivity is changed.

Leeds and Clarke (11) found that a satisfactory solution for gold on copper was a solution of 5% sodium sulphate with 0.1% Rochelle salts, and linear V - I graphs were obtained with potential displacements of up to 100mV. It is a relatively complicated test to carry out since a series of values of V and I must be determined before the value of $\frac{dV}{dI}$ can be found. Its main application has been in the field of research where it has been particularly useful in determining the effect of process variables on the porosity of gold electrodeposits (9, 11, 14). The test specimens are not damaged in any way and may be re-tested or subjected to another type of test such as a gas test. Electrochemical tests, when used alone, give no indication of the number, size, and distribution of pores, although the cross sectional area of the pores can be calculated from the resistivity of the electrolyte if the pores are assumed to be cylindrical. Additional tests can subsequently be used to assess the number of pores making up that area.

2. 5. Electroplating Using Modulated Currents.

2. 5. 1. Introduction.

Electrodeposition is normally considered to take place using a direct current, but in practice, due to inefficiences in commercial rectifiers, there is always a small ripple of modulated current present. In some cases, however, electrodeposition is carried out with a deliberately produced modulated current which is considered to have beneficial effects on the properties of the deposit. In these cases the modulated current is much larger than rectifier ripple and often involves a change in the polarity of the electrodes during the cycle, though there is no reversal in interrupted and pulsed currents. Modulated currents showing a reversal of polarity may be classified into three types :-

a) alternating current
b) periodic reverse current
c) superimposition of alternating current on direct current.

While deposition using a symmetrical alternating current can take place in some systems where differing degrees of anodic and cathodic polarisation rectify the alternating current, it is not generally practicable and need not be considered further. Periodic reverse and superimposed alternating currents have been in use since about 1890. Their use has been described by Baeyens (25) who reviewed the literature on the use of modulated currents for electrodeposition.

2. 5. 2. The Development of Plating with Modulated Currents.

Early workers such as Rosing (26) who used a periodic reverse current noted a refining of the structure of the deposit, and that deposits of zinc and copper from sulphate baths were more coherent and less prone to nodule formation. He used relatively low frequencies, 14-30 c.p.s., and cathodic: anodic time ratios varying from 9:1 to 19:1. His work was not immediately followed up but Baeyens emphasises that many other workers subsequently confirmed the smoother less porous deposits. Baeyens pointed out that from the results obtained before 1954 it appeared that most effects produced by modulated currents were more noticeable when :-

a) a definite reversal of polarity took place, some effects not being evident at all without reversal.

b) low frequencies, i.e. below 100c.p.s., were being used. He suggested that the most interesting region probably lies between 10^{-2} and 10^{2} c.p.s., and in that region the effect passes through a maximum, then decreasing with lower frequency.

The use of modulated currents did not become widespread until Jernstedt (27) took out his patents in 1945. These patents concerned the use of periodic reverse currents for electroplating, and the major innovation claimed was to state that the anodic part of the cycle should be long enough to remove at least 10% of the metal deposited during the cathodic part of the cycle. The advantages he claimed were smoother deposits, sounder structure and improved throwing power. The work on which his claims were based was carried out on the deposition of copper from cyanide solution. (28,29) He found it necessary to remove 10% minimum of the metal deposited during each cycle, and a typical average cycle time was 15 secs. cathodic followed by 3 secs. anodic (deplating). Using periodic reverse current he produced smooth, bright, ductile deposits whereas previously bright deposits had often indicated stressed or brittle material. The deposits were also harder and of higher tensile strength than those obtained by conventional direct current plating. Jernstedt emphasised the improved throwing power brought about by periodic reverse plating. Scratches and nodes on the substrate surface were smoothed out and there was less build up on corners. It is interesting to note that these improvements were obtained with cyanide copper, and when acid copper solutions were used instead the improvements were not so marked.

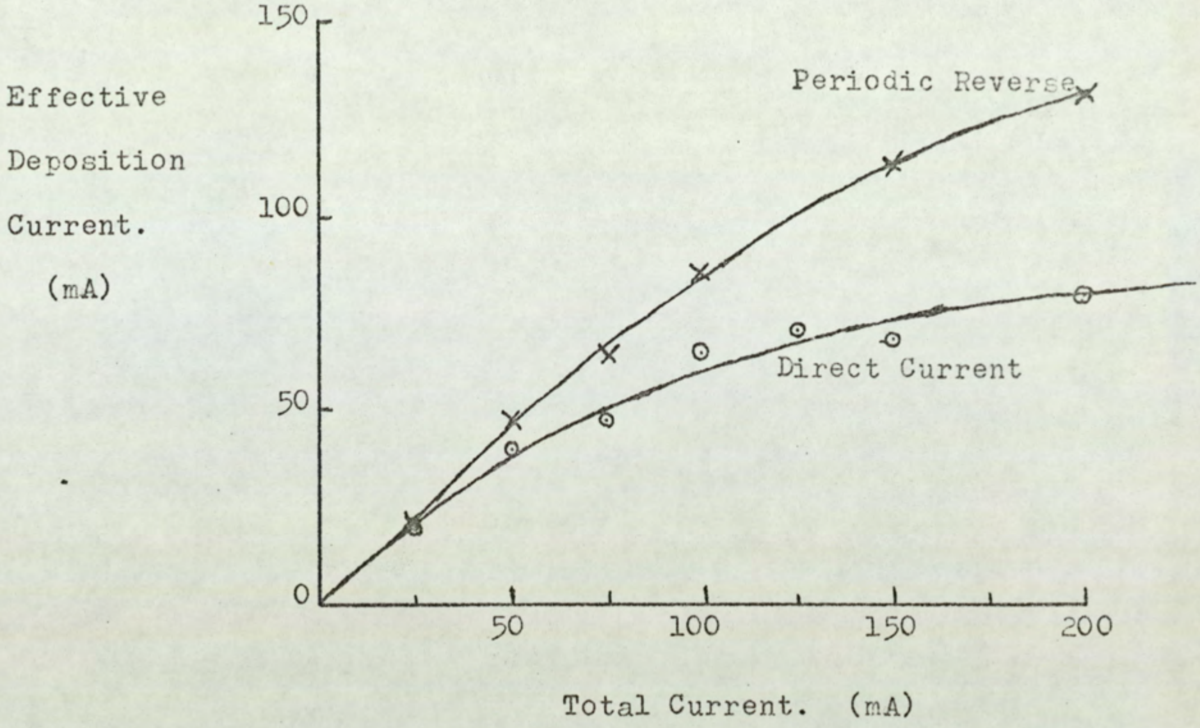
Modulated currents have been used for electrolysis of gold solutions since 1909 when Wohlwill (30) took out patents making use of superimposed alternating current in the refining of gold. He claimed that anodic corrosion was accelerated enabling lower concentration electrolytes to be used. The patent claim stated that the ratio of alternating and direct currents must be selected to ensure that current reversal took place during each cycle. More recently Shenoi et al. (31) have reported the use of an asymmetric alternating current in the deposition of gold from ferrocyanide solutions. They claimed an increase in reflectivity from 60% to 75% and a 'tremendous increase in hardness' without quoting any figures. Shenoi suggested that the use of alternating currents had no effect on porosity but did not indicate how this conclusion was reached, there being no mention of porosity testing or at what level the porosity remained constant. The statement must therefore be treated with caution.

Since the initial work of Jernstedt, the metallurgical and electrochemical aspects of periodic reverse plating have been studied more thoroughly.

2. 5. 3. Periodic Reverse Plating.

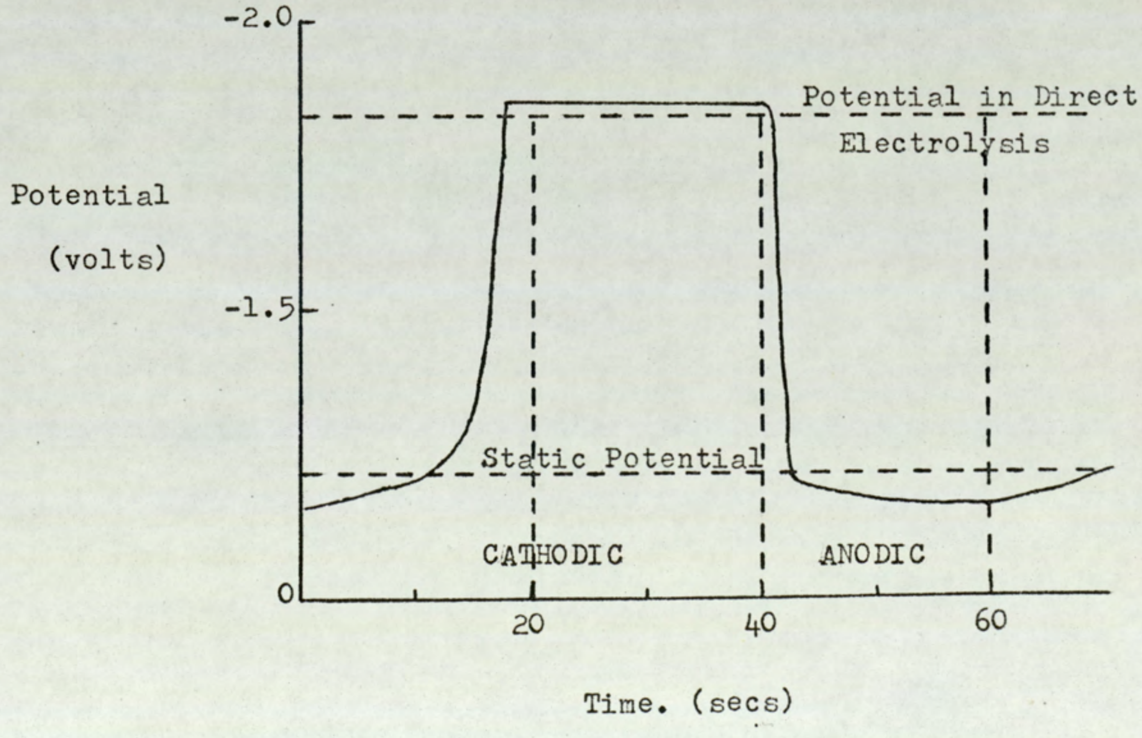
Hickling and Rothbaum (32) looked into the mechanism of the levelling action produced by periodic reverse plating, and the influence of periodic reverse on concentration polarisation. They chose to work on a cyanide solution, and studied the deposition of silver from a solution of 0.5N AgCN and 0.5N KCN. Silver was selected since it should dissolve with 100% efficiency during the anodic part of the cycle. (the anodic polarisation of silver in potassium cyanide is almost zero). The quantity of current passed was measured by a copper coulometer, and by comparing the weight of silver deposited with the weight which should have been deposited by the number of coulombs passing through the coulometer, the cathodic current efficiency was determined. Assuming 100% efficiency during the anodic part of the cycle, the efficiency during the cathodic period was calculated. They found that this was considerably higher than for direct current plating once the current density exceeded the limiting value at which hydrogen evolution commences in direct current plating. Their results are summarised in fig. 2.I.

Hickling and Rothbaum concluded that concentration polarisation was reduced in periodic reverse plating because the metal ions removed during the anodic period increased the metal ion concentration in the diffusion layer adjacent to the cathode surface. Thus,



The relationship between the total and effective deposition currents for the deposition of silver from cyanide solution. (32)

Fig. 2.1.



Potential/time curve for the deposition ofssilver from a cyanide solution.. (32)

Fig. 2.2.

the onset of concentration polarisation was delayed. They confirmed their ideas by plotting the electrode potential / time graph during electrolysis. (see fig. 2.2.). It can be seen that tha cathodic polarisation during the first part of the cycle is approximately equal to the steady potential, but then increases suddenly to much more negative values approaching the direct current potential. The low values of cathode polarisation were observed after every anodic period. Deposition at these low potentials takes place at almost 100% efficiency, and hence the greater effective current density when plating with reversing current as opposed to direct current. Similar results were obtained when depositing copper from cyanide solutions, but when depositing nickel from simple salts the large increase in effective current was not observed, probably because the polarisation of nickel is of the chemical type and not the concentration type found in cyanide solutions of copper and silver.

Interrupted current should produce similar effects, but it was found to be slight unless there was a long period of interruption. Generally, the effect of periodic reverse was diminished by factors which accelerate diffusion, such as higher temperature and agitation. Agitation decreases concentration polarisation and, when agitation and periodic reverse are employed simultaneously much shorter cycle times must be used if the effective current density is to be raised appreciably.

It must be realised that while Hickling and Rothbaum claim large increases in current efficiency at currents greater than the limiting current density, the increase applies only to the cathodic part of the cycle taken separately, the deplating of the anodic period being ignored. If the cycle is considered as a whole then there is little difference between the overall effective current density during cyclic electrolysis and the current density during direct electrolysis. This can be explained by reference to fig. 2.2. where the period for which the cathodic polarisation remains very low is seen to be approximately equal to the time for which the specimen is anodic. Hence the period for which deposition takes place with 100% efficiency merely cancels the period of anodic dissolution at 100% efficiency. Closer examination of the results bears this out since the effective cathode efficiency (overall) using periodic reverse is in all cases similar to that using direct current. (see table 2.I.).

Almost all the work described previously relates to electrodeposition from cyanide solutions. Deposition from simple salts was thought to bring about a finer grain size. Early work on nickel brought no significant improvement in the quality of the deposit, although it will be shown in the following section that more recent work has produced much more interesting results.

2. 5. 4. Plating with a Superimposed Alternating Current.

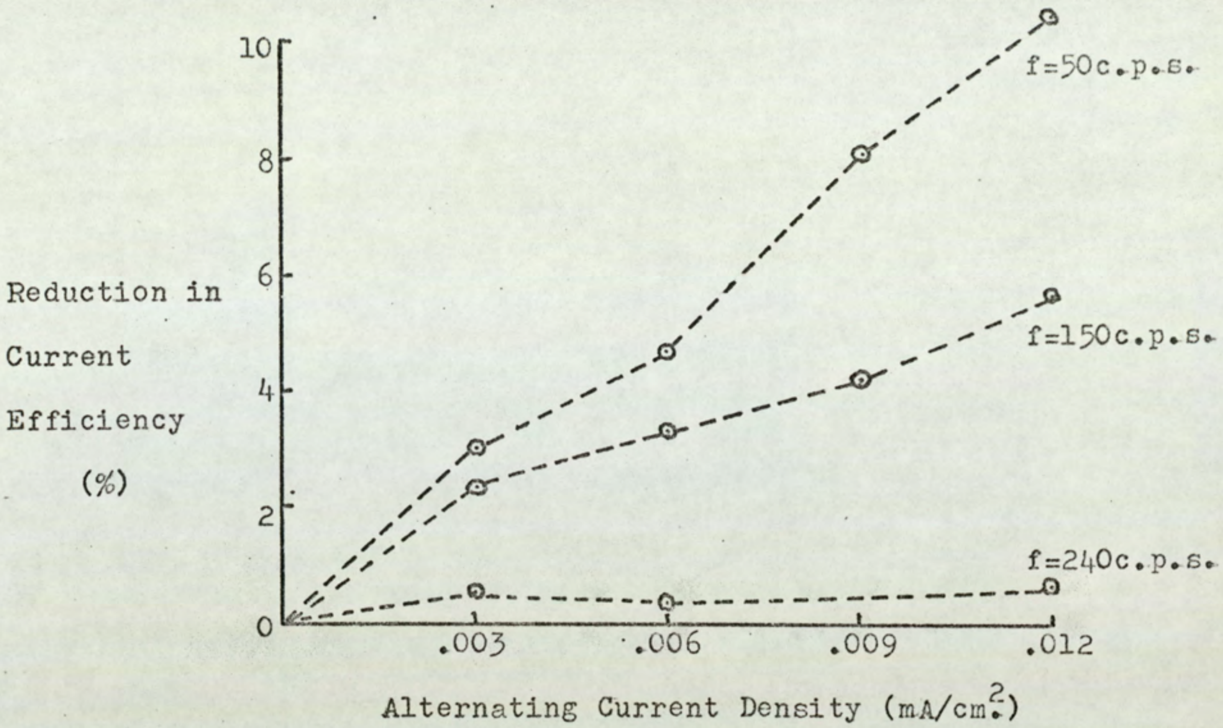
The deposition of nickel using superimposed alternating currents has been widely studied. Izgaryshev and Kudryavstev (33) have shown that the cathodic current efficiency is reduced by its use. Their results are shown in fig. 2.3. which also demonstrate the greater effect of decreasing frequencies. They suggested that during anodic polarisation, a certain amount of oxygen separates out at the electrode which subsequently, during the cathodic period,

Current Applied mA	D.C. Electrolysis Efficiency %	Cyclic Electrolysis	
		Overall Efficiency %	Efficiency during Cathodic Period %
200	39.0	32.0	66.0
150	45.6	48.8	74.4
100	63.0	61.0	80.5
75	63.8	68.5	84.3
50	84.0	91.0	95.5
25	93.0	86.0	93.0

Cathodic current efficiencies during direct and cyclic electrolysis.

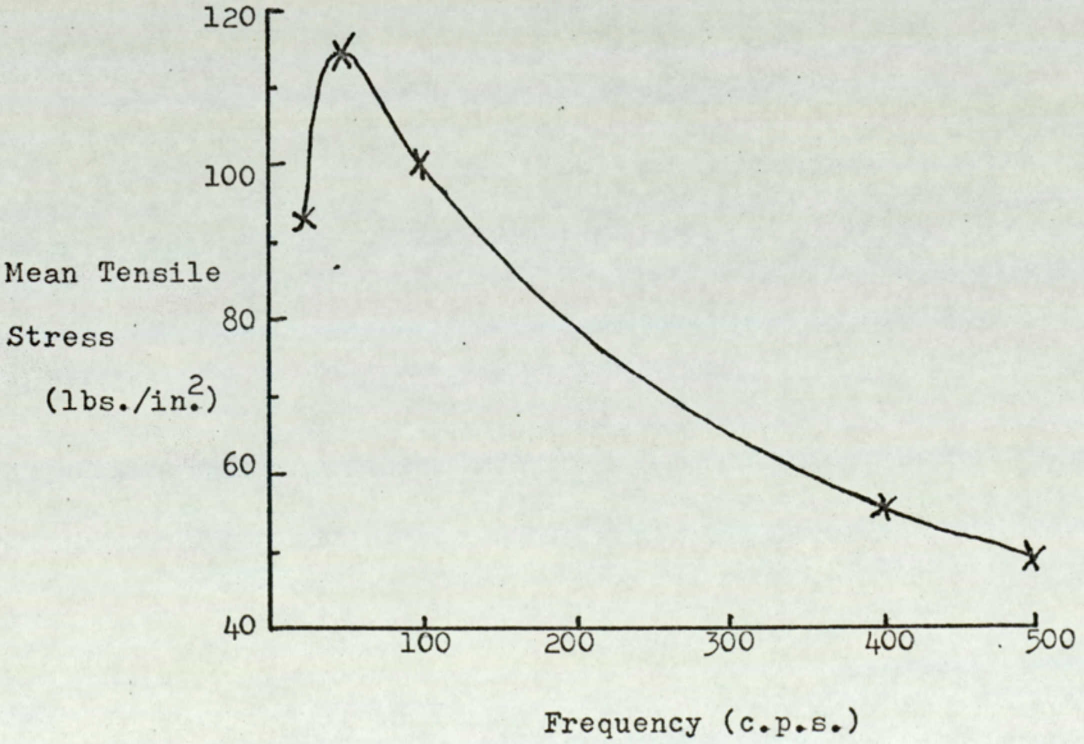
From Hickling and Rothbaum (32)

TABLE 2. 1.



The effect of increasing alternating current density on current efficiency. Direct current density 0.015 amps/dm.^{2} Izgaryshev and Kudryavstev.(33)

Fig, 2.3



The relation of stress to alternating current frequency for nickel deposition. Kendrick.(36)

Fig. 2.4

acts as a depolariser on the discharge of hydrogen, as a result of which the discharge of hydrogen is facilitated and the current efficiency of metal deposition is reduced. However, Hickling and Rothbaum's explanation appears to be more satisfactory, and the reduction in efficiency may be attributed to the efficiency of anodic dissolution being greater than the efficiency of metal deposition in the period immediately following the anodic part of the cycle.

Marchese (34) showed that the internal stress in nickel deposits could be reduced in certain conditions of superimposition and this was accompanied by a change in the structure of the deposit. Vagramyan and Sutuyagina (35) found that if the current density of the superimposed alternating current exceeded that of the direct current, then grain coarsening took place, and that at certain values of the alternating current density, a reduction in porosity occurred. Increasing the frequency of the alternating current increased the porosity until at 500c.p.s. and above it had no effect, another example of the beneficial effect of low frequencies.

The structure and properties of nickel deposited from chloride solutions have been studied by Kendrick (36). He used an asymmetric square wave alternating current on which the anodic : cathodic current density ratio and the anodic current pulse width could be varied, the former from 0.25 to I.5 and the latter from 10% to 30%. The frequency was varied from 10-500c.p.s. By statistical analysis of the results, the effect of individual parameters of the alternating current on the internal stress and ductility were derived. He found that increases in frequency, anodic : cathodic current density ratio, and anodic pulse width all tended to increase the internal stress. The general conclusions were as follows :-

a) Small amounts of deplating were associated with increased tensile stress which was reduced as deplating increased.

b) At low frequencies, 100c.p.s. and below, there was a considerable increase in stress, whereas at high frequencies, 400c.p.s. and above, there was a reduction in stress.

c) Deposits produced at 100 c.p.s. or below were hard and brittle compared with the ductile deposits obtained at 400c.p.s. Increased amounts of deplating tended to improve ductility.

d) At 100c.p.s. or below, deposits were bright or semi-bright changing to white matt at 400c.p.s.

e) Deposits at low frequency were hard compared to those at high frequency.

These results are interesting, particularly those for the effect of frequency which are shown graphically in fig. 2.4. Kendrick suggested that there is a reduction in stress at high frequencies and an increase at low frequencies, but the graph (fig. 2.4.) shows that the stress at 10 c.p.s. is lower than that at 50c.p.s., there being a maximum at 50c.p.s. Baeyens (25) has pointed out that graphs of effect against frequency should not be extrapolated back to zero from frequencies above 100c.p.s. since there may be an inversion, as happens in this case. In fact the use of frequencies below 10c.p.s. may give rise to similar lowering of stress to that produced by higher frequencies. Kendrick did not examine frequencies below 10c.p.s., presumably because of limitations imposed by his power supply.

Kendrick suggested that the explanation for the alteration of the properties by variation in the alternating current lay in the nucleation and growth of the electrodeposit. With Crossley and Mitchell he carried out further work to determine the influence of alternating current on the structure of the deposit. (37) The nickel electrodeposits were examined by transmission electron microscopy, and deposits produced by direct current showed heavily distorted grains and a high density of dislocations. In contrast, deposits produced by low frequency alternating currents were fine grained and had low dislocation density but a high degree of twinning. High frequency deposits were characterised by coarse grain size and a high degree of twinning.

These results show a clear correlation between microstructure and the abrupt change in tensile stress brought about by increased frequency. Kendrick explained the correlation by assuming that deplating either removed the cause of the stress or introduced a balancing compressive stress. The latter alternative seems unlikely in view of the greater purity and simpler structure of the deposits produced by alternating currents. He assumed, therefore, that the source of the tensile stress is removed during plating. To understand this, the mechanisms by which an atom can be deposited on the surface of an existing crystal must be considered. Three possible ways exist :-

a) by incorporation in the lattice site of an existing crystal, probably at steps in the surface.
b) by random deposition and subsequent movement to the correct lattice site by a process of surface diffusion or by diffusion within the electrodeposit itself.

c) by random deposition and subsequent incorporation in the nucleus of a new crystal.

Process (a) has the lowest activation energy and atoms deposited in this way would be difficult to move. Process (b) permits the introduction of tensile stress. There is no need for every vacant site to be filled and diffusion of the deposited nickel atoms can take place within the interior of the crystal after further layers have been deposited. The vacant sites may be left in the lattice and their collapse and removal would cause a decrease in volume and an increase in tensile stress.

Process (c) is dependent on there being an adequate number of dischargeable ions at appropriate points on the surface. While it may predominate at low rates of deposition, as the rate increases a point in reached where the diffusion of ions to the appropriate points is insufficient for this type of growth. At this point, despite the lower activation energy of process (a), process (b) tends to dominate and tensile stresses will develop. If the lattice contractions are such as to cause deformation of the crystal during plating, continuous formation of new surface at slip steps will favour the growth of existing crystals. A brief deplating period provided by the alternating current will permit relaxation and subsequent deposition will take place in conditions favouring process (c). Thus the introduction of an alternating current should lead to a refinement in grain size. During the deplating period, atoms in high energy sites will be selectively removed, and there will be a reduction in stress. These results are borne out in practice, low frequency alternating currents producing fine, undistorted grains, and high frequency alternating current coarser grains but still undistorted when compared to those produced by direct current.

2. 6. Electrocrystallisation.

2. 6. I. Ion Discharge.

The discharge of an ion during metal deposition takes place in three stages :-

a) transport of the ion to the cathode surface.

b) discharge of the ion to form an adion.

c) incorporation of the adion into the growing crystal structure as an adatom.

Three mechanisms operate to transfer the ion from the bulk of the electrolyte to the cathode :-

I. transport by means of electric current.

2. diffusion.

3. convection, which may be due to density gradients within the electrolyte (natural convection) or induced by the use of agitation and/or increased temperatures. (forced convection).

When the ion approaches the cathode surface it enters the diffusion layer, and within this layer transfer to the cathode surface is by diffusion or electric transport, convection playing no part in the diffusion layer. The thickness of the diffusion layer varies considerably, depending on the cathode configuration, temperature, degree of agitation and electrolyte composition. In stirred solutions, the layer has a thickness of approximately IOum, whereas in an unstirred electrolyte this may increase to 500um.

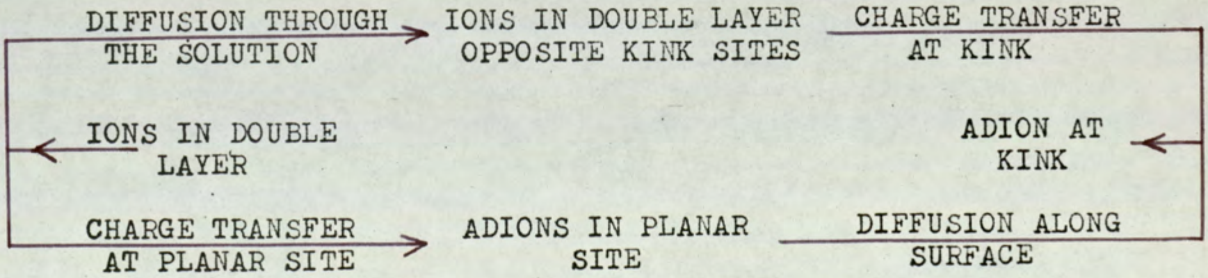
When the ion reaches the cathode surface it is discharged by the acceptance of an electron to form an adion, and ultimately to become an atom in the growing crystal lattice. The sites on the crystal surface at which the ion may be discharged can be summarised as follows :-

a) planar sites,	coordination	number	3
b) edge sites	"	"	5
c) kink sites	"	"	6
d) vacancies	"	"	9

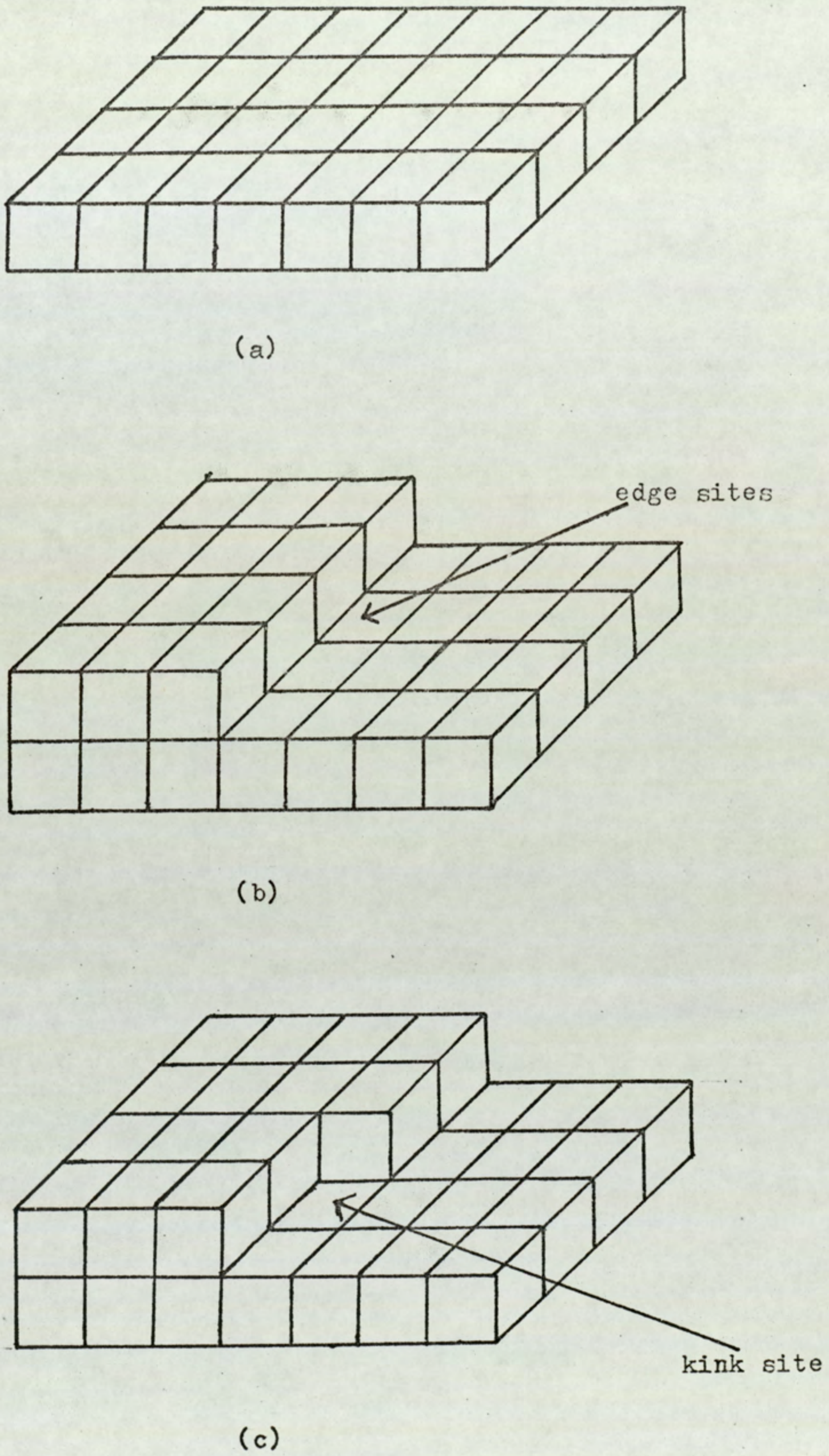
(coordination numbers quoted refer to a III plane in a face centred cubic lattice).

These sites are shown diagrammatically in fig. 2.5., and often arise from the emergence of screw dislocations on the substrate surface.

It can be seen from the coordination numbers that the most stable final position for the atom would be at a vacancy or kink site where the coordination number is high and the energy low giving strong bonding. However, it does not follow from this argument that the ion is in fact discharged at one of these sites. It may be discharged at a planar site and subsequently diffuse to the more stable kink site. Two paths exist for the discharge of ions :- (38,40,)



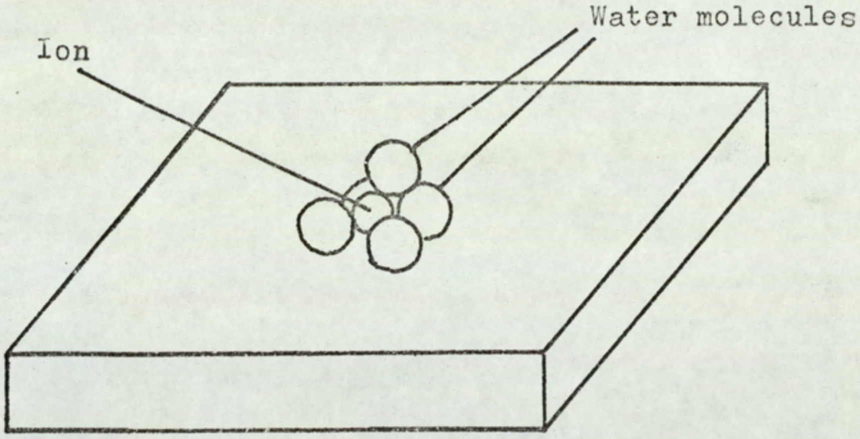
The important question is whether surface diffusion or diffusion through the solution is the controlling factor.



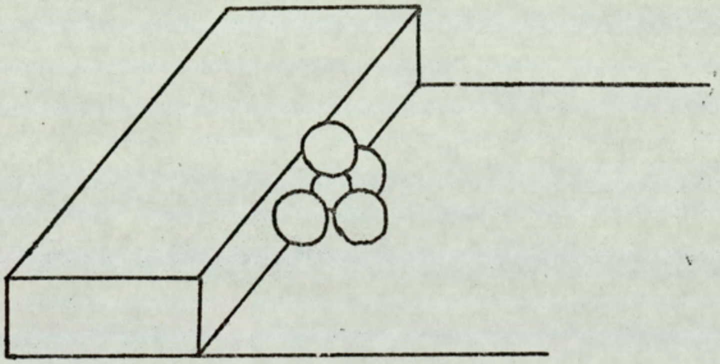
Diagrammatic representation of possible discharge sites on the surface of a crystal showing a) a planar surface b) edge sites and c) a kink site. Conway and Bockris. (40)

Fig. 2.5

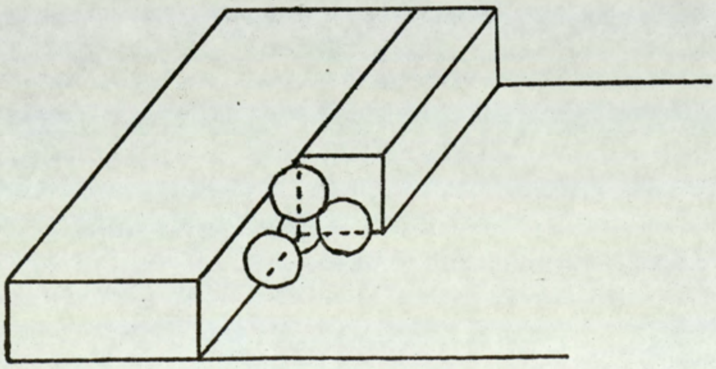
Fleichsmann and Thirsk (39) imply that direct transfer to kink sites is likely preceded by diffusion through the solution. Their deduction is based on the fact that there is a lower heat of activation for discharge at a growth site. This suggestion arose from qualitative consideration of the greater coordination number of an atom at a growth site, i.e. greater bonding lowering the energy in the final state. While this may be true for the final state, it does not necessarily hold true for the intermediate stages when a further factor must be considered. Most metal ions in solution are hydrated and before an ion can be discharged the hydration sheath must be removed. During the transfer process the ion must displace part of its hydration sheath. The amount of displacement will depend on the type of site at which the ion is discharged, and the more displacement needed, the greater the energy required for discharge at that type of site. (see fig. 2.6.) Conway and Bockris (40) showed that this altered the energy levels pertaining during deposition. Although a kink site possesses the lowest final energy, the extra energy necessary to displace the sheath of water molecules is high. Conversely, although planar sites would be high energy final sites, less displacement of the water sheath is required for discharge at this point. Conway and Bockris concluded that the heat of activation for transfer to a planar site was much less than that to an edge or kink site. The difference in calculated heats of activation was large so that the rate constant for transfer to a planar site is likely to be at least 10^6 times greater than to any other type of site. Thus Bockris and Razumney (41) conclude that ions are discharged at planar surface sites, and diffuse along the surface to growth sites. If the overpotential is small,



a) planar surface site



b) edge site



c) kink site

Diagrammatic representation of possible modes of hydration of adions at various sites on the crystal surface. (40)

Fig. 2.6

surface diffusion is the rate determining step, but at higher overpotentials charge transfer becomes rate controlling. Mehl and Bockris (52) showed that this was so for silver deposition.

2. 6. 1. 1. Influence of the Substrate.

The growth sites mentioned, such as steps and edges, are provided by screw dislocations emerging at the surface. It has been shown (42) that there is a critical radius r_c such that a growing layer must have a radius of curvature, r_I , larger than r_c in order to continue growing.

The radius of the critical nucleous is given by

$$r_c = \frac{A . \gamma_{edge}}{\rho_s . R.T. \ln \left[C(\eta) / C_o \right]}$$

where A is the atomic weight of the metal, γ edge is the edge free energy, ρ_s is the surface density in a two dimensional nucleous, $C(\eta)$ is the maximum possible value of the surface adion concentration at overpotential η and C_o is the adion concentration at the reversible potential (i.e. in equilibrium with a straight step). The value of $C(\eta)$ will be related to the overpotential by :-

$$\frac{R.T}{Z.F} \ln \frac{C(\eta)}{C_o} = -\eta$$

It follows from these two equations that as , the overpotential, increases, the value of the critical radius at which the growing layer accepts adions for growth decreases.

If it is assumed that the steps present in the surface arise mainly from pairs of emergent screw dislocations, the average length will be given by

$$\bar{l} = \left(\frac{1}{N_{dis}} \right)^{\frac{1}{2}}$$

where N_{dis} is the density of dislocations intercepting the surface.

However, not all the steps arising from the pairs will be active. If a pair of dislocations is distance l apart, the radius of curvature of the step joining them decreases as the step grows and will pass through a minimum equal to $\frac{l}{2}$. Therefore only those steps for which $l \geqslant 2r_c$ will be able to accept adions for continuous growth. Assuming random distribution of dislocations, the fraction of steps on the surface with length greater than $2r_c$ will be :-(43)

$$P = \exp\left[-\left(\frac{2r_c}{l}\right)^2\right]$$

introducing the previous equations this becomes

$$P = \exp\left[-\frac{4\,N_{dis}\,A^2\,\gamma^2_{edge}}{Z^2\,F^2\,\rho_s^2}\cdot\frac{1}{\eta^2}\right]$$

This equation shows that the fraction of steps which are active increases very rapidly as the overpotential increases and this makes the rate constant for surface diffusion higher, making charge transfer the rate controlling step at higher overpotentials.

2. 6. 2. The Growth of the Crystal Structure.

A wide range of growth forms have been observed on single crystals such as pyramids, layers, spirals, whiskers, and dendrites. The growth form is dependent on the following factors

1) The adion concentration and local current density, which are determined by the overpotential.
2) The activity of the steps and the fraction of the steps which are active. This has been shown to

depend on the critical nucleus size which is in turn a function of overpotential

3) The surface concentration of the different species present in the electrolyte, particularly organic substances. Again this depends on the overpotential.

Thus if a relationship is to be found betwen crystal growth and electrochemical parameters, the overpotential rather than the current density should be considered as the controlling variable, though both are in fact inter-related. The role of the substrate is also important, since while the overpotential is independent of position, the local current density may be dependent on position, thus affecting the structural characteristics. Impurity effects are also important to all normal deposition mechanisms as only a small amount of impurity considerably modifies both the morphological and kinetic aspects of electrolytic crystal growth.

2. 6. 2. I. The Effect of Adsorbed Substances on Electrocrystallisation.

It is well known that the addition of certain organic substances affects to a very large extent the physical properties and conditions of formation of electrodeposits. (44) An important characteristic of these effects is the low concentration needed for their action, Concentrations as low as 10^{-12} moles/cm^3. have been found to produce significant changes in the structure of an electrodeposit. (45)

Two kinds of effect produced by the additive can be discerned :-

a) morphological i.e. changes in microscopic or even visual appearance of the deposit as well as in the structural properties (grain size, stress, orientation and dislocation density.)

b) electrochemical, resulting in changes to the potential / current curves for the particular electrode reaction.

The basic action of addition agents arises almost invariably from their adsorption onto the electrode surface, and hence modification of the steps of the crystallisation process following that of mass transport in the solution. Grain size is often reduced, and this may be qualitatively interpreted as an increase in the frequency of nucleation which results from a higher concentration of adions on the surface. An increase in the adion concentration can only be explained by assuming that the inhibitor hinders a step for which adions are a reactant i.e. surface diffusion or incorporation at a growth site. This in turn requires that the inhibitor be absorbed on the surface to be effective.

Levelling and brightening are important applications of the effect of additives. During electrodeposition without additives, the different rates of growth of different crystallographic faces leads to faceting of the growth surface and hence roughening. Brightening can therefore be explained as an equalisation of the rates of growth of the different crystal planes present in the deposit surface. This assumes that brightening of a surface occurs when growth is uniform at a crystallographic level, an assumption which is supported by the relationship between brightness and texture. The conditions for uniform growth are satisfied when faceting is absent, and hence no preferred orientation develops, (46) or when only one crystal face is present on the surface, i.e. when a smooth single crystal surface grows or when a strong preferred orientation is developed. Correspondingly, bright electrodeposits were observed both in the case of deposits with strong texture and in the absence of any preferred orientation, as well as for smooth crystal faces. (47)

2. 6. 3. The Nucleation and Growth of Gold Deposits.

The growth of gold deposits has been studied by Pashley et al. Their initial work was concerned with deposition from the vapour phase which they were able to observe directly as it took place in the specimen chamber of an electron microscope. (48) They found four stages in the growth of a vapour deposit :-

a) Nucleation. Triangular nuclei were formed in an initial burst during deposition at 400°C. There were between 10^{10} and 10^{12} nuclei / cm^2.

b) Coalescence of the nuclei occurred in less than 0.1 secs. and gave a decrease in the projected area of the nuclei, and therefore an increase in height. Thus the nuclei covered less of the substrate than before, and secondary nuclei were formed in between the islands.

c) Channel Formation. The islands became elongated and joined to form a continuous network structure in which the deposit was separated by channels 50-200 Å wide. Renucleation occurred in these channels and bridging took place at some points.

d) Hole Stage. Most channels were eliminated leaving an almost continuous film containing many irregularly shaped holes. Renucleation took place in these holes and the deposit eventually became hole free.

Pashley followed up this work by examining the electrodeposition of gold from a chloride solution onto a silver / mica substrate. (49) Obviously this process could not be observed in an electron microscope as it took place, and the nucleation and growth was followed by a series of replicas. A constant current generator producing 200 µ amps was used, giving a growth rate of 3.5Å / sec. according to Faraday's Laws. They found that their results were very similar to those for vapour deposition, despite the much lower temperature involved. Embury and Duff, working on copper, have confirmed the similarities of nucleation and growth between vapour and electro-deposition. (50)

Pashley et al. found that the first 10-15Å of deposition made no contribution to the observed film, and suggested that the layer might form an alloy with the substrate, a finding supported by Thomson and Lawless. (51) At 15 Å the deposit was in the form of very thin plates, like islands, giving clear, arced diffraction spots. At 20 Å, the diffraction spots were less arced. The population of nuclei was approximately 4×10^{10} / cm^2 and 22% of the surface was covered. At 50Å, all record of the original nuclei had disappeared, the structure being best described as a continuous deposit containing irregular shaped holes and channels, as was the vapour deposit. Further deposition led to the filling in of the holes and at 80-100Å a complete hole free film was formed.

The continuous pore free deposit at such a low thickness contrasts sharply with the 1500 pores / mm^2 reported by Ashurst and Neale in 400Å deposits. (6) There are probably two reasons for this, the low current density used by Pashley and the perfect, single crystal substrate.

3. EXPERIMENTAL PROCEDURE.

This section is divided into two parts. The first covers the practical details of the electrodeposition and the second the examination and testing of the deposits so produced.

3. 1. Electrodeposition.

3. 1. 1. Solutions.

Acid and neutral electrolytes have been used in this investigation. Both commercially available solutions and solutions made up in the laboratory have been used. They may be summarised as follows :-

a) acid citrate solution

gold as $KAu(CN)_2$	8 gms. / l.
tri-ammonium citrate	100 gms. / l.

pH adjusted to 4 by the addition of citric acid.

b) neutral phosphate solution

gold as $KAu(CN)_2$	8 gms. / l.
ammonium phosphate	90 gms. / l.
phosphoric acid to pH 6	

These two solutions made up in the laboratory from reagent grade chemicals and de-ionised water. A further two solutions, both commercially available, were used, though the exact composition of these solutions is not known.

c) Sel-Rex Autronex CI - an acid citrate solution containing cobalt as an alloying element and also organic addition agents.

d) Sel-Rec Pur-A-Gold - a neutral solution depositing, as the name implies, pure gold but in fact probably containing small amounts of silver and possibly organic addition agents.

The majority of the work described here has been carried out on bath (a) used exactly as defined. In addition this particular solution was used with higher gold concentration of 16 gms./l., and with 1 gm./l of nickel added as citrate to provide comparison with the commercial alloy gold bath (c).

3. 1. 2. Electrodes.

Both electrodes were in the form of rectangular sheets which filled the cross section of the plating cell. Several materials are used as anodes in acid gold plating, the common ones being gold, platinised titanium, carbon, and stainless steel. The last two named are found to contaminate the solution over a period of time, (53) and platinised titanium was therefore selected as the anode material. Practical difficulties which arise from the use of platinised titanium are associated with the breakdown of the platinum film to expose a passive titanium layer. Examination of the platinised titanium in the scanning electron microscope did reveal denuded areas, but these constituted only a very small percentage of the surface area, and were not considered large enough to present any problems.

In any study of the porosity of gold electrodeposits, the cathode material must be carefully chosen and prepared. The reasons for this have been described in section 2. 3. 2. Leeds and Clarke (9) found that the reverse or matt side of electroformed copper foil was ideal for this purpose, but for the present work a surface similar to that used in the production of electrical components was desired. Hence it was decided to use copper sheet as the cathode material, and to use it in a condition which was easily reproduced. Therefore oxygen free high conductivity copper (OFHC) sheet was rolled and annealed to produce a cubic texture. To obtain this, copper sheet supplied 0.2 ins. thick and 50% cold reduced was further cold rolled to a total reduction of 95%. The resulting sheet was annealed for 6 hours at 600°C in a muffle furnace to produce the cubic texture.

After annealing, panels 75 mm. x 35 mm. were cut from the sheet, descaled by pickling in dilute sulphuric acid and polished mechanically down to 600 grade emery paper. This polishing technique was found to reduce the thickness of the sheet to 0.006 ins., leaving the surface approximately in the centre of the original as rolled sheet, thus eliminating the 'zone' effects found in the extreme surface layers of rolled sheet by Leeds and Clarke.(9)

Finally, the copper panels were electropolished to produce a smooth surface and to remove any 'zone' effects arising from the mechanical polishing operation. An area of 2.5cm. x 2.5cm., was marked out and the remaining area stopped off with 'Lacomit'. A 900gms./l. orthophosphoric acid solution was used for electro-polishing, a potential of 1.8 volts being applied across the electrodes for a minimum time of 15 minutes. This treatment was found to remove approximately 1uM of copper per minute. After a few minutes polishing, particles of polishing compound were released from the surface of the copper, and these were removed by washing with a water jet before polishing was resumed. After polishing, the panels were washing in 10% phosphoric acid, tap water and finally deionised water to remove any phosphate films from the surface. The cathodes were transferred wet to the plating cell and used for deposition immediately.

3. 1. 3. Power Supply.

Deposition was carried out with two types of current :-

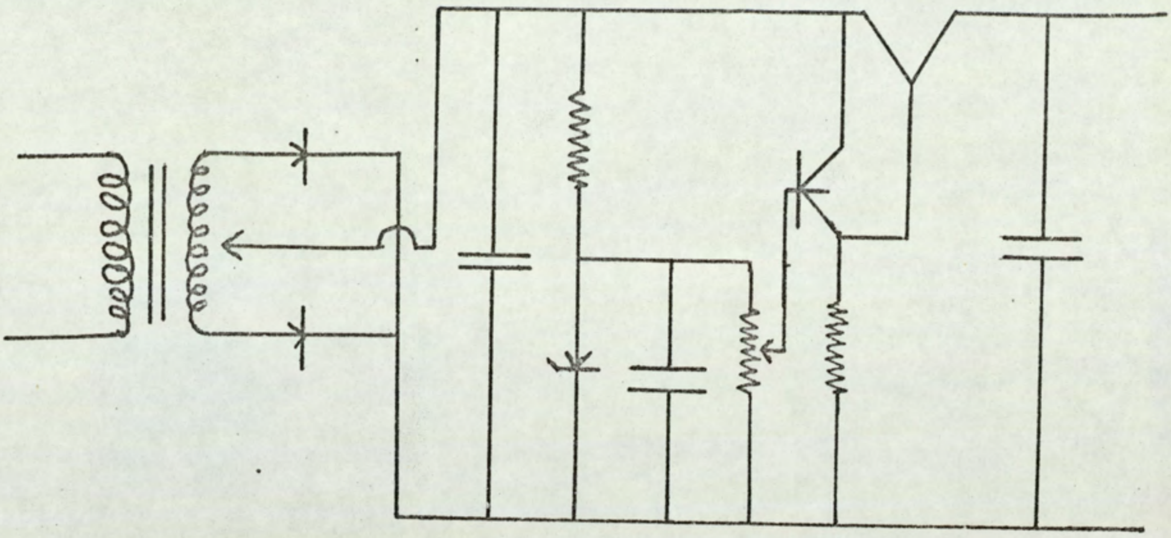
a) direct current

b) asymmetric square wave alternating current

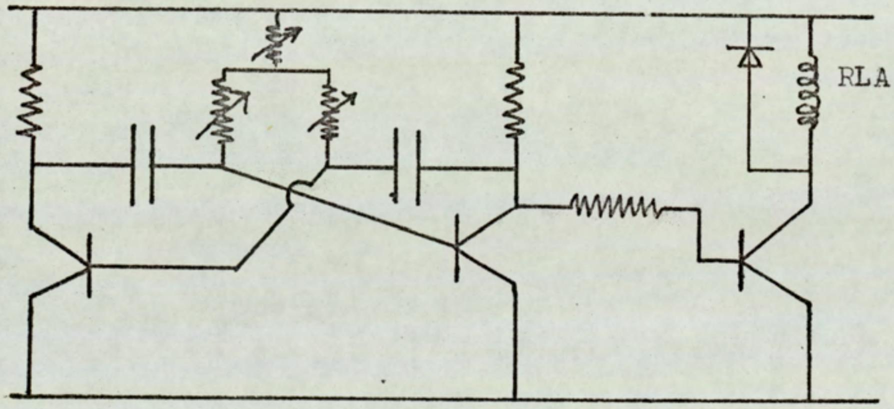
Batteries were used as the power supply for conventional direct current plating since they are known to produce a smooth ripple free current. The current flowing was adjusted by a rheostat in the circuit and measured by a milliammeter.

A specially designed generator was used for plating with an alternating current. Briefly, this generator consisted of two transformers and rectifiers, each producing a smoothed direct current from the mains supply. An electronic 'flip flop' switch was then used to switch the 'positive' output terminal of the generator alternately to the positive side of one direct current output and the negative side of the other. Thus a square wave current was produced. The frequency of the current could be varied from 30c.p.s. upwards to 50,000 c.p.s., and the current flowing in each direction could be altered independently to produce an asymmetric square wave current. The use of transistors in the generator limited the current available in either direction to 100 mA. A circuit diagram of the generator is shown in fig. 3.1.

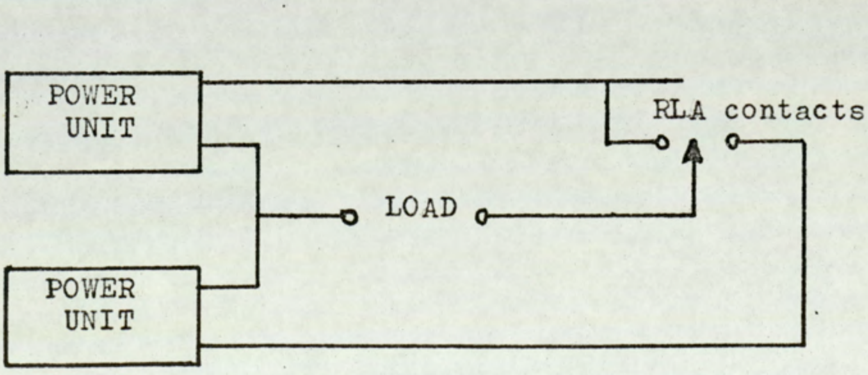
The frequency and shape of the alternating current was checked by an oscilloscope, and very little surge was found at the start of each cycle. Fig. 3.2. is



a) power unit

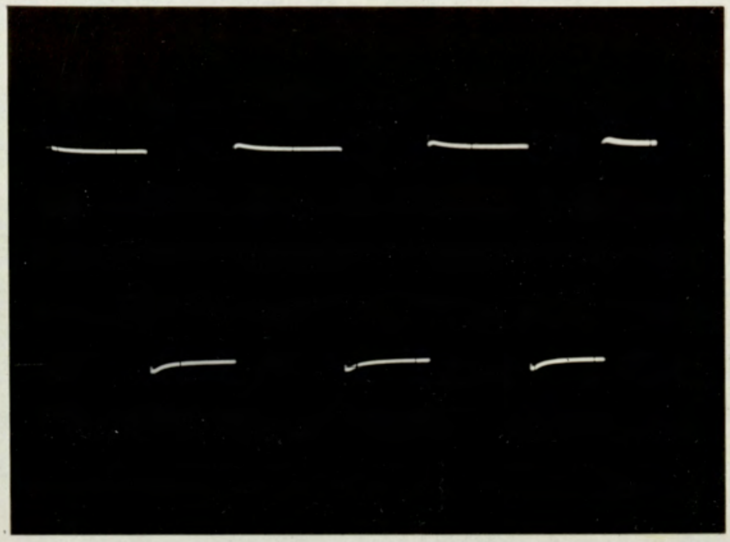


b) electronic 'flip flop'



Circuit diagram of square wave alternating current generator

Fig. 3.1



Photograph of an oscilloscope screen showing a typical waveform produced by the square wave generator.

Fig. 3.2

a photograph showing a typical waveform delivered from the generator. The oscilloscope was placed across a standard resistance in series with the plating cell. By reading the value of the voltage drop across this resistance, the current flowing in each half of the cycle was determined by a simple application of Ohm's Law.

In practice, the most useful frequencies were found to be below 100 c.p.s. At 100 c.p.s., the use of alternating current was found to have very little effect on the structure of the deposit compared to that produced by direct current plating. In view of this, and the small range of the generator below 50 c.p.s., it was decided to use a standard frequency of 33 c.p.s., the lowest produced by the generator. The actual waveforms used are shown in the following chapter in fig. 4. 19.

3. 1. 4. Plating Conditions and Thickness Determinations.

The laboratory solutions described in section 3. 1. 1. were made up as required into 175 ml. samples. Plating was carried out in a rectangular perspex cell containing the 175 mls. of solution. The cell was placed into a thermostatic water bath heated to the desired temperature. Vigorous agitation was provided by a glass propellor rotated at several hundred r.p.m. The exact conditions of temperature and current density at which each sample was plated are set out in the appropriate section of the results in the following chapter.

When a new solution was used, the cathode current efficiency was first determined. To do this, a sample was plated for a time estimated from previous experience to give a deposit about 10uM thick. The copper substrate was then dissolved away in dilute nitric acid, and the gold foil weighed. The thickness was calculated from the weight and area of the deposited foil assuming the density of gold to be 19.1 gms./cc. This procedure was satisfactory for pure gold, but in the case of alloy gold, two difficulties arose. The deposits were highly stressed and broke up when the substrate was dissolved, and the density of an alloy is not 19.1 gms./cc. The first problem was overcome by filtering the nitric acid after dissolution of the copper, burning off the filter paper and weighing the gold. The density of an alloy gold is more difficult fo assess, and since the alloys plated were over 99% gold, it was decided to assume a density of 19 gms./cc. The thickness of all deposits was in any case checked by metallographic examination of cross sections. These were mounted in 'araldite' under vacuum and prepared for examination on the Vickers projection microscope by conventional metallographic techniques. This examination confirmed that the thicknesses determined by weighing, which are average figures, were true for the whole area of the electrodeposits.

After determination of the cathode current efficiency, a series of samples was plated over a range of thicknesses designed to show the development of the structure of the electrodeposit. In general it was not found necessary to examine deposits thicker than 5uM, since it appeared that the structure had reached its final form by this point. Finally a series of panels for porosity testing were prepared as described later.

No additions were made to the plating solution during its period of use. Each 175 mls. contains 1.35 gms. of gold assuming 8 gms./l., and in no case was a solution used after 0.2 gms. had been plated out from it. At this point, or at the end of a series if sooner, the solution was discarded.

3. 2. Examination of the Electrodeposits.

The colour and brightness of the deposits was assessed by visual examination. The structure of the deposit was examined in the 'Stereoscan' scanning electron microscope, and porosity tests were also carried out.

3. 2. 1. Examination of the Structure of the Electrodeposits.

The scanning electron microscope was used to study the structure of the gold electrodeposits. Samples approximately 1cm.x 1cm. were cut from the centre of the plated panels and mounted in the 'Stereoscan' for direct observation. This procedure avoided any non-uniformity at the edge of the electrodeposits, and the use of a guillotine prevented any damage or deformation during the actual cutting of the sample. Since samples could be examined immediately after plating, the risk of damage was virtually nil.

The specimens were mounted in the 'Stereoscan' at an angle of 45° to the electron beam. It should be noted that this gives rise to a fore-shortening effect in the vertical direction on the electron micrographs shown. The magnifications in the vertical direction is reduced by a factor of $\frac{1}{\sqrt{2}}$ compared with those shown for the horizontal direction. The microscope itself was used at 20Kv, and the specimens examined by the secondary electrons emitted from the surface of the sample.

3. 2. 2. Porosity Testing.

A quick reliable test was required to assess the porosity of the gold plated copper panels. Electrographic testing is often used for this purpose, but the pressure used during this type of text is thought to damage the deposit during the test. Gas tests, on the other hand, cannot possibly cause mechanical damage to the electrodeposits, and have the added advantage of being more searching than liquid tests. The sulphur dioxide test described by Leeds and Clarke (20) was therefore chosen to assess the porosity of the electrodeposits.

The basis of this porosity test is to attack the substrate through the pores, the corrosion product marking the pores and enabling them to be counted. The test was carried out in a large glass desiccator of 7 litres capacity. An atmosphere containing 10% sulphur dioxide was generated in this vessel by the reaction of 20% sodium thiosulphate solution with 50% sulphuric acid. Leeds and Clarke recommended a mixture of 4 volumes of thiosulphate to 1 volume of acid for normal use. However, such a mixture was found to produce wet films which spread over the surface making pore counting impossible. A drier gas was found to be more suitable. Leeds and Clarke reported that a higher proportion of sulphuric acid was permissible to produce a drier gas without invalidating the test. A mixture of 125 mls. of thiosulphate with 50 mls. of sulphuric acid was used making 175 mls. or $\frac{1}{40}$ of the desiccator volume in all. This mixture generates an atmosphere containing 10% sulphur dioxide within minutes of the start of the test and maintains it at this level throughout the 24 hours of the test.

In practice, for each set of plating conditions for which porosity tests were carried out, six panels were plated, all of the same thickness. It was decided to standardise the thickness of the deposits tested for ease of comparison, and 1.25µM was chosen. This is somewhat thinner than the normal commercial gold coating, and it therefore gives rather high porosity values. However, this does enable differences in porosity to be detected more easily. The six panels were suspended in the desiccator at least 3 ins. from the bottom and 1 in. from the sides to ensure uniform gas concentration. The reactants were then added and the desiccator sealed. After 24 hours the panels were removed and the number of pores in the central 4 $cms.^2$ of each panel was counted. These figures were averaged to give the final figure quoted in the results as pores / $cm.^2$ A proportion of the samples were examined in the 'Stereoscan' after exposure to the gas test. The exact details of the techniques used for this examination are given in section 4. 3. 2.

4. RESULTS AND DISCUSSION

The results of the examination of the gold electrodeposits in the scanning electron microscope are presented as a series of electron micrographs. The plating conditions relating to individual micrographs are set out beneath the micrograph concerned. Thicknesses quoted were estimated from the cathodic current efficiency for the appropriate conditions. The structures shown were found to be uniform over the whole of the cathode surface, and this uniformity was found to be a feature of the deposits, the substrate having no marked effect on the structure of the electrodeposit.

The first series of results shown all relate to the simple acid citrate solution described in section 3. 1. 1. and illustrate the effect of plating variables on the structure. Later, other laboratory solutions and some commercial solutions are included for purposes of comparison.

4. 1. Electrodeposition With a Direct Current.

The two temperatures used for direct current deposition will be considered separately.

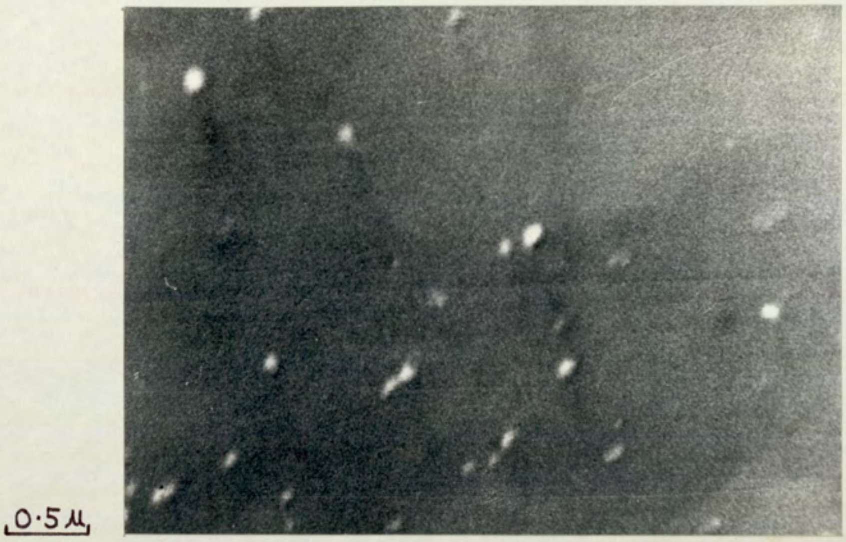
4. 1. 1. Deposition at 20°C.

The cathodic current efficiency of the solution at 20°C was found to be 83% at a current density of 3 amps/ft.^{2} giving rise to a growth rate of 10uM per hour. Thicknesses quoted are based on this growth rate.

The initial bright yellow colour of the electropolished copper substrate began to dull after only 3 minutes plating. (equivalent to a thickness of 0.5uM at 3 amps/ft.^{2}) After 10 minutes (1.5uM) the deposit was a dull brown colour. This colour did not alter appreciably as deposition continued beyond 10 minutes.

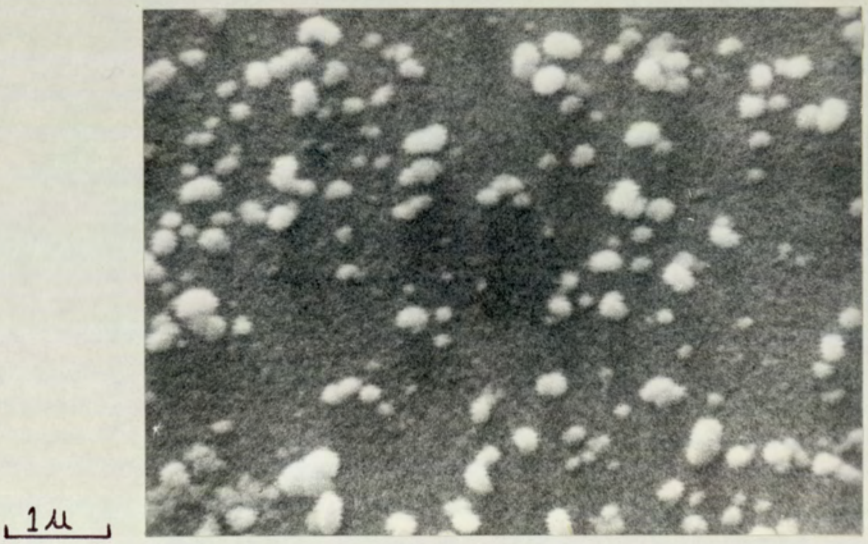
The nucleation and growth of the gold deposit at a current density of 3 amps/ft.^{2} is shown in figs. 4. 1. - 4. 8. Fig.4. 1. illustrates the substrate surface before any plating had taken place. The surface was almost featureless, there being only a few small particles on which to focus. Fig. 4. 2. shows the surface after 30 secs. plating had taken place. Small globular nuclei of no particular crystallographic shape were deposited, the average diameter of the nuclei being 0.25µM. After 1 minutes plating, fig. 4. 3., the number of nuclei had increased considerably and the size ranged up to 0.5µM. Fig. 4. 4. after 1.5 minutes shows that the number of nuclei did not increase significantly between 1 and 1.5 minutes and the size of the nuclei also remained constant during this period. However, closer examination of fig. 4. 4. reveals a fine structure growing between the globular nuclei. This structure must have nucleated during the first few seconds of plating, but until growth had taken place for 1-1.5 minutes and the nominal thickness was 0.25µM, it could not be resolved by the scanning electron microscope because its surface topography was a replica of the featureless copper substrate. At some point between 1 and 1.5 minutes, the growth rate of this structure accelerated and that of the globular nuclei slowed down, leaving them the same diameter after 1.5 minutes as after 1 minute. The fine structure can be seen in more detail in fig. 4. 5. after 3 minutes plating. It was found to consist of small elongated laths, and at this stage it was beginning to overgrow the globular nuclei, reducing the degree of contrast between these nuclei and the background.

Fig. 4. 6. nominal thickness 1.6µM, and 4. 7. thickness 5µM, illustrates the structure finally reached with this solution at 20°C. The structure consisted of tangled laths and the result of further deposition was to coarsen the laths (see figs 4.7. and 4. 8). The surface of the electrodeposit was found to be very rough microscopically which explains the dull brown colouration



electropolished copper substrate

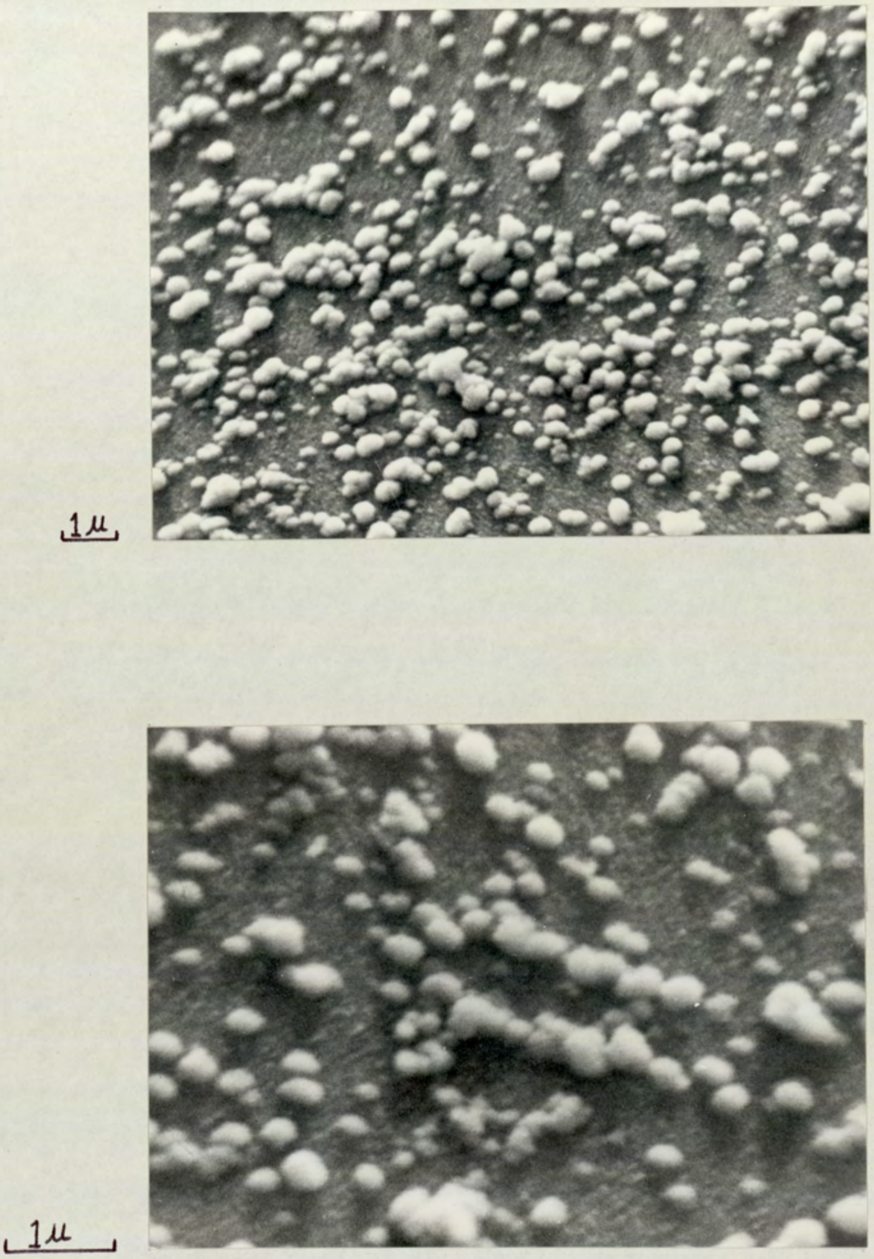
Fig. 4.1



thickness : 0.08μM

temperature : 20°C

Fig 4.2



thickness : 0.16µM

temperature : 20°C

Fig. 4.3

thickness : 0.25μM

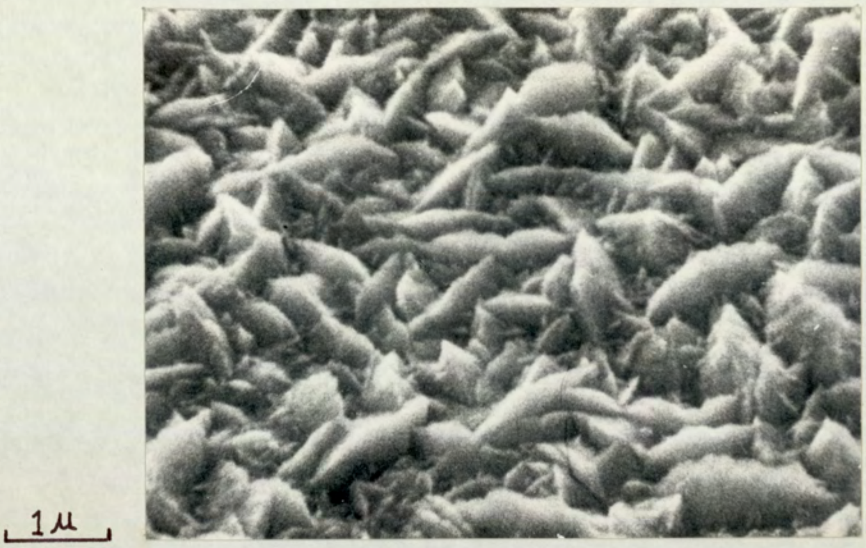
temperature : 20°C

Fig. 4.4

thickness : 0.5μM

temperature : 20°C

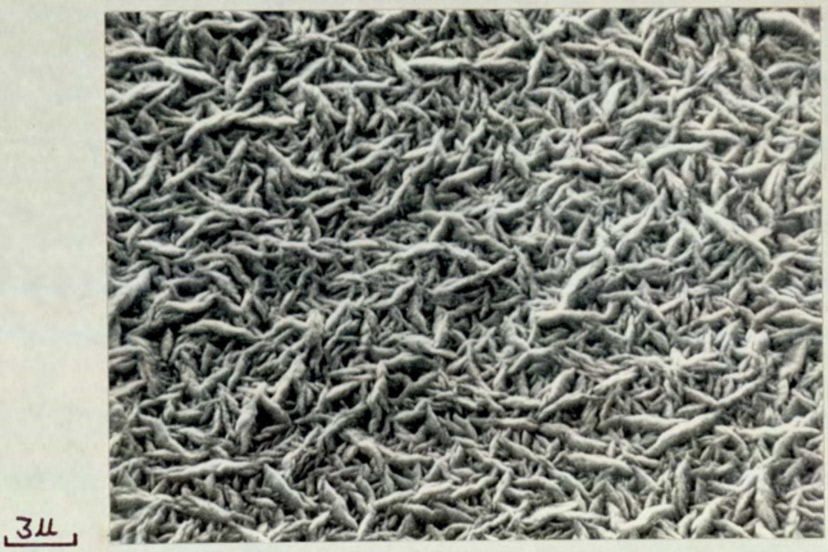
Fig.4.5



thickness : 1.7μM

temperature : 20°C

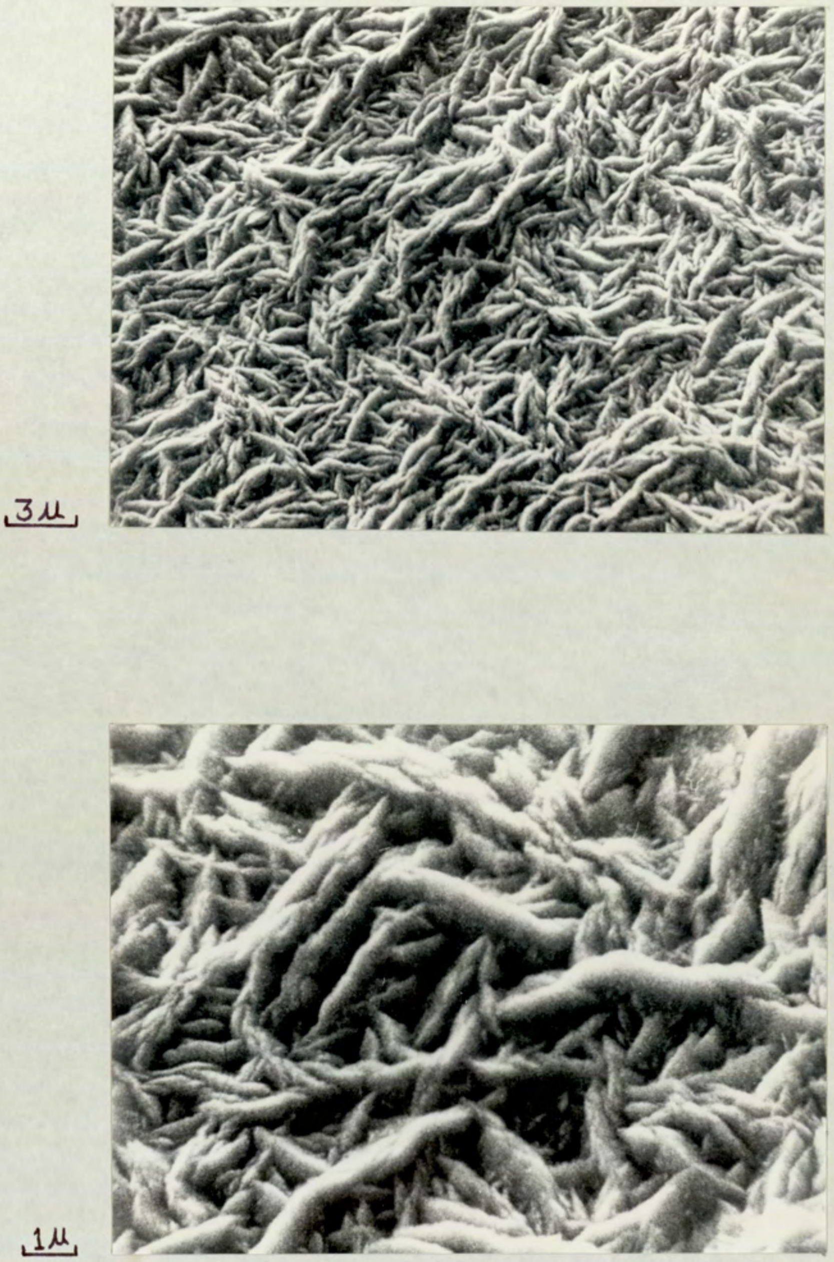
Fig. 4.6



thickness : 5.0μM

temperature : 20°C

Fig. 4.7



thickness : 10.0μM

temperature : 20°C

Fig. 4.8

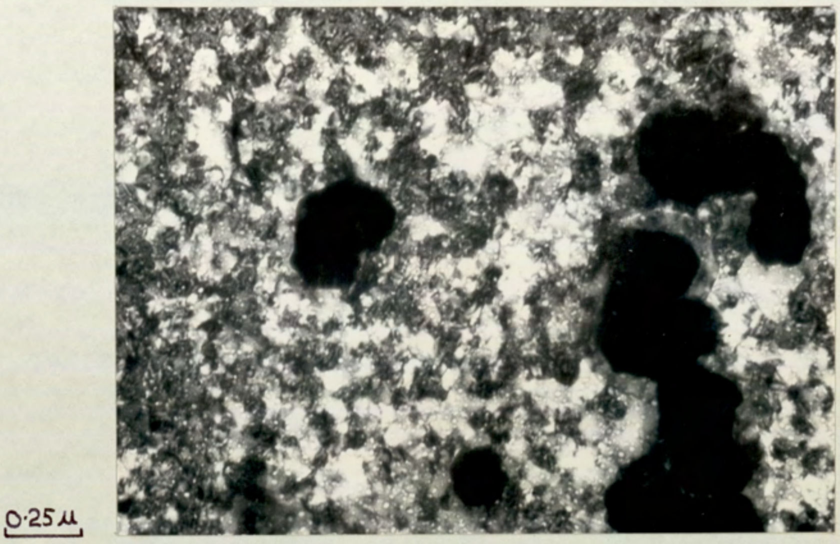
of the specimens. The original bright surface of the copper became bright yellow with an initial flash of gold. This brightness was retained to a thickness of 0.5uM when the lath type structure became predominant and the brightness faded to its final dull brown as it did so.

Examination of the structure at high magnification, fig. 4. 8. showed that the thickness of the deposit was by no means uniform, and the gaps between the laths suggested that some areas of the substrate were covered by coatings far thinner than the nominal value, which could give rise to the higher porosity associated with this type of structure. This point will be discussed more fully in section 4. 3. 4.

4. 1. 2. <u>Discussion</u>.

The type of nucleation found at this temperature is very similar to that observed by Pick and his co-workers in their work on the deposition of copper from acid solutions. (54) They also used OFHC copper substrates and found nuclei of three types, two of which had a definite crystallographic shape and one which did not. They suggested that the positions of these nuclei corresponded to those of inclusions present in the OFHC copper substrate and confirmed this by plating onto high purity substrate from which the oxides had been removed. It seems likely that the nuclei observed in the present work also form on substrate inclusions since they may be seen in fig. 4. 4. to lie in stringers, which is typical of the distribution of inclusions in rolled sheet. Since these nuclei form extremely quickly, it is probable that the energy required for nucleation on the oxide is lower than on the copper itself. Hence many of the gold atoms deposited in the initial layer go to these points. In the scanning electron microscope these nuclei collect and reflect a large proportion of the electrons giving them a bright appearance on a dark background.

It is not suggested that these particles are the only points at which gold is nucleated during the early stages of deposition. Although there is no evidence from the electron micrographs of any nucleation between the large globules, this is due to the inability of the microscope to resolve the structure rather than a failure to nucleate. To confirm that this was so, a panel was plated with gold for a period of 15 seconds in order to obtain a deposit of nominal thickness 0.04μM which should be suitable for examination by transmission electron microscopy. The copper substrate was dissolved away in dilute nitric acid, and although the gold film broke up, fragments sufficiently large to be examined remained. These fragments were collected on electron microscope specimen grids, washed, dried, and examined in an A.E.I. EM 6G electron microscope. A typical transmission micrograph is shown in fig. 4. 9. The structure of the foil was very fine and produced ringed diffraction patterns. Small black particles, too thick to transmit the electron beam, were a feature of the micrographs. These particles could be the globular nuclei seen on the scanning electron micrographs or small particles of undissolved copper. The transmission micrographs show that gold is nucleated over the whole of the substrate surface, and that the areas between the



Transmission electron micrograph of a thin gold electrodeposit. (0.04uM)

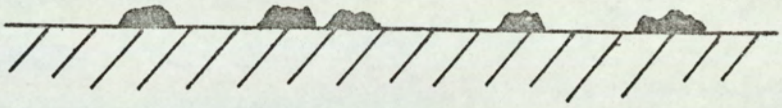
Fig. 4.9

globular nuclei is covered in the first seconds of deposition.

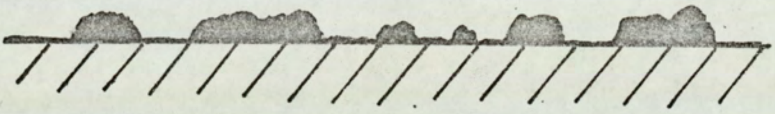
Thomson and Lawless (51) have carried out similar work but plating for much shorter times. Transmission electron micrographs of copper coated with a few angstroms of gold showed that initially gold was deposited in small areas. At 50Å thickness the gold appeared as randomly distributed circular nuclei of no particular crystallographic shape. Their substrate was free from inclusions and hence the nuclei correspond to those in the present work which are formed between the globular particles and which cannot be resolved by the scanning electron microscope. Thomson and Lawless did not continue their work to show the agglomeration of the nuclei, but Pashley et al. did so using a replica technique. (49) Their results have been described earlier (see section 2. 4. 3.), but they also found nuclei in the very early stages and a continuous film by a thickness of 100Å. In the current work with a less ideal substrate, a continuous film containing holes or pores would be expected, as found by Ashurst and Neale. (6) This was in fact found to be the case, although the micrograph in fig. 4. 9. does not show any holes and was selected to avoid doing so.

The whole process of nucleation and growth at 20°C can be summarised as follows and is shown diagrammatically in fig. 4. 10:-

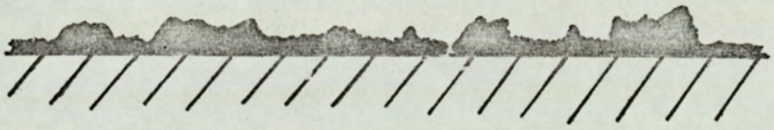
a) The formation of large gold nuclei, probably on inclusions present in the copper substrate. The area between these globular nuclei is covered by much smaller unresolvable nuclei. At this



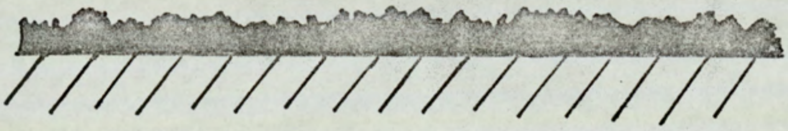
thickness 0.08uM



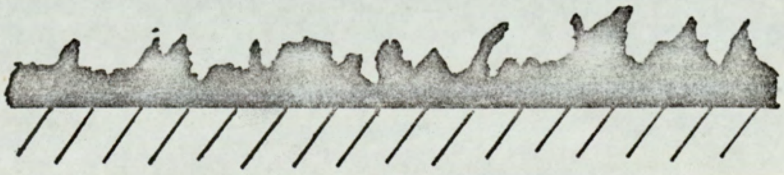
thickness 0.16uM



thickness 0.25uM



thickness 0.5uM



thickness 1.6uM

Diagrammatic representation of deposition from an acid citrate solution at 20°C with direct current.

Fig. 4.10

stage the growth rate of the larger nuclei is faster than that of the smaller ones.

b) The growth of the larger nuclei slows down and that of the structure between then accelerates. There is probably a certain critical size which the small nuclei must exceed before rapid growth can take place, and when this size is reached, the growth of these nuclei becomes energetically favourable and proceeds at the expense of the growth of the original nuclei.

c) At a thickness of 0.5uM the lath type structure overgrows the original nuclei and covers the whole of the substrate surface, becoming coarser as time proceeds.

4. 1. 3. Deposition at 50°C.

The cathodic current efficiency was not significantly altered by increasing the deposition temperature to 50°C, and remained at 83%. However, the electrodeposits remained bright to a greater thickness than at 20°C, becoming semi-bright at 1.25uM and a dull yellow at 2.5uM.

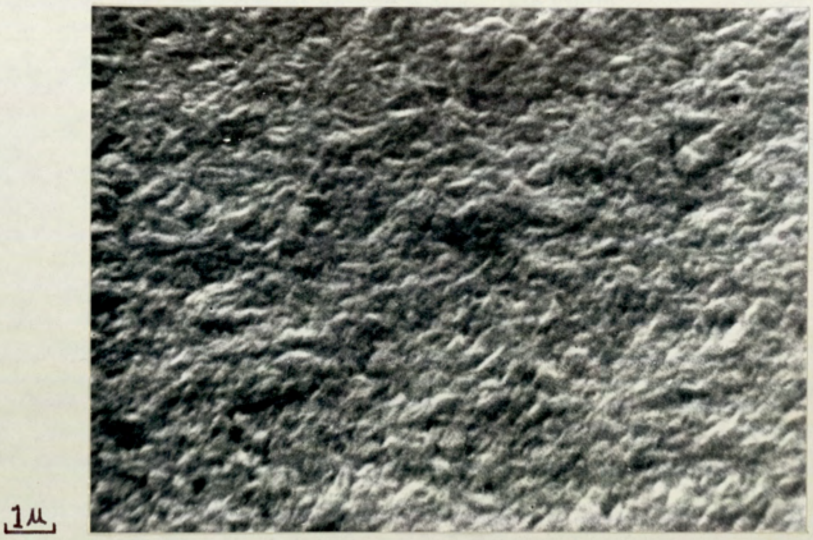
The nucleation and growth was again studied at 3 amps/ft^2. The mechanism was considerably modified by the change in temperature to 50°C which is the temperature recommended for commercial solutions of this type. The globular nuclei found at 20°C and thought to form on impurities in the substrate were not present and examination of the deposit after short plating times revealed a surface similar to that of the polished copper substrate i.e. almost featureless. The structure was clearly too fine to be resolved, and therefore no micrographs are included until a thickness of 1.25uM. (fig. 4. 11), Fig. 4. 12 shows the structure at 3.3uM and figs. 4. 13 at 5uM. At the two latter thicknesses there was little difference between the deposits except for a roughening to the surface as deposition proceeded.

The appearance of the deposits plated at the higher temperature followed a similar trend to that at 20°C, as described above, but the final colour was orange-yellow rather than brown. The 50°C. deposit was more compact and had a smoother surface than at 20°C., but the surface was not sufficiently smooth to give a bright deposit.

4. 1. 4. Discussion.

The main influence of altering the deposition temperature is to modify the diffusion rates, both of ions in the solution and of adions deposited on the growing crystal surface which must move from planar sites to low energy sites in the lattice. The result of altering the temperature is seen as a roughening of the surface at the lower temperature when diffusion rates would be expected to be considerably slower since diffusion rates are approximately doubled by a 20°C rise in temperature. In both cases the surface of the electrodeposit is rougher than that of the original substrate and energy is required to create new surface, the effect being more pronounced on the rougher 20°C deposit.

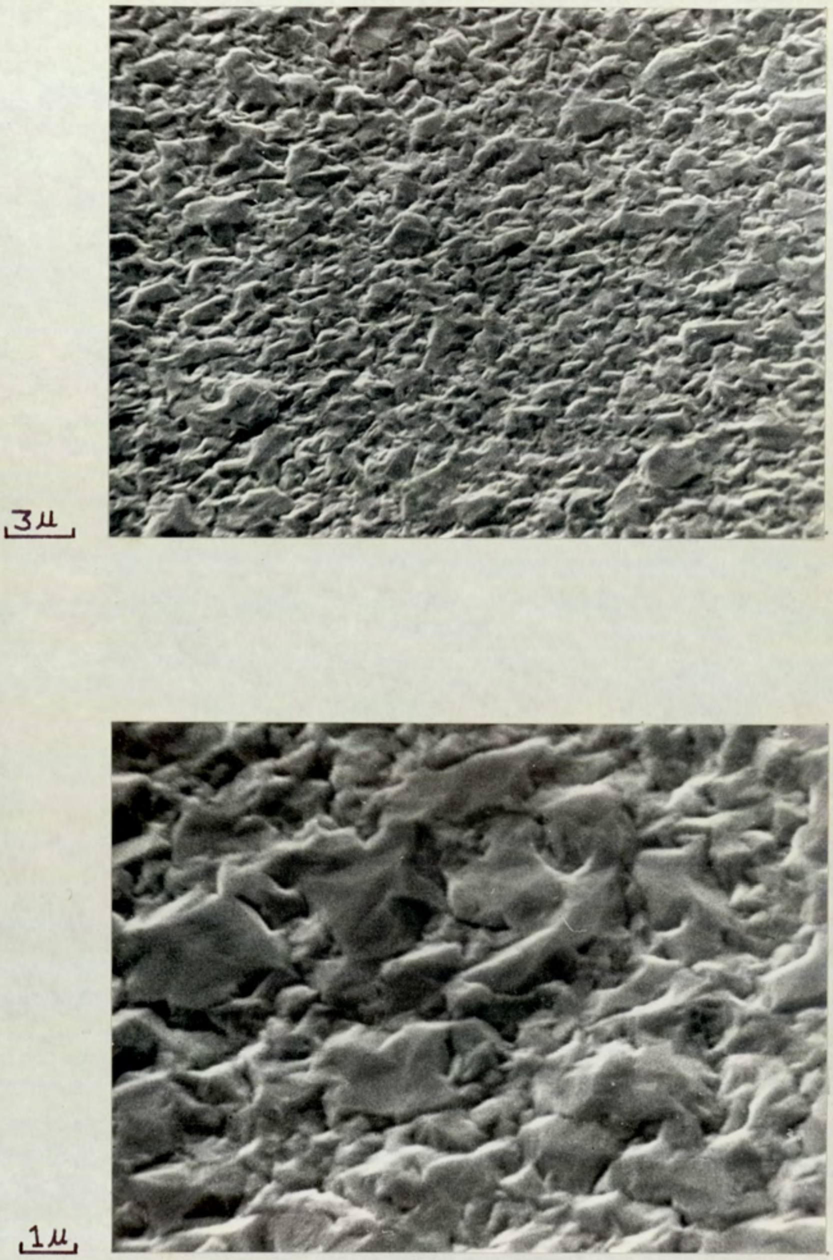
In order to explain the difference in structure brought about by the change in temperature, it is necessary to consider the deposition of individual atoms, a process which has been fully described in section 2. 6. It was



thickness : 1.25μM

temperature : 50°C

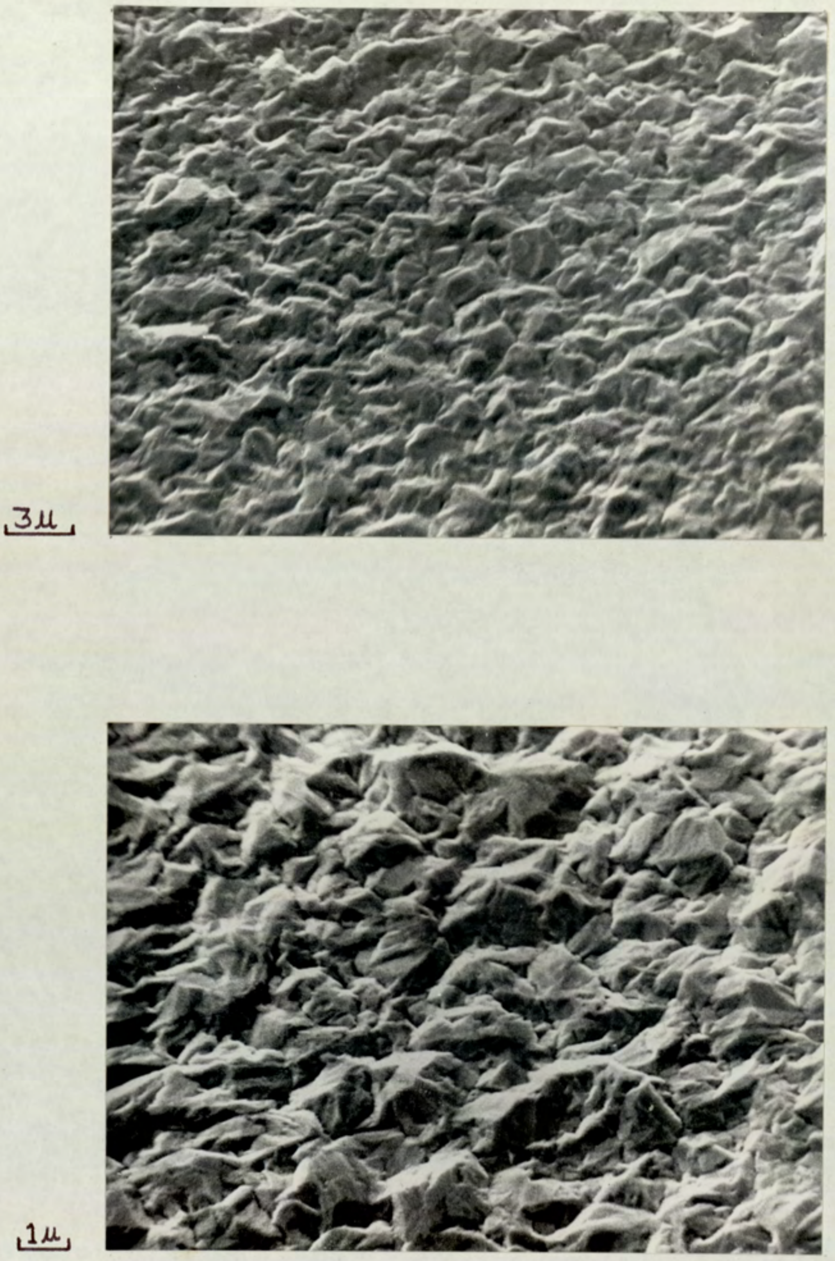
Fig. 4.11



thickness : 3.3μM

temperature : 50°C

Fig. 4.12



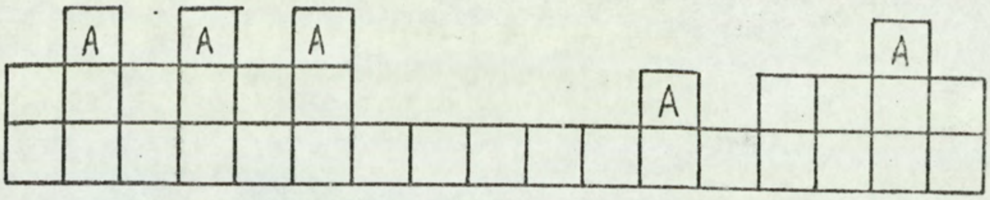
thickness : 5.0μM

temperature : 50°C

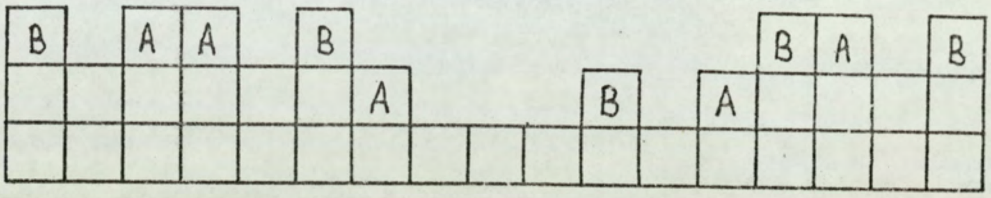
Fig. 4.13

shown that an ion is most likely to be discharged at a planar site and then to diffuse over the surface of the growing deposit to its low energy stable site at a kink or edge on the surface. It can be seen from fig. 4.14 that an atom at a planar site, such as that labelled A, will create new surface, whereas that at an edge site creates less and that at a kink or vacancy none. Thus, if an atom were to remain at a planar site, the surface would be roughened and new surface created on an atomistic scale. However, Bockris and Razumney (43) have concluded that after charge transfer the adion diffuses to its stable site at a kink or vacancy and in this case there will be no increase in surface area. Bockris and Razumney's work relates to perfect equilibrium condition. In practice, at higher current densities, many thousands of atoms will be deposited every second. Thus once an atom is deposited at a planar site it may be trapped by following ions before it has time to diffuse to a low energy site. Once the atom is trapped, diffusion in the solid state is much more difficult than surface diffusion, especially at the relatively low temperatures at which electrodeposition normally takes place. At 50°C, the chances of an adion diffusing over the surface to a stable low energy site are much higher since although the distance to be covered in the same, the diffusion rate is faster. Thus atomistically, the surface will be rougher at 20°C than at 50°C and the surface energy will be higher at the lower temperature.

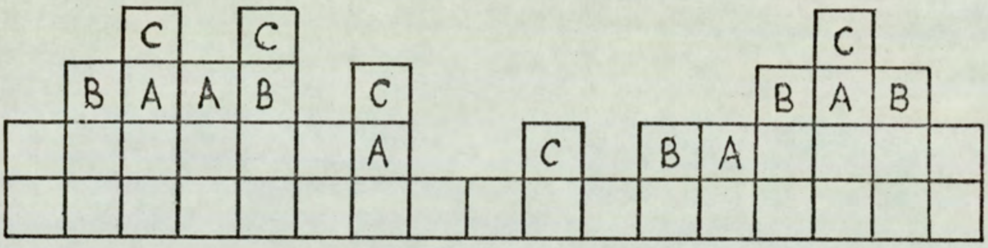
Fig. 4.14 shows the proposed deposition process schematically. In stage 1, atoms marked A are discharged at planar sites. At stage 2 these atoms have started to



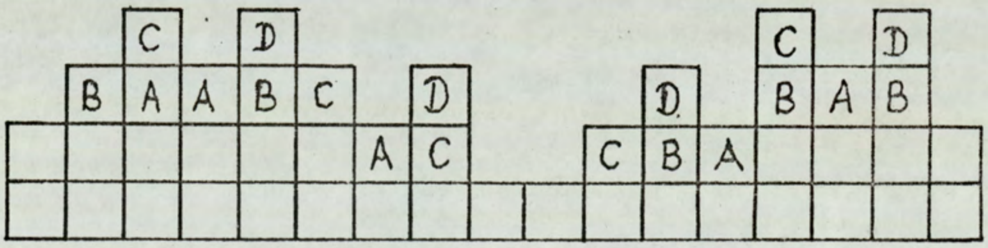
stage 1



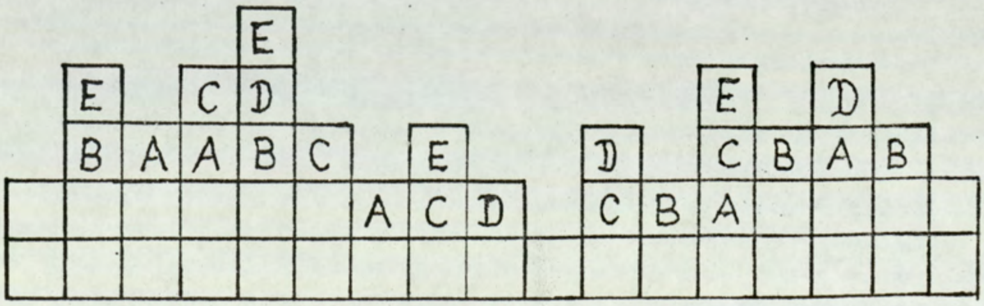
stage 2



stage 3



stage 4



stage 5

Schematic representation of the deposition of ions showing roughening of the surface on an atomistic scale.

Fig. 4.14

diffuse to edge sites but their path may be blocked by the arrival of more atoms marked B. These new atoms create more planar and edge sites for subsequent deposition in stages 3 and 4, cutting the distance which an atom must diffuse in order to reach a low energy site. Thus deposition onto the initially deposited layers is made easier and these areas continue to grow, leading to a roughening of the surface atomistically. Meanwhile, some atoms will diffuse to the original edge sites so that the whole of the substrate surface is covered. Since diffusion rates increase with increasing temperature, the number of atoms reaching low energy sites will be increased by raising the temperature of deposition and therefore the degree of roughness of the surface would be expected to fall as the temperature rises, as has been shown to occur in practice.

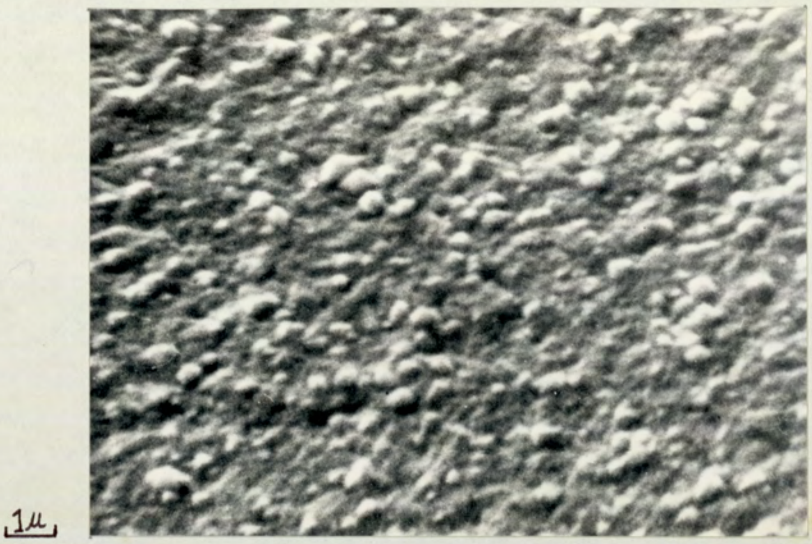
The creation of new edge sites and the reduction in the distance which an atom must diffuse to reach a stable site makes outward growth of the projecting areas easier, possibly explaining the sudden increase in the growth rate of the fine structure observed at 20°C. The tendency for the outward growing areas to continue growing will be increased in gold cyanide solutions by the effect of concentration polarisation which causes a shortage of gold ions available for discharge. The growing nuclei will grab any available ions leaving surrounding areas to grow at a slower rate. The effects of concentration polarisation will also be more pronounced at 20°C since the faster diffusion rate of the ions in the electrolyte will reduce the effect at 50°C.

4. 1. 5. Effect of Variation of Plating Parameters.

Since 50°C produced a more solid, compact deposit structure the current density was varied at this temperature to determine its effect on the structure of the deposit. Some panels were also plated without agitation. Fig.4.15 shows a 1.25uM deposit at 6 amps/ft^2. Compared with deposits of the same thickness produce at 3 amps/ft^2. (fig. 4.11) the surface is rougher. This may be due to the greater effect of concentration polarisation at the higher current density.

At a lower current density of 1.5 amps/ft^2., (figs. 4.16) these was very little change from the structure at 3 amps/ft^2 although a smoother surface might have been expected. It appears that current density changes within the range 1.5-3 amps/ft^2 do not significantly alter the structure of the resultant electrodeposit.

The effect of agitation was studied by removing the mechanical stirrer and plating panels with only the natural agitation provided by gas bubbles leaving the electrode surfaces. Fig. 4.12 shows the structure produced without agitation at 3 amps/ft^2. The surface of the deposit was much rougher and many of the crystals, which were elongated, appeared to have grown outward at the expense of surrounding areas. The lack of agitation considerably reduces the supply of gold ions arriving at the cathode surface ready for discharge and therefore existing crystals which protrude into the electrolyte will grab those ions which arrive and continue to grow at the expense of the surrounding areas. Such an effect

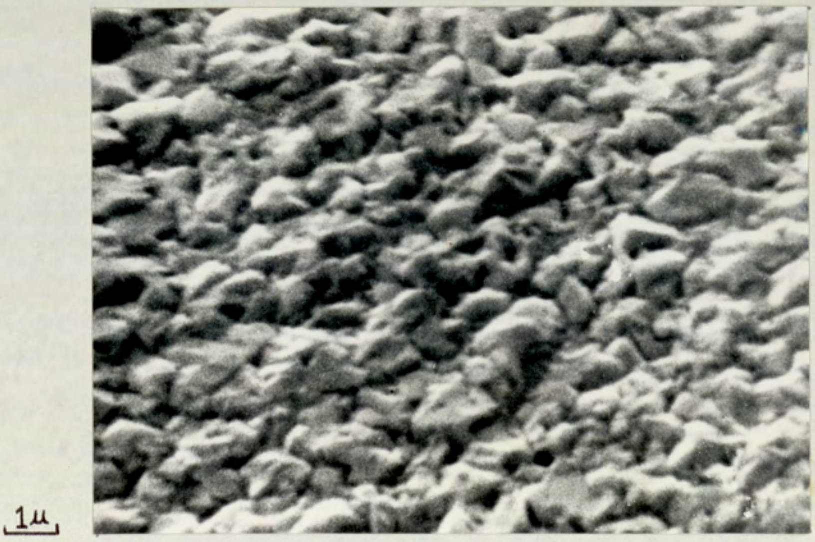


thickness : 1.25μM

temperature : 50°C

current density : 6 amps/ft.^{2}

Fig. 4.15



thickness : 2.5μM

temperature : 50°C

current density : 1.5 amps/ft.^{2}

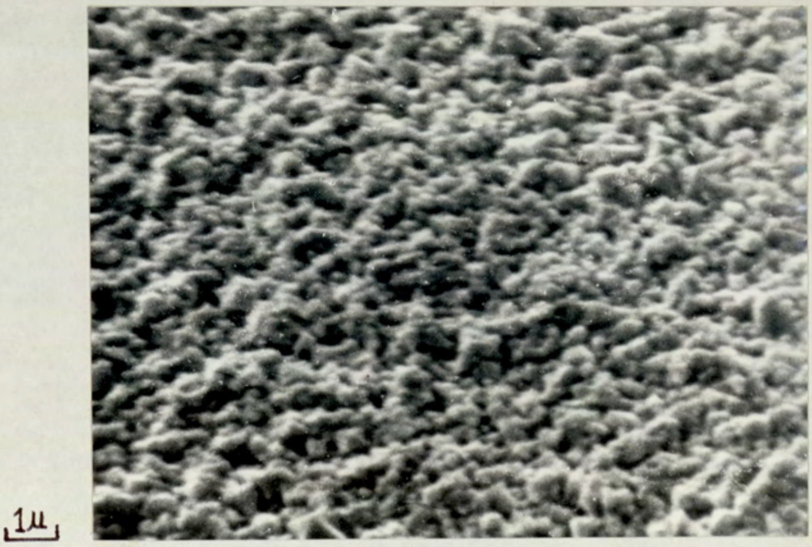
Fig. 4.16

thickness : 1.25µM

temperature : 50°C

current density : 3 amps/ft.^{2} (no agitation)

Fig. 4.17



thickness : 1.25µM

temperature : 50°C

current density : 1.5 amps/ft.^{2} (no agitation)

Fig. 4.18

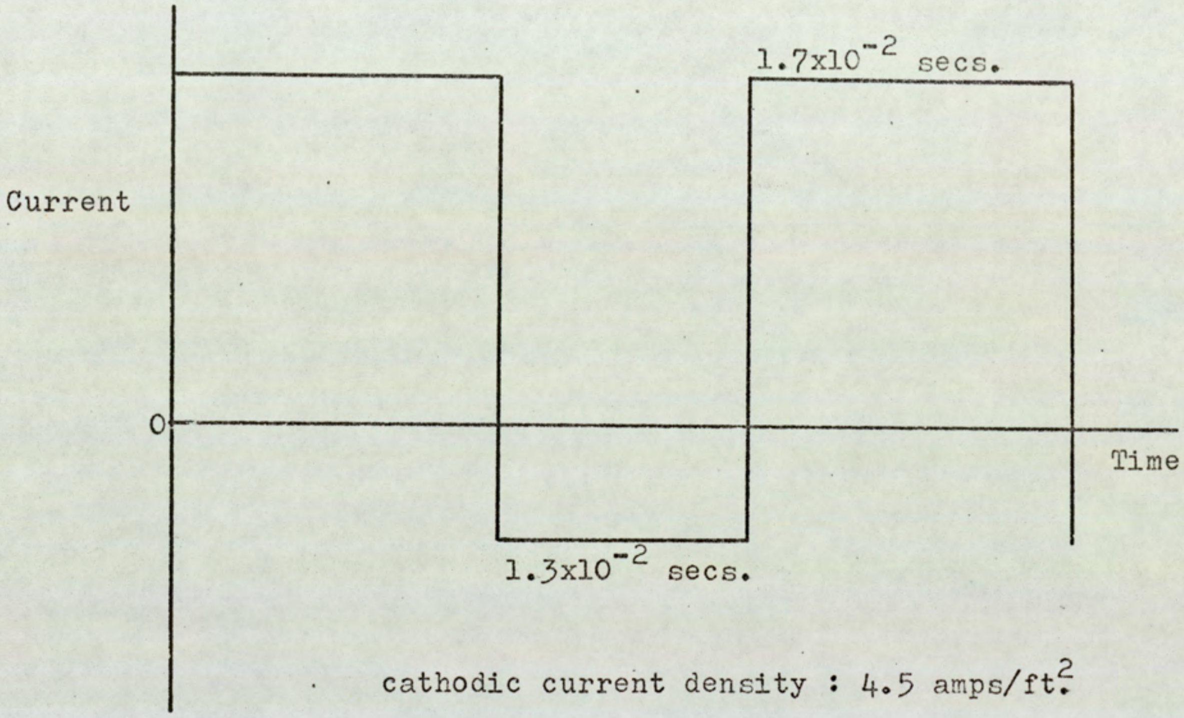
would be expected to be less pronounced at low current densities when fewer ions are discharged in a given time, and fig. 4.18 shows the structure at 1.5 amps/ft^2. In this case the lack of agitation again led to a rougher surface than when vigorous agitation was used.

4.2. Deposition with Superimposed Alternating Current.

The waveform used in the majority of these experiments was an asymmetric square wave alternating current which gives the effect of a symmetrical alternating current superimposed on a direct current. The characteristics of the wave form are shown in fig. 4.19. Where any deviation from this standard waveform has been made the characteristics of the waveform have been quoted at the appropriate place.

The calculation of cathodic current efficiencies for alternating current deposition is difficult since the efficiency with which gold dissolves during the anodic period is not known. It was therefore assumed to be 100% and the current efficiencies have been calculated on this basis.

In the following discussion, the term 'anodic period' is used to refer to the period during the alternating cycle in which the polarity of the electrodes is reversed from that normal in direct current plating, i.e. the copper onto which the gold is being plated becomes anodic for this part of the cycle. The current densities applying in each direction are quoted beneath the electron micrographs e.g. 4.5 : 1.5 amps/ft^2. A.C. refers to a current density of 4.5 amps/ft^2. in the cathodic period and 1.5 amps/ft^2. in the anodic period.



cathodic current density : 4.5 amps/ft.^{2}

anodic current density : 1.5 "

frequency : 33.3 c.p.s.

Fig. 4.19

4. 2. 1. Deposition at 20°C.

The cathodic current efficiency assuming 100% dissolution in the anodic period was found to be 85%, The use of alternating current did not therefore greatly affect the overall current efficiency. The visual appearance of the gold coating was not radically altered and the initial brightness faded to a dull yellow as deposition proceeded.

The early stages of nucleation and growth of the deposit at 20°C were similar to that obtained with direct current in that globular nuclei were first formed on the surface, see fig. 4.20 (1 minutes plating). In this case, the nuclei were smaller and fewer. Again the structure growing between them could be seen at a thickness of 0.25µM (fig. 4.21). Fig.4.22 at 1.25µM thickness shown the initial nuclei being overgrown and the final structure developed under these conditions is shown in fig.4.23 at a nominal thickness of 5µM. This structure shows no evidence of the tangled laths found with direct current at 20°C, and was similar to that produced by direct current at 50°C although the scale of the structure was finer. Thus the use of alternating currents has had two effects :-

a) The early nucleation of globular particles was still present but the number and size of the nuclei were both reduced.

b) the structure growing between the nuclei was changed from tangled laths to a more solid compact structure.

4. 2. 2. Deposition at 50°C.

The cathodic current efficiency at 50°C with alternating current was found to be 85%, exactly as for the lower temperature of 20°C. Deposits were still bright at 1.25µM, but by 2.5µM this had dulled to semi-bright, although

thickness : 0.12μM

temperature : 20°C

Fig. 4.20

thickness : 0.25μM

temperature : 20°C

Fig. 4.21

thickness : 1.25μM

temperature : 20°C

Fig. 4.22

thickness : 5.0μM

temperature : 20°C

Fig. 4.23

the deposit remained brighter than with direct current plating.

At 50°C there was again no nucleation on substrate inclusions and there was a much less marked difference between the structures produced by alternating and direct current. Figs. 4.24-4.27 illustrate the structure of the deposit at various stages of growth up to 7µM thickness. The main difference between alternating and direct current lies in the scale of the structure produced which can be seen by comparing figs. 4.27 and 4.13 when the alternating current structure was much finer than the direct current structure.

4. 2. 3. Discussion.

The mechanisms for the changes in structure brought about by the use of alternating current must now be considered. The most pronounced change occurs at 20°C and this will be discussed first. The initial nucleation was modified by the reduction in the number of particles and the reduction in their size. This type of nucleation was removed altogether by raising the deposition temperature, with or without alternating current. It appears that at 20°C the energy required for nucleation on copper oxide is less than for copper itself and hence the gold ions are discharged on the inclusions. Once these nuclei have been formed they continue to grow by 'robbing' the surrounding solution. At 50°C, however, this is not the case, and the energy for nucleation on copper and its oxide are about the same since there is no record of the position of the inclusions in the structure of the electrodeposit. However, at 50°C another factor is

thickness : 0.62μM

temperature : 50°C

Fig. 4.24

thickness : 1.25μM

temperature : 50°C

Fig. 4.25

introduced. The structure of the deposit nucleated at this temperature is entirely different to that at 20°C. It has already been shown that because of increased diffusion rates at 50°C the deposit is smoother and possesses less surface energy. Since less surface energy is required for its formation, this type of structure can nucleate more easily. Thus it appears that the tangled lath type structure experiences difficulty in growing in the initial stages of nucleation due to the difficulty of the adions diffusing to low energy sites at the lower temperature. As deposition proceeds, more low energy kink and edge sites are generated reducing the distance which an adion must diffuse to a stable site and increasing the growth rate.

The final structure produced by alternating current at 20°C is similar to that produced by direct current at 50°C. It has been shown that this structure arises from the increased diffusion at the higher temperature. Alternating current will produce the same effect in three ways :-

a) During the anodic period which constitutes 43% of the alternating cycle, there will be further time for diffusion to take place. Re-arrangement of atoms is known to continue after deposition has finished.(49)

b) There will be dissolution of a proportion of the deposited gold atoms during the anodic period. The atoms which are removed will be those in the high energy positions and not those in stable sites. The net result will be an increase in the proportion of atoms deposited in stable sites, thereby producing a structure with lower surface energy.

c) During the anodic period, more ions will diffuse from the bulk of the electrolyte to the cathode diffusion layer, particularly as the gold is in a negatively charged complex. These ions together with those removed from the deposit surface will increase the concentration and therefore the activity of the gold ions in the diffusion layer leading to more uniform deposit structure.

The use of alternating current can therefore be said to have aided the progress of the discharged adions to low energy sites in the lattice and to have increased the activity of the gold ions in the diffusion layer to offset the increased rate of deposition in the cathodic part of the cycle.

At the higher temperature of 50°C the effect of alternating current was much less noticeable, there being merely a refining of the structure. Kendrick et al. (36,37) predicted that the introduction of an alternating current would lead to a refinement in grain size from their work on nickel. (see section 2. 5. 4.) In this case, all the factors leading to a stable structure are operating at the same time, and hence nucleation would be expected to take place at a large number of places. Growth would take place from these nuclei in a uniform manner leading to a very fine grain size and a smooth deposit, which is found in practice.

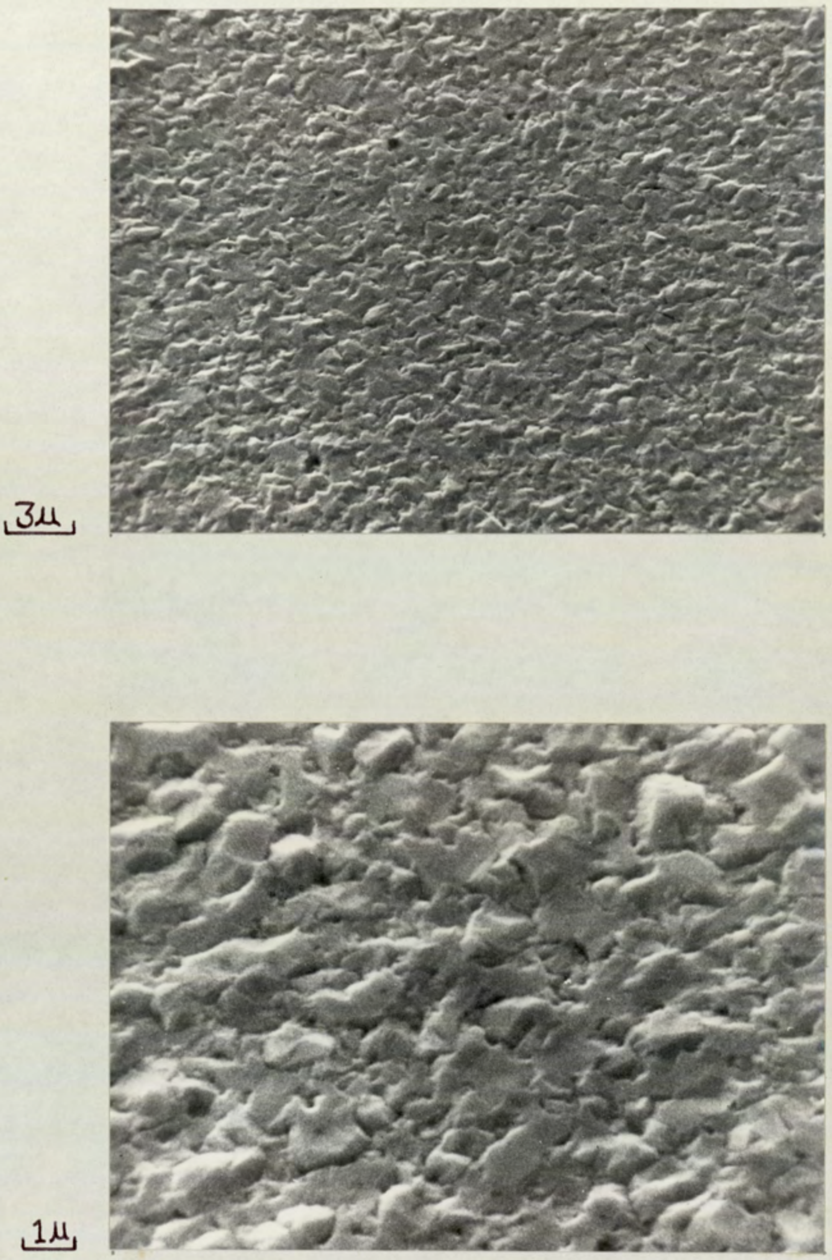
4. 2. 4. Variations in the Characteristics of the Alternating Current.

The two parameters of the alternating current which were varied were the frequency and the size of the current flowing during the anodic period.

· The effect of increasing the frequency from the 33c.p.s. used previously is shown in fig. 4.28 which show the structure produced by the waveform shown in fig. 4.29a, the frequency being 600c.p.s. The structures were very little different from those produced by direct current at 50°C, figs.4.12 and 4.13. It was concluded that the effect of alternating current was more pronounced at low frequencies. In tests carried out at 20°C it was found that the tangled lath structure was not modified until the frequency fell below 100 c.p.s. Fig. 4.30 shows a 20°C structure at 400 c.p.s. (fig.4.29b) to be exactly the same as the direct current structure. The reason for the lack of sensitivity to high frequencies is presumably the lack of time for diffusion to take place. This effect was also noted by Baeyens.(25)

Since the equipment available would not generate a frequency below 33 c.p.s., no work was carried out at frequencies below this figure. In his survey of the literature, Baeyens noted that there was often an inversion of an effect as the frequency fell below 1 c.p.s. If lower frequencies had been used in the present work it is probable that there would have been a frequency below which no modification of the structure took place. At low frequencies a relatively thick layer would be deposited in the cathodic period, and since diffusion takes place far more easily on the surface, there would be very little re-arrangement of the layer plated first. As a result the modofication of the structure would be less marked.

The size of the current during the anodic period was also increased and fig. 4.31 shows the result

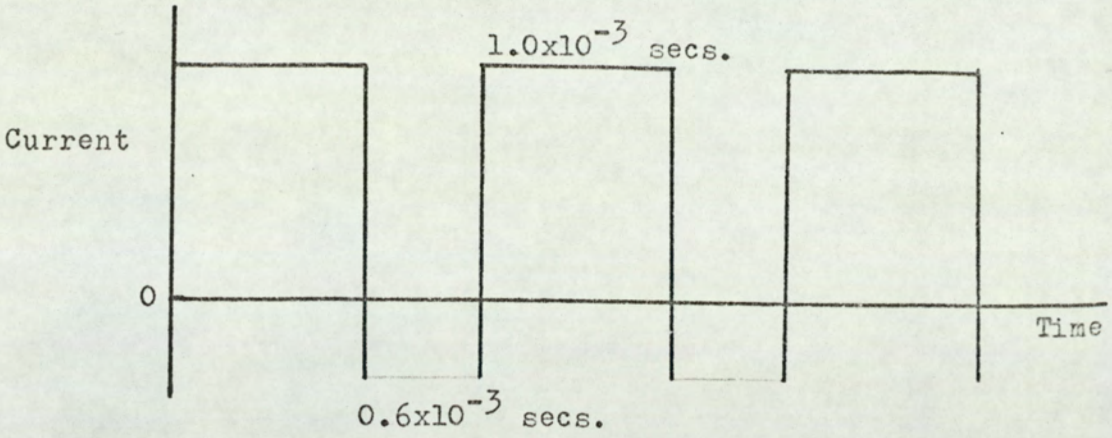


thickness : 2.5µM

temperature : 50°C

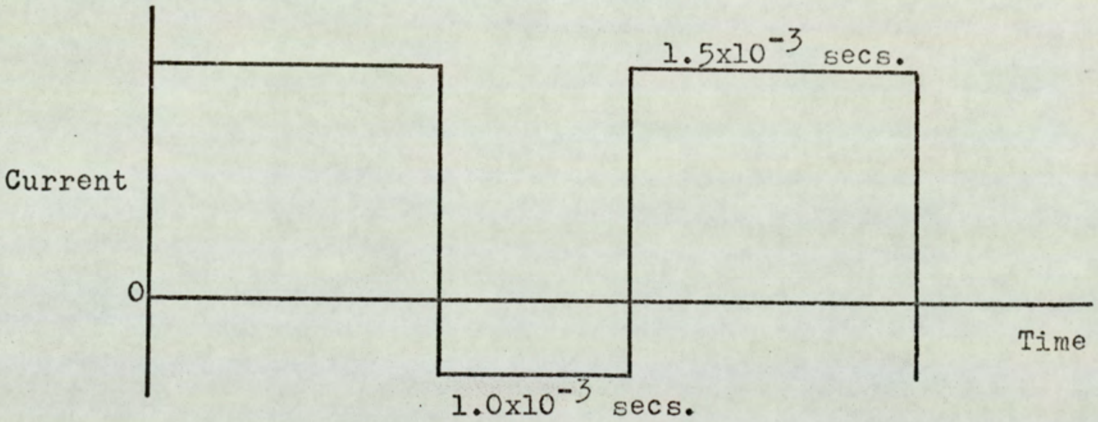
alternating current frequency : 600 c.p.s.

Fig. 4.28



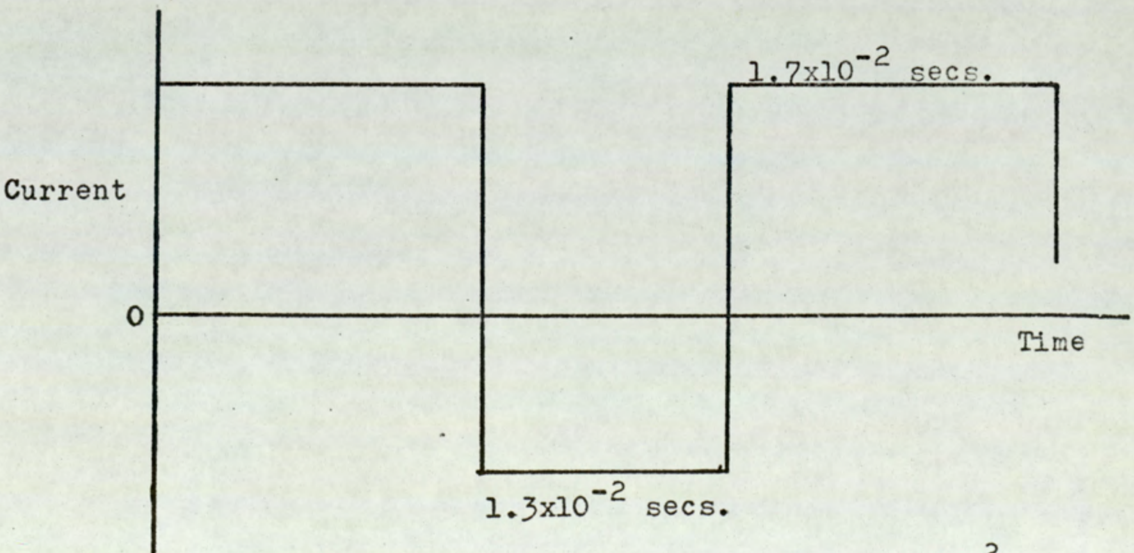
cathodic current density : 4.5 amps/ft.^{2}
anodic current density : 1.5 "
frequency : 600 c.p.s.

(a)



cathodic current density : 4.5 amps/ft.^{2}
anodic current density : 1.5 "
frequency : 400 c.p.s.

(b)



cathodic current density : 4.5 amps/ft.^{2}
anodic current density : 3 "
frequency : 33.3 c.p.s.

(c)

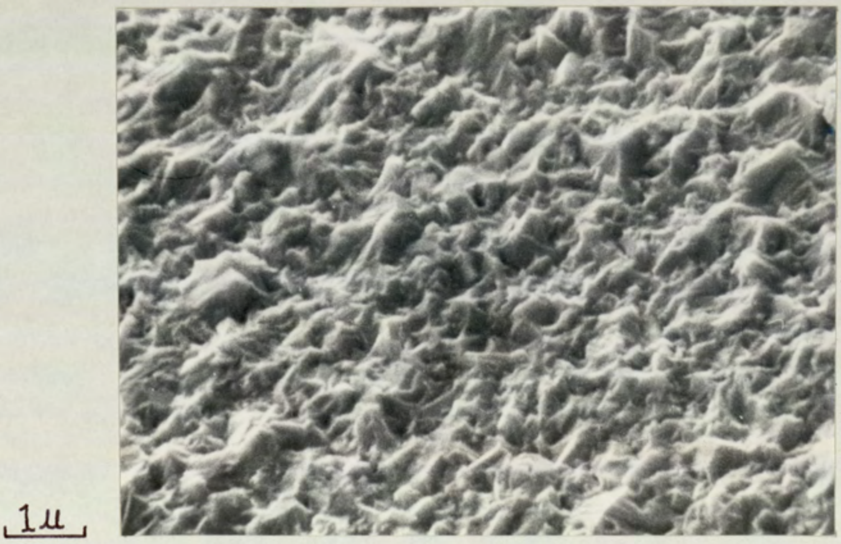
Fig. 4.29

thickness : 5.0μM

temperature : 20°C

alternating current frequency : 400 c.p.s.

Fig. 4.30



thickness : 5.0μM

temperature : 50°C

current density : 4.5/1.5 amps/ft.^{2} a.c.

Fig. 4.31

to be a fine grained deposit. The waveform used is shown in fig. 4.29c. Generally, it was found that if the cathodic current efficiency during the cathodic part of the cycle was assumed to be 85%, a figure based on the efficiency for direct current plating, then the efficiency of anodic dissolution was 100%. Since gold anodes do not dissolve appreciably in acid solutions (53) it might be thought that little dissolution would take place during the anodic period. However, it must be remembered that the anodic period lasts for only 0.015 secs., and that the anode is a gold electrodeposit on which deposition has only just ceased. Many of the adions will be very loosely attached to the growing structure and these will be removed easily giving rise to 100% dissolution. This high efficiency might not be continued if the anodic period was extended into seconds rather than fractions of a second.

4. 3. Porosity Test Results.

The results of the sulphur dioxide porosity test described earlier are given in table 4.1.

The following points emerge from the figures quoted :-

a) The use of higher plating temperatures reduced the level of porosity whether or not alternating current was used for plating. Porosity levels on panels plated at 50°C were lower than those plated at 20°C despite the fact that the coatings under test were only half as thick at 50°C. At a thickness of 1.25µM the porosity of 20°C deposits was too high to be measured, the spots of corrosion product tending to merge into a continuous corrosion film.

b) The porosity of the gold plate was considerably reduced by increasing the gold content of the electrolyte. The

Temperature ^{o}C	Current Density amps/ft.^{2}	a.c. or d.c.	Thickness uM	Pores/cm.^{2}
20	3	d.c.	2.5	19
"	4.5 : 1.5	a.c.	"	12.5
50	3	d.c.	1.25	13.75
"	4.5 : 1.5	a.c.	"	9.75

a) acid citrate solution containing 8 gms/l. of gold.

Temperature ^{o}C	Current Density amps/ft.^{2}	a.c. or d.c.	Thickness uM	Pores/cm^{2}
50	3	d.c.	1.25	2.75
"	4.5 : 1.5	a.c.	"	2.25
"	3	d.c.	2.5	2.25
"	4.5 : 1.5	a.c.	"	2.5
"	6	d.c.	1.25	8.0
"	7.5 : 3	a.c.	"	5.0
"	6	d.c.	2.5	3.25
"	7.5 : 3	a.c.	"	6.5

b) acid citrate solution containing 16 grms/l of gold

Temperature ^{o}C	Current Density amps/ft.^{2}	a.c. or d.c.	Thickness uM	Pores/cm^{2}
70	3	d.c.	1.25	6.0
"	4.5 : 1.5	a.c.	"	2.0

c) neutral phosphate solution containing 8 gms/l. of gold.

Porosity test results for laboratory solutions.
Alternating Current Waveform as shown in fig. 4.19.

TABLE 4. 1.

solution containing 16 gms./l. of gold gave very low values of porosity with direct current. Tests were carried out on thicker deposits and these were found to be only marginally less porous. With regard to the spread of the results which made up the average, the results for the 16 gms./l. gold solution could be regarded as constant.

c) The neutral phosphate solution (8 gms./l. of gold) gave lower values of porosity than the corresponding acid citrate solution. Leeds and Clarke (9) also noticed this effect and attributed it to the higher pH value of the phosphate solution.

d) In all cases except one the use of alternating current reduced the level of porosity. The effect was most marked when alternating current was used on the 8 gms./l. solution at 20°C, but was also true at 50°C, and for the phosphate solution. The 16gms,/l. citrate solution showed different results, there being a slight increase in porosity which in view of the almost constant low level of the porosity may be ignored. At higher current densities alternating current brought about a markedly higher level of porosity with the 16 gms./l. solution. This increase is difficult to explain, but may be due to the fact that the panels for this particular test were the last to be plated from the solution and the depletion of the gold ions which occurred may have resulted in an abnormally high porosity value.

e) The effect of varying the plating current density is shown by the figures for the 16 gms./l. electrolyte.

Generally the porosity was increased as the current density increased, and this applied to thicknesses of 1.25µM and 2.5µM. Thicker deposits were less porous except for the high current density alternating current sample where the figure for the 2.5uM deposit was abnormally high as described earlier.

The factors which reduce porosity may be summarised as follows :-

1. increased plating temperature.
2. increased gold concentration in the solution.
3. use of alternating current for deposition.
4. use of lower current densities.

All of these factors have one common effect - they increase the activity of the gold ions in the diffusion layer adjacent to the cathode surface. It may be concluded therefore that the porosity of gold electrodeposits is reduced by factors which increase the activity of the gold ions in the plating solutions.

4. 3. 1. The Relation of Porosity to Structure.

The most porous electrodeposits were those from direct current at 20°C. Examination of the structure of these deposits reveals a mass of tangled laths, (see figs. 4.7 and 4.8.), with the thickness of the coating varying considerably from the nominal thickness, though the relationship is parabolic rather than linear. (4) For a given nominal thickness on the 20°C deposit, there are areas where the thickness is below the nominal value giving increased porosity. To compensate for this there are areas where the thickness is greater than the average and the porosity reduced. The parabolic relationship between thickness and porosity means that this reduction in porosity will not offset the increased porosity brought about by the thinner areas, and this is one reason for the high porosity of these electrodeposits. More important, however, pores can reach the substrate by following a tortuous path between the laths and this is the major reason for the high porosity.

Raising the deposition temperature brings about a change to a more solid and compact form, where the thickness is more uniform. A similar effect occurs if alternating current is used. These structures look more sound than the lath type structure and it is reasonable to expect them to be less porous as is found to be the case.

The lowest porosity figures were found to arise from electrolytes containing 16gms./l. of citrate gold and from neutral phosphate solutions. Typical micrographs illustrating the structures of these deposits are shown in figs. 4.32 and 4.33. Generally it was found that the more uniform and compact the structure appeared to be the less porous was the electrodeposit, but it was not possible to predict the level of porosity from the structure unless tangled laths were present when high porosity could be predicted.

4. 3. 2. Examination of Pores in the 'Stereoscan'.

It has already been stated that the size of the pores present in a gold coating is very small. Ashurst and Neale (6) found that 95% of the pores in a 0.25uM coating were about 200Å in diameter. Leeds (4) indicated that the exposed area of the substrate in a total area of 1 in^2. was equivalent to a parallel sided cylindrical pore of 2uM diameter for a 0.25uM deposit. In fact there is not one parallel sided pore but many irregularly

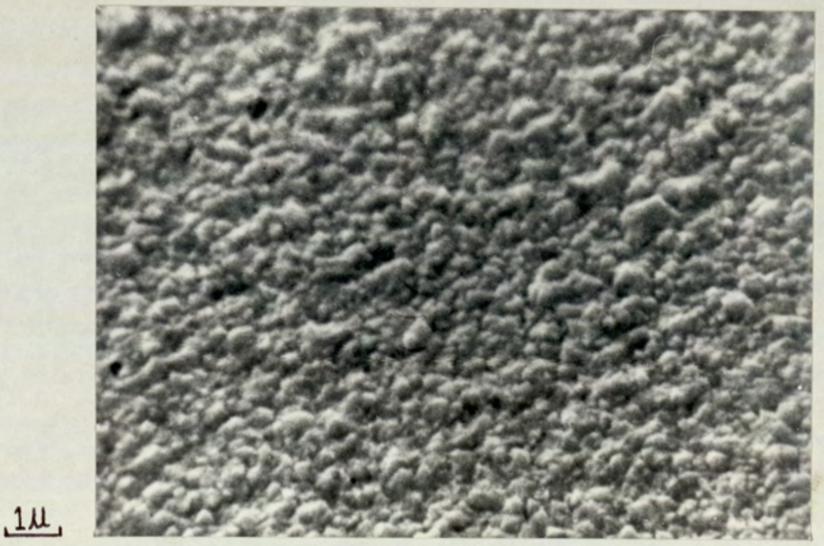
thickness : 2.5μM

temperature : 50°C

current density : 3 amps/ft.^{2} d.c.

solution : acid citrate (16gms. Au/l.)

Fig. 4.32



thickness : 2.5uM

temperature : 70°C

current density : 3 amps/ft.^{2} d.c.

solution : neutral phosphate

Fig. 4.33

shaped pores. It would be expected that such small pores would be difficult to locate even with an instrument such as a scanning electron microscope. Three techniques were used in an attempt to examine porosity, and they will be described in turn :-

a) Examination of panels after exposure to the sulphur dioxide porosity test. This technique did not prove successful owing to the large amounts of corrosion product which obscured the pores from which it originated. To overcome this problem, panels were left in the corrosive atmosphere for a shorter period of 2 hours before being removed and examined. Results from this test are shown in 4.34 and 4.35. Fig. 4.34 features a 20°C direct current electrodeposit with a tangled lath structure. A patch of dark corrosion product can be seen on the surface of the deposit. Close examination reveals that beneath the corrosion film the structure carries on apparently unaltered. Clearly the pore which has given rise to the corrosion film is very small and would not be detectable without first using a corrosion test to mark the pore site. This pore may well be typical of those in this type of deposit where the pores can follow tortuous paths through the laths to the substrate surface. Fig. 4.35 shows a similar patch of corrosion product on a 2.5µM direct current 50°C deposit. Again there is no evidence of any defect in the structure of the deposit beneath the corrosion film.

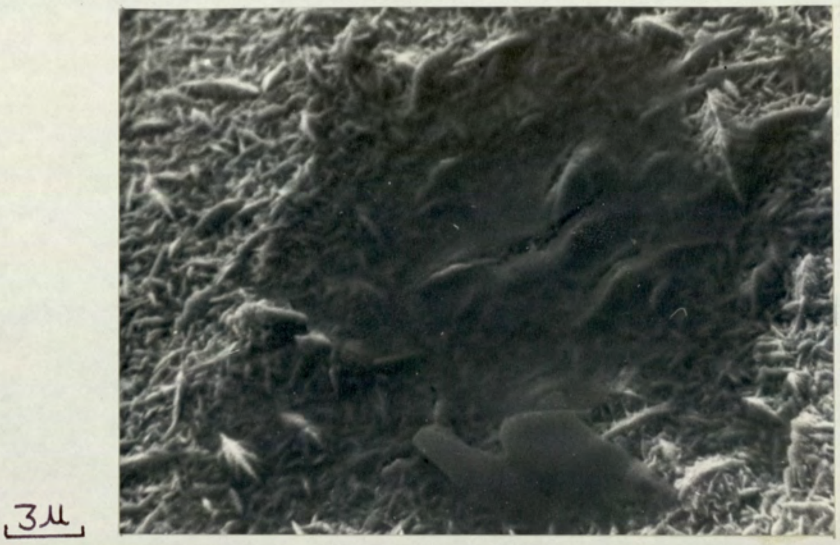
b) The second technique was to dissolve away the corrosion film arising from the sulphur dioxide test in dilute nitric acid. This technique was difficult to control, and in some cases attack started on the substrate through the pore before all the corrosion product had been removed from the surface. An example of this is shown in fig. 4.36 where a hole can be seen in the top of a lump of sulphide covering a pore. The technique did however reveal some pores and defects. Fig. 4.37 shows a fairly large wedge shaped pore, 4uM across and 8µM long. This pore has a particularly uniform shape with very straight edges. At the higher magnification the walls of the pore can be seen to be straight and vertical. This would suggest that the pore was formed round an inclusion which has subsequently fallen from the deposit to expose the substrate. The inclusion may have been a particle of polishing compound (silicon carbide) which was only loosely attached to the substrate surface.

A further pore detected by this technique is shown in fig. 4.38 and this pore can also be seen to have formed on a substrate inclusion. In this case the offending inclusion has remained at the base of the pore where it can clearly be seen at the higher magnification. The pore is approximately rectangular, 2uM x 0.5uM and has straight edges.

c) The final technique used to locate pores was to scan the surface of an untreated panel in an attempt to find any discontinuities which occurred. Two definite defects were found by this method, and both arose in a 2.5uM thick deposit from the simple acid citrate solution to which had been added 1 gm./l. of nickel for comparison with the commercial solutions described later in section 4. 4. The first of these, fig. 4.39 is another rectangular pore with two straight sides. The pore in this case has occurred at the top of a large group of protuberances which were typical of alloy deposits. The size of the pore is approximately 3μM x 4μM. There is no indication of why this pore should have formed, but the straight sides suggest that a small piece of gold may have fallen out. Some commercial alloy deposits were found to be cracked due to high stress, the cracks often being associated with the protuberances. (see fig. 4. 47.) In this case the cracks may have joined up to allow the gold to fall out.

Fig. 4.40 shows a pore which has formed on a substrate defect. A triangular pit in the surface has been covered over by the gold coating but this coating appears to have collapsed after plating had finished. This pore arises from a combination of a substrate defect and post plating damage.

Other areas located by the direct examination technique were not such definite pores. Figs. 4.41 and 4.42 show two areas of weakness in a deposit from the 16 gms./l. citrate solution. It can be seen that on these micrographs there are areas which are not covered with the same amount of gold as the remainder of the sample. These areas are quite large, and examination at higher magnifications reveals that they are sited over small pits in the substrate surface. It is not suggested that the whole of these weak areas is devoid of any gold coating and this is unlikely since if there were no gold covering there would be sharp contrast between the gold and the copper. However, the area around these small defects is certainly covered by a thinner layer of gold than elsewhere, and no detail of the structure can be seen. In other cases the structure of

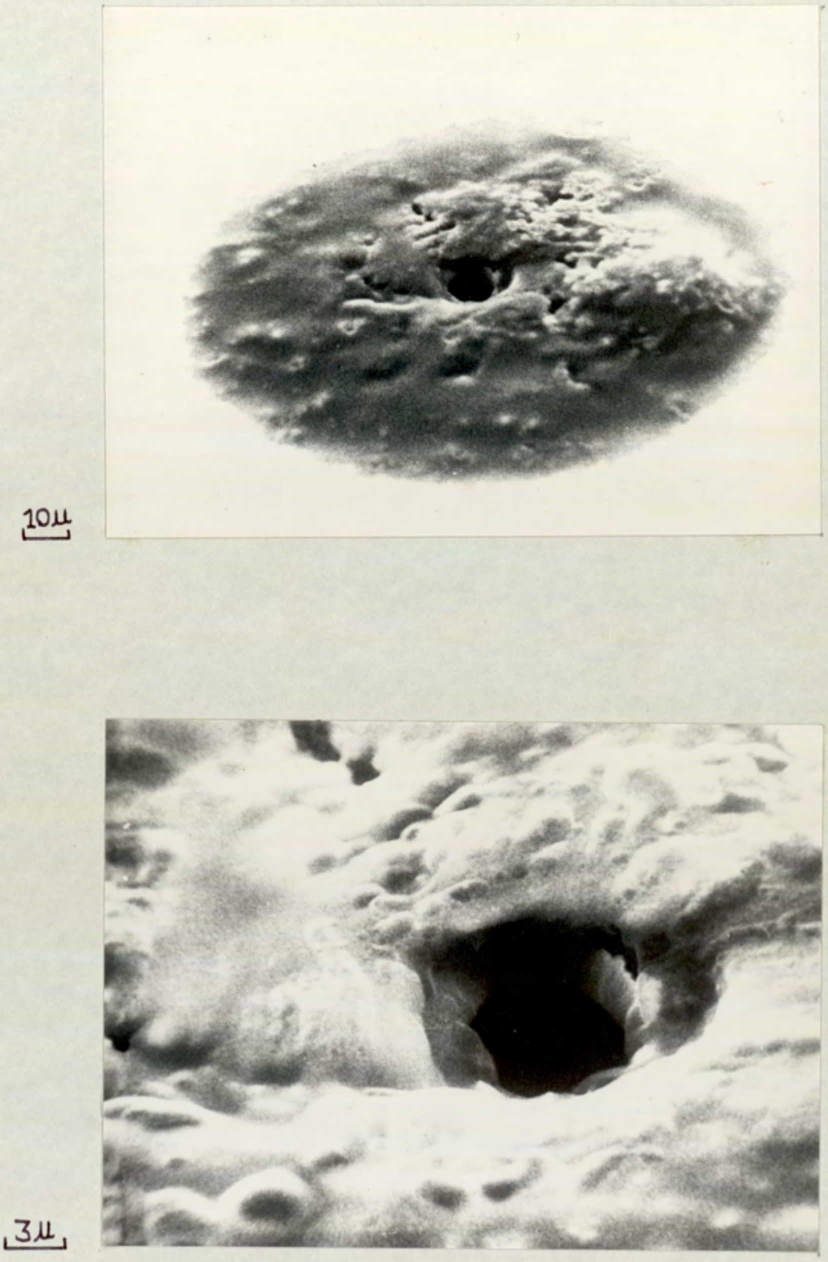


Film of corrosion product on the surface of a 5.0μM deposit from acid citrate solution at 20°C.

Fig. 4.34

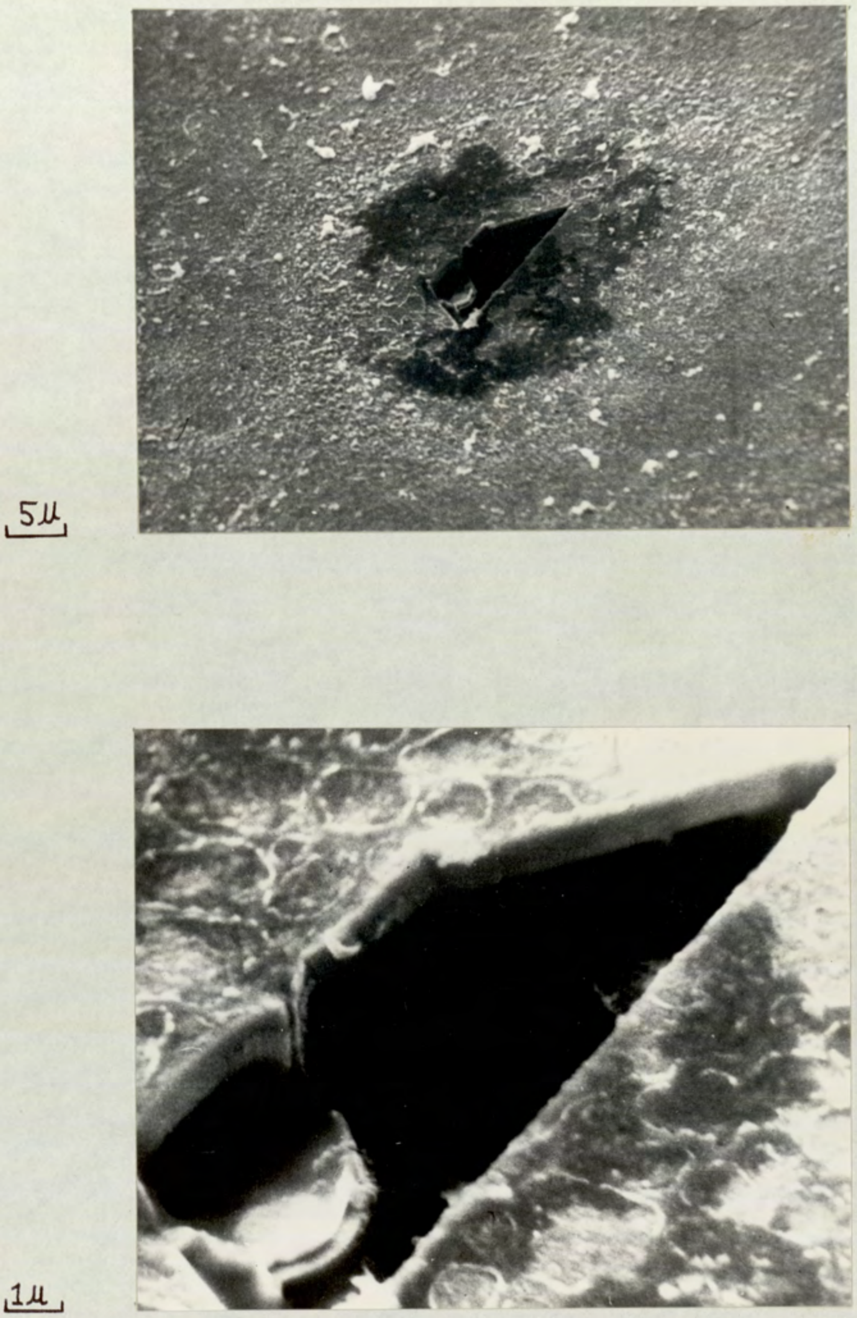
Film of corrosion product on the surface of a 2.5μM deposit from acid citrate solution at 50°C.

Fig. 4.35



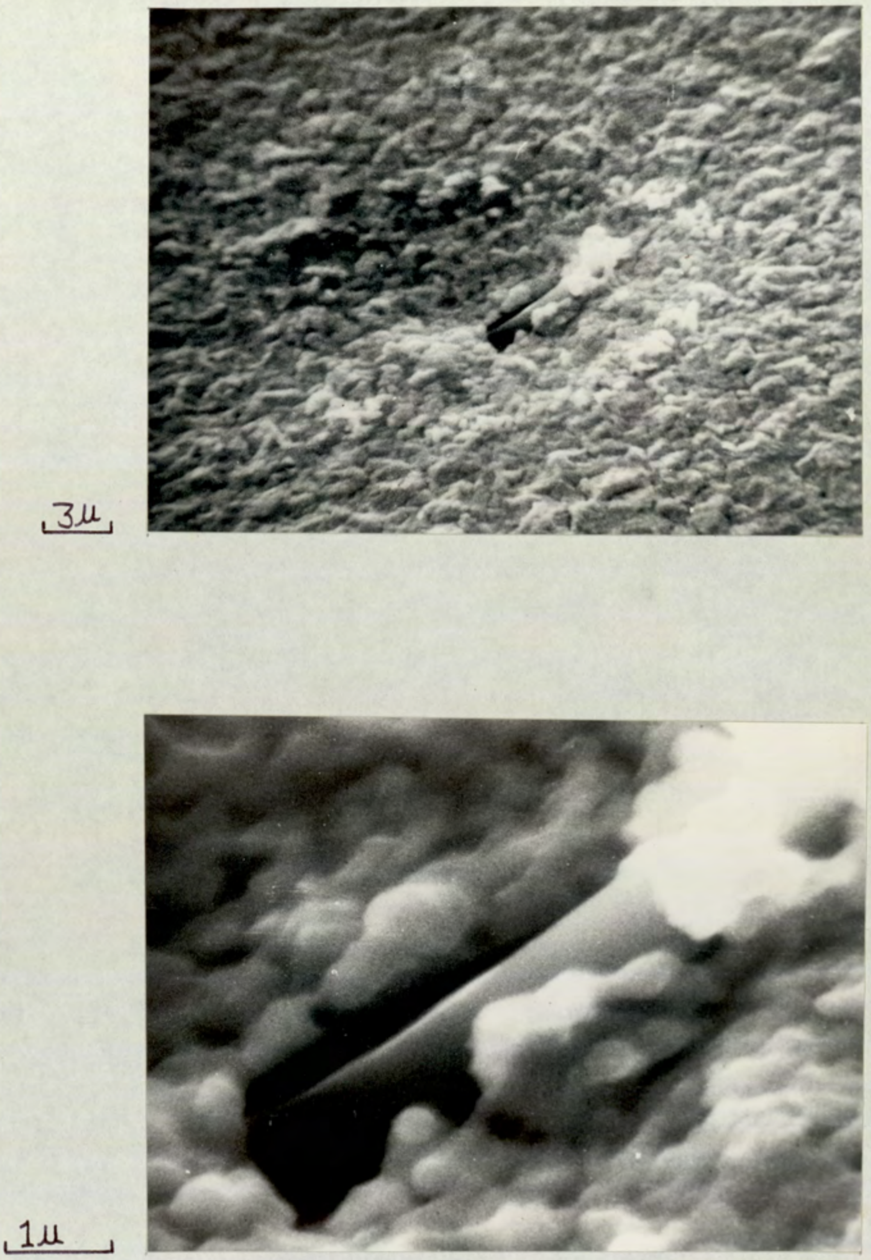
Attack on the corrosion product surrounding a pore after immersion in dilute nitric acid.

Fig. 4.36



An angular pore thought to have formed round an inclusion.

Fig. 4.37



A pore formed round an embedded inclusion.

Fig. 4.38

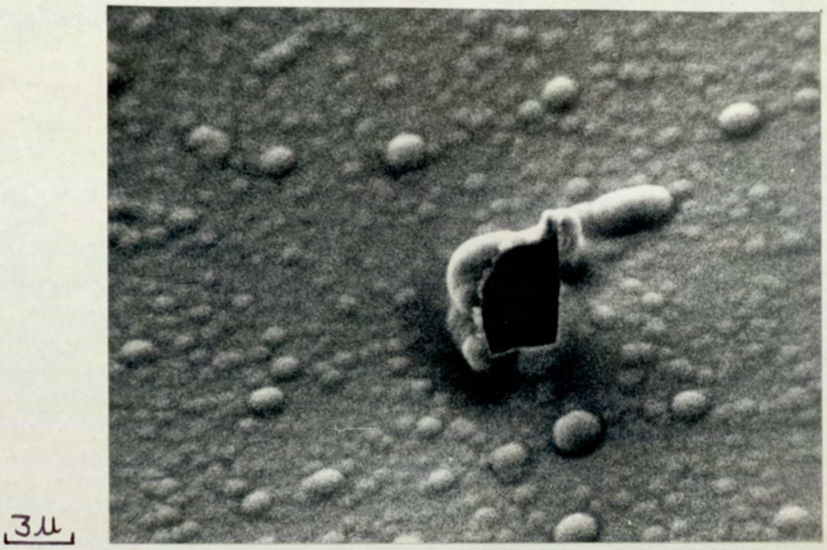
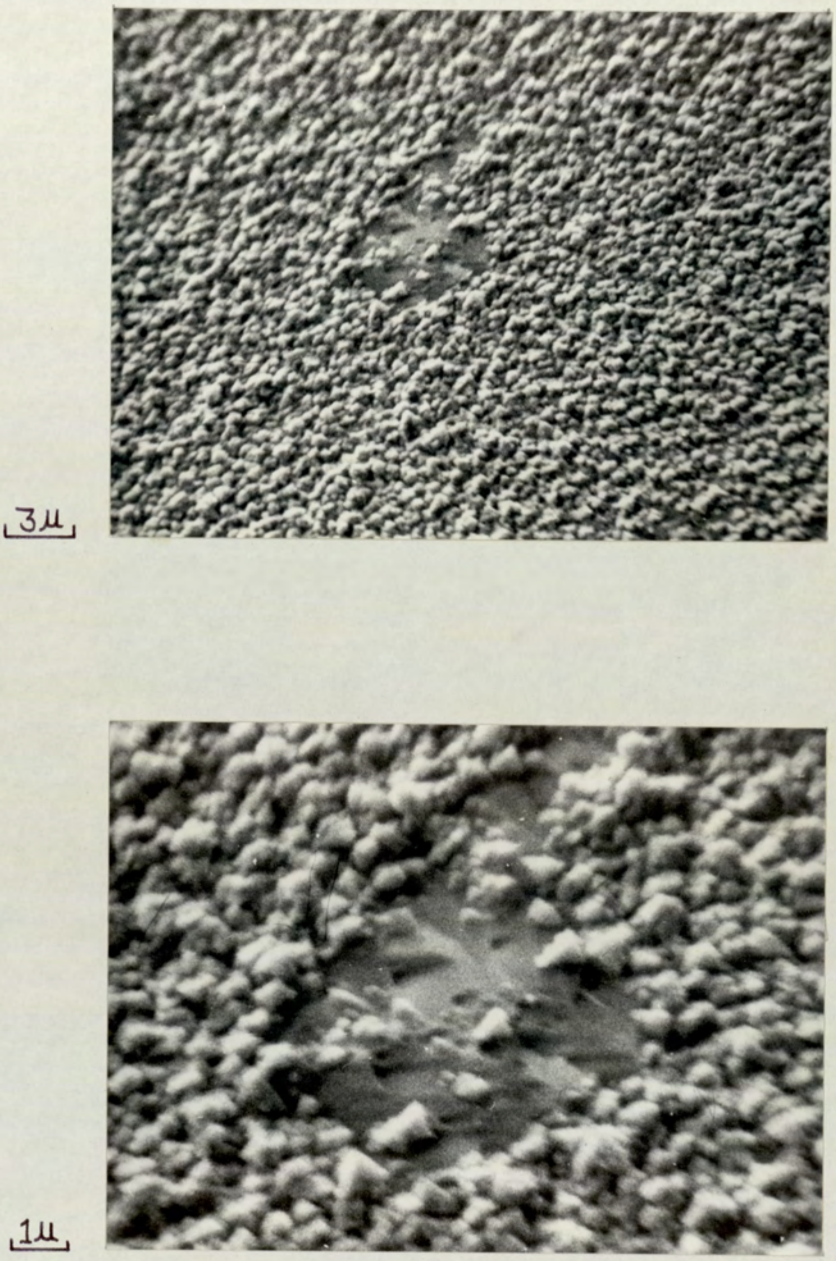


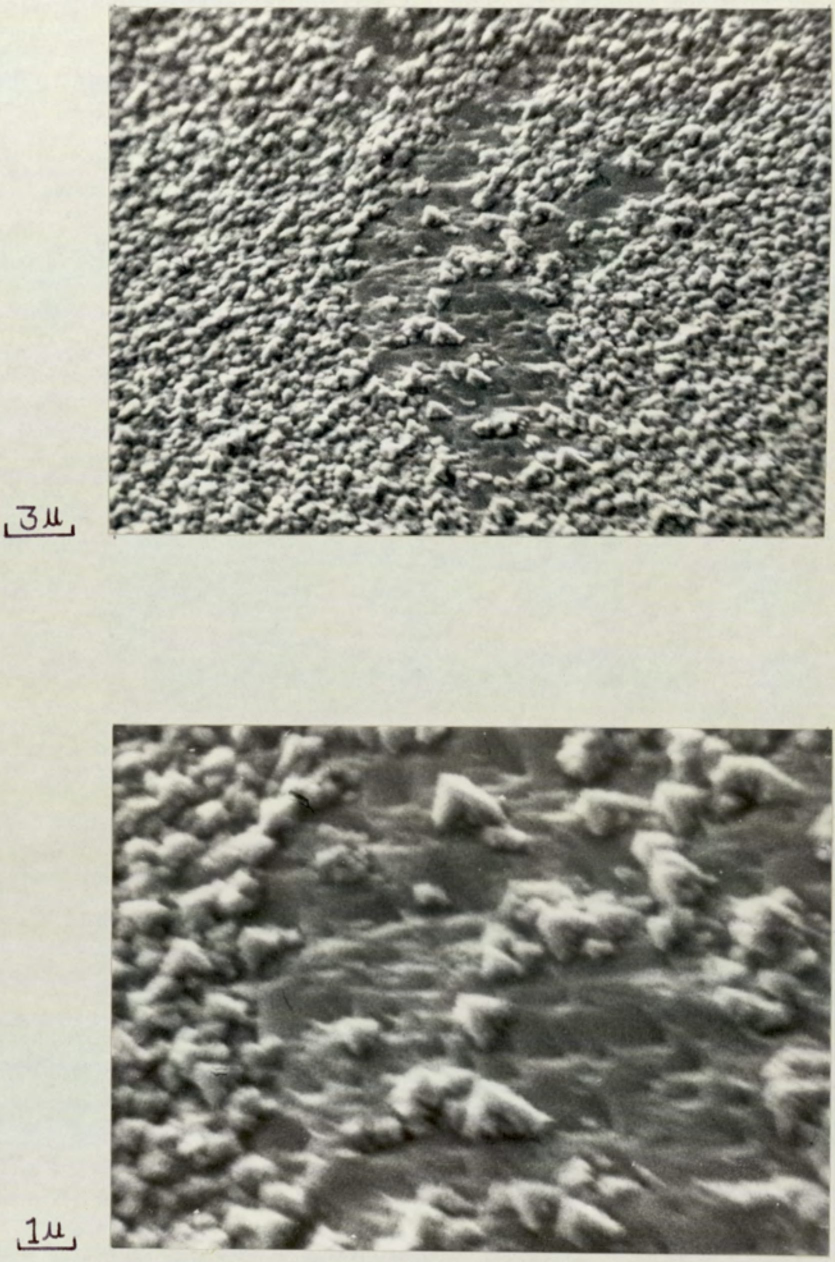
Fig. 4.39

Fig. 4.40



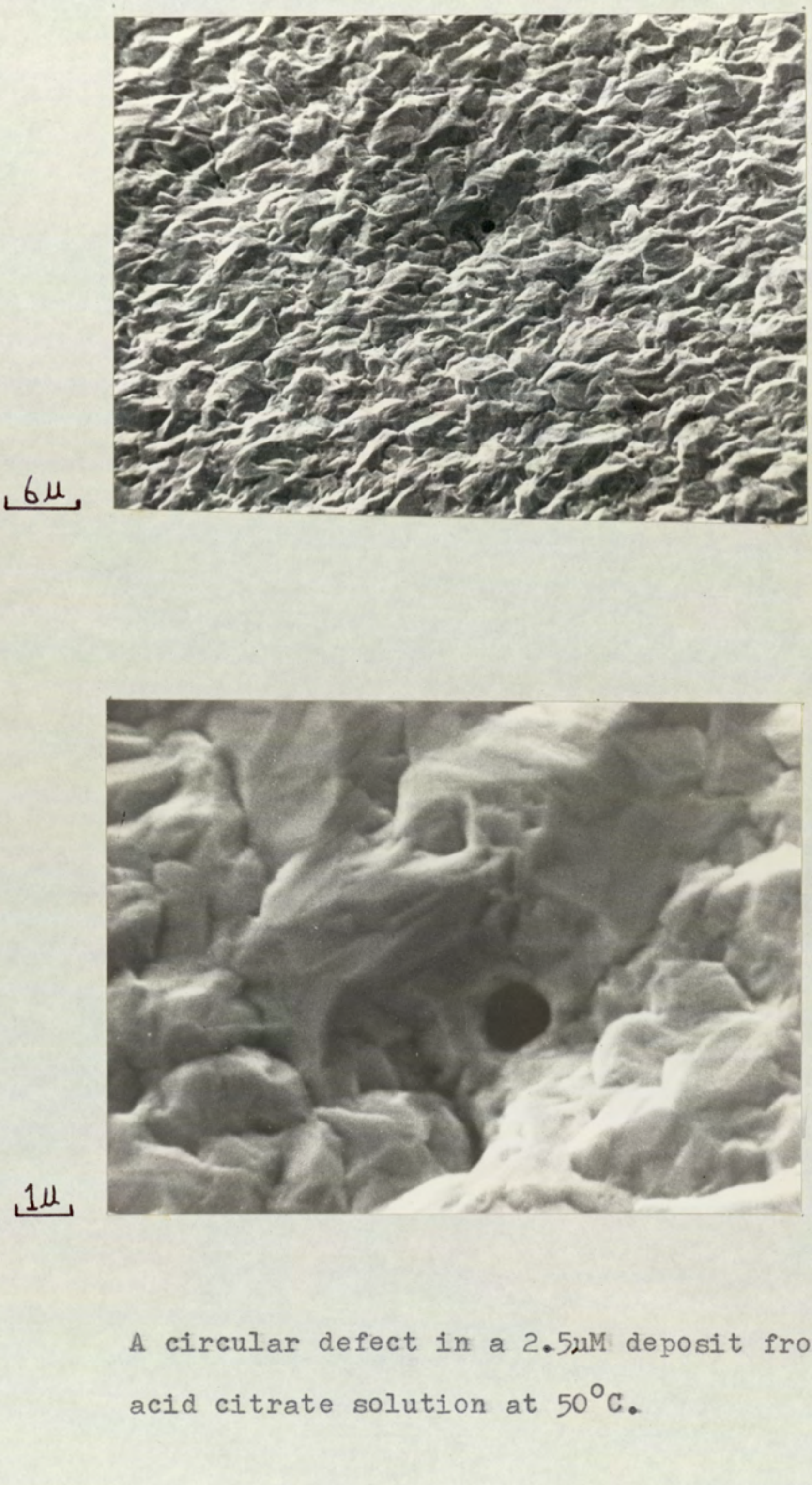
A weak area in a 1.25μM deposit from an acid citrate solution containing 16gms/l. of gold.

Fig. 4.41



A weak area in a 1.25μM deposit from an acid citrate solution containing 16gms/l. of gold.

Fig. 4.42



A circular defect in a 2.5μM deposit from acid citrate solution at 50°C.

Fig. 4.43

the deposit becomes evident at a thickness of 0.25µM, and it is reasonable to assume that these weak areas are covered by a layer of gold less than 0.25µM thick. Ashurst and Neale (6) found 21 pores mm^2 in deposits 0.25µM thick, and since there are visible surface defects in these areas it is very likely that small pores of less than 100Å diameter will exist in these regions. Such an area will also be susceptible to damage in service as an electrical contact.

Fig. 4.43 shows a further defect located by direct examination. A small circular hole was found in a 2.5µM deposit from acid citrate solution ay 50°C. The hole has a diameter of luM but there is no apparent reason for its existence.

4, 4. Deposition From Commercial Solutions.

Two commercial electrolytes were used experimentally in the laboratory as described in section 3. 1. 1. The results of the sulphur dioxide porosity tests carried out on these solutions are given in table 4. 2. The thicknesses quoted are based on the assumption that the density of the alloy deposits was 19 gms./cc. Since only low alloys were used the assumption did not introduce a significant error as was confirmed by the examination of cross sections.

The results given in table 4.2. are surprising in some respects such as the high level of porosity in some cases, and the fact that the use of alternating current has led to an increase in the porosity, contrary to what was found with laboratory solutions. These results can be explained by reference to the structures of the deposits.

Solution	Temperature ^{o}C	Current Density amps/ft.^{2}	a.c. or d.c.	Pores/cm^{2}
Autronex CI	20	2.5	d.c.	14
"	"	4.5: 1.5	a.c.	16
"	"	5	d.c.	44
"	"	7.5: 2.5	a.c.	29
Por-A-Gold	50	2.5	d.c.	11
"	"	4.5: 1.5	a.c.	15.5

Porosity test results for commercial solutions. All figures relate to a standard thickness of 1.25 uM.

TABLE 4. 2.

Solution	Current Density amps/ft.^{2}	a.c. or d.c.	Current Efficiency %
Autronex CI	2.5	d.c.	34
"	4.5 : 1.5	a.c.	33.1
"	5	d.c.	36.8
"	7.5 : 2.5	a.c.	33.2
Por-A-Gold	2.5	d.c.	75
"	4.5 : 1.5	a.c.	61

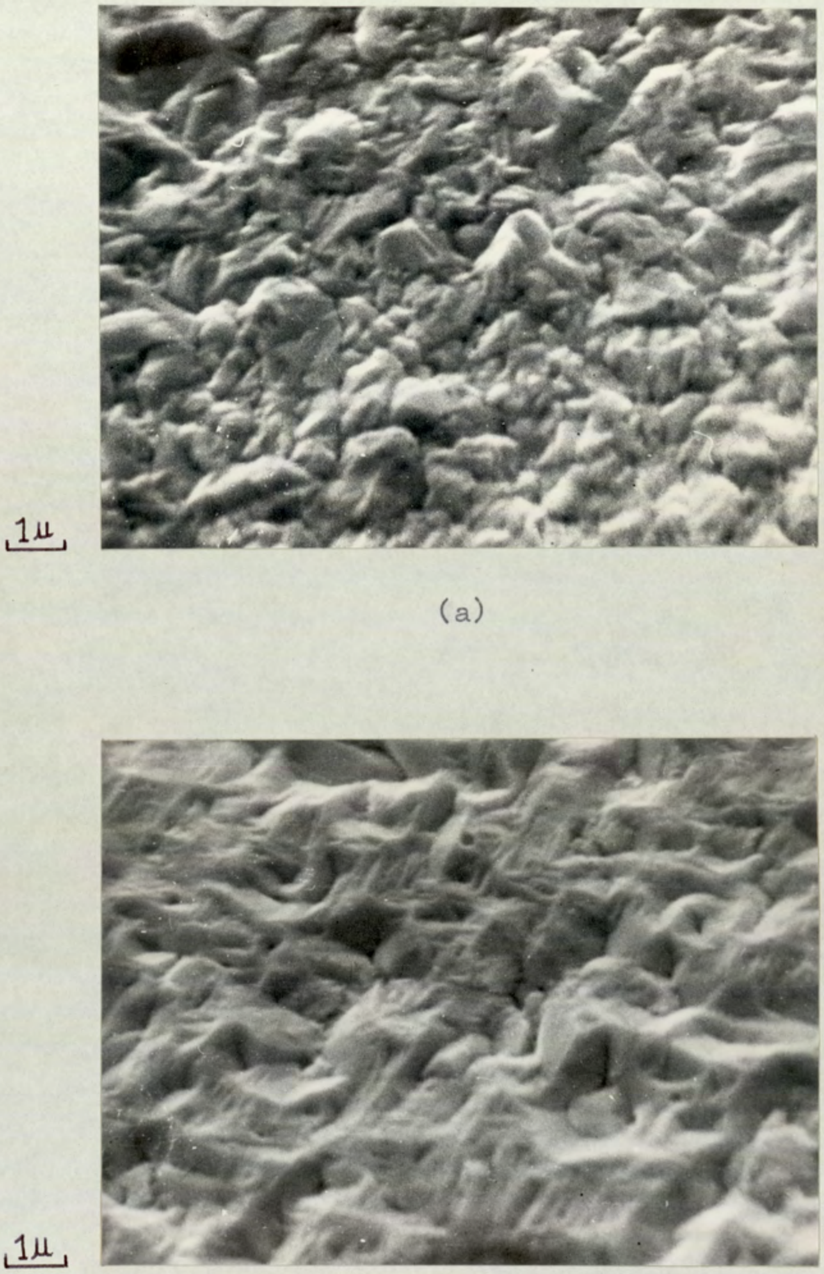
Cathodic current efficiencies for commercial solutions

TABLE 4. 3.

4. 4. 1. Pure Gold Deposits.

The commercial pure gold solution was of unknown composition but it is probable that small quantities of silver were present as well as organic addition agents. The solution produced bright electrodeposits up to a thickness of 2.5µM, with direct current but only 1.25µM with alternating current. The cathodic current efficiencies obtained with all the commercial electrolytes are shown in table 4.3. For the pure gold solution, the current density was reduced to 2.5 amps/ft.^{2} in the direct current plating, but the alternating current densities were kept the same as for the laboratory solutions.

The porosity tests showed that the figures for direct current were of the same order as those obtained from the laboratory prepared pure gold solution at 50°C. The structure of the direct current commercial deposit is shown in fig. 4.44. It is very similar to that of the laboratory solution, and hence the similar porosity level is not surprising. When alternating current was applied to the laboratory solution the porosity was reduced and the structure little altered, except for a refining of the features. With the commercial solution this was not the case. Alternating current brought about a marked increase in porosity accompanied by a complete change in structure. The solid compact structure became broken up into individual particles which appeared to have been scattered at random over the surface (fig. 4.45.), tending to roughen the surface. This effect explains why dulling set in earlier when alternating current was used. By the time the coating was 5uM thick, most of the surface was covered by the particles which did not join together but still had the

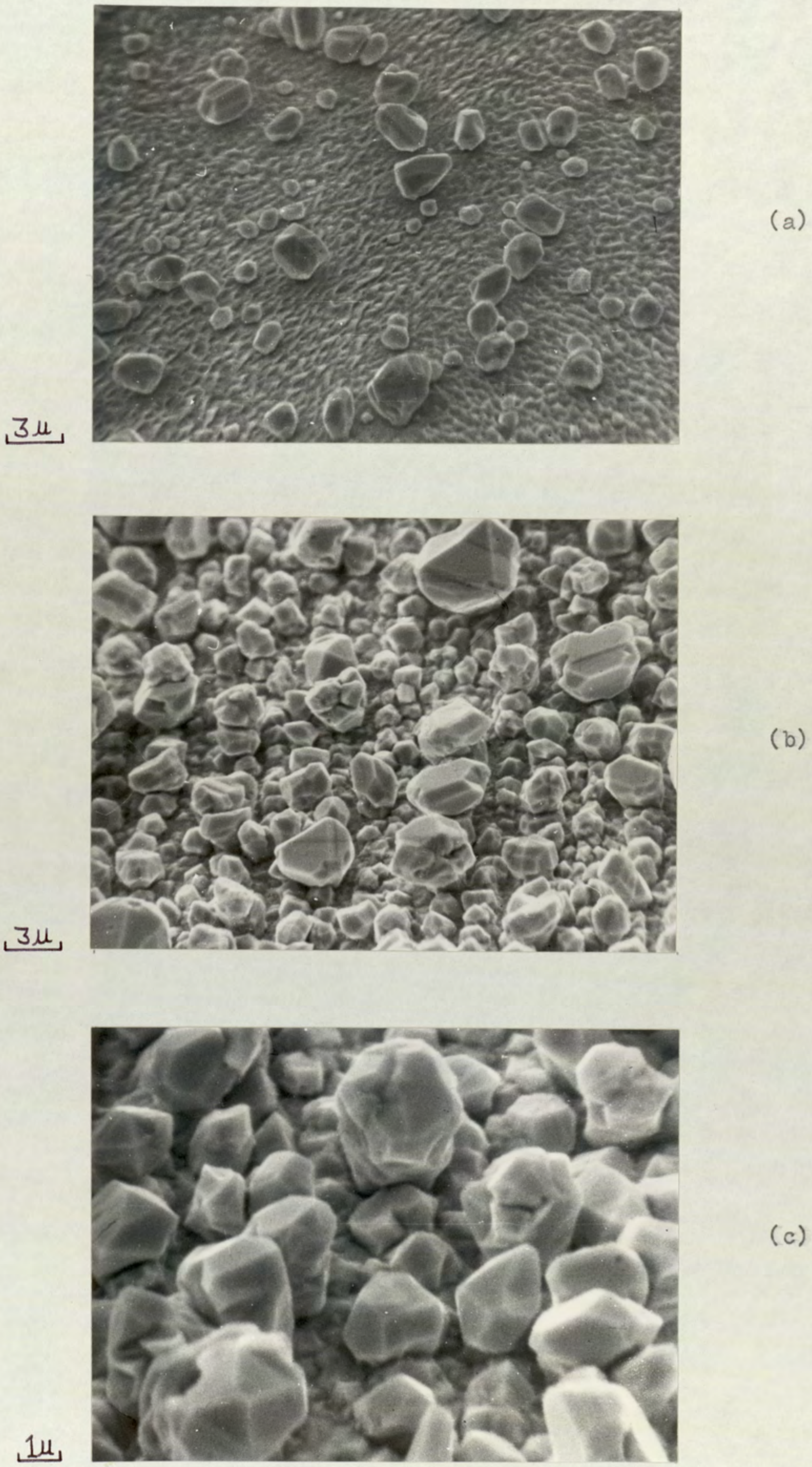


(a)

(b)

Direct current deposits from 'Pur-A-Gold' solution used at 50°C and 2.5 amps/ft^2. Thickness (a) 2.5μM ; (b) 5.0μM

Fig. 4.44



Alternating current deposits from 'Pur-A-Gold' solution used at 50°C and 4.5/1.5 amps/ft.^{2} a.c. Thickness (a) 1.25uM ; (b) and (c) 5.0uM

Fig. 4.45

appearance of having been scattered over the surface. The channels between these particles offer an obvious path for pores to reach the substrate surface. In the 1.25µM deposit, there was only a thin layer of gold between the particles and this is one reason for the high porosity of these deposits, as found in the sulphur dioxide porosity test. The failure of the crystallites to merge in thicker deposits would be expected to give rise to high porosity in these deposits.

The fact that the use of alternating currents leads to a roughening of the surface when applied to commercial electrolytes, but does not do so when applied to laboratory solutions, leads to the assumption that the roughening arises from some form of interaction between the alternating current and the addition agents present in the commercial solutions. It is significant that the current efficiency falls when alternating current is used, an effect not present with simple solutions, which suggests that something is interfering with the deposition process. Possibly the alternating current causes a breakdown of the addition agent during the anodic period leading to inhibition during the cathodic period.

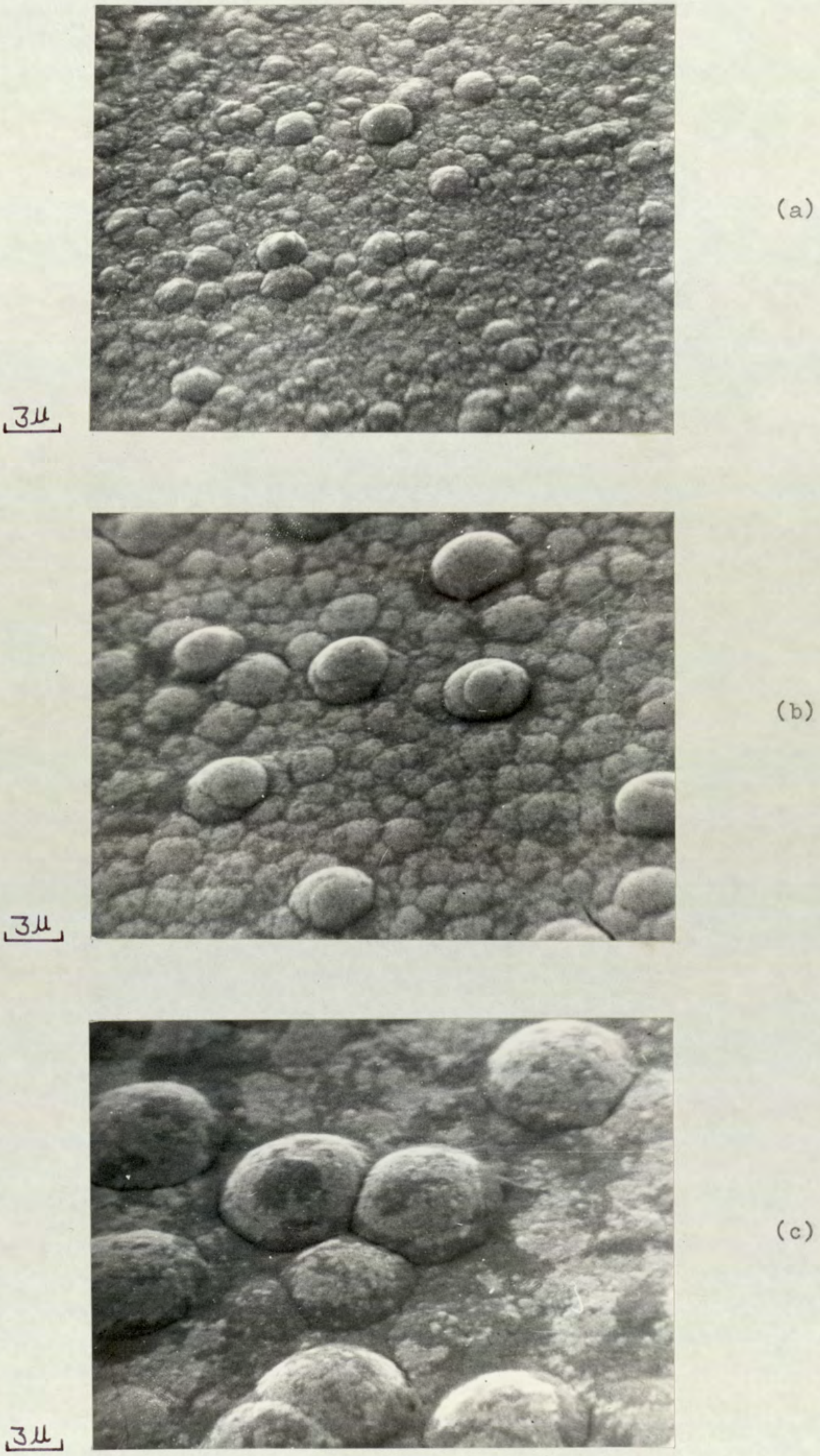
4. 4. 2. Alloy Gold Deposits.

The alloy gold deposits were brighter to a greater thickness than pure gold deposits, being semi-bright at 5uM. The use of alternating current enabled bright deposits to be produced at thicknesses up to 7uM. The alloy solutions were used at two current densities and the cathodic current efficiencies are quoted in table 4.3.

At both current densities with direct current the structure produced was of fine grains. At 2.5amps/ft.^{2} a few of these grains grew preferentially and protruded from the surface somewhat, although the surface of the grains themselves always remained very smooth. (fig.4.46). At 5 amps/ft^2. all the grains grew uniformly to give an exceptionally smooth bright deposit at 5µM (see fig.4.47.) A feature of both deposits was that when the copper substrate was dissolved away, the unsupported gold broke up due to the high internal stress. This feature was never observed with pure gold deposits and was presumably due to the alloying element introducing a strain into the lattice of the deposit. The effect was more noticeable at the higher current density, and examination of the deposit in the scanning electron microscope revealed that the stress had been sufficient to cause cracking of the deposit. These cracks account for the very high level of porosity recorded for these deposits (44 pores/cm^2.). See fig. 4.47.

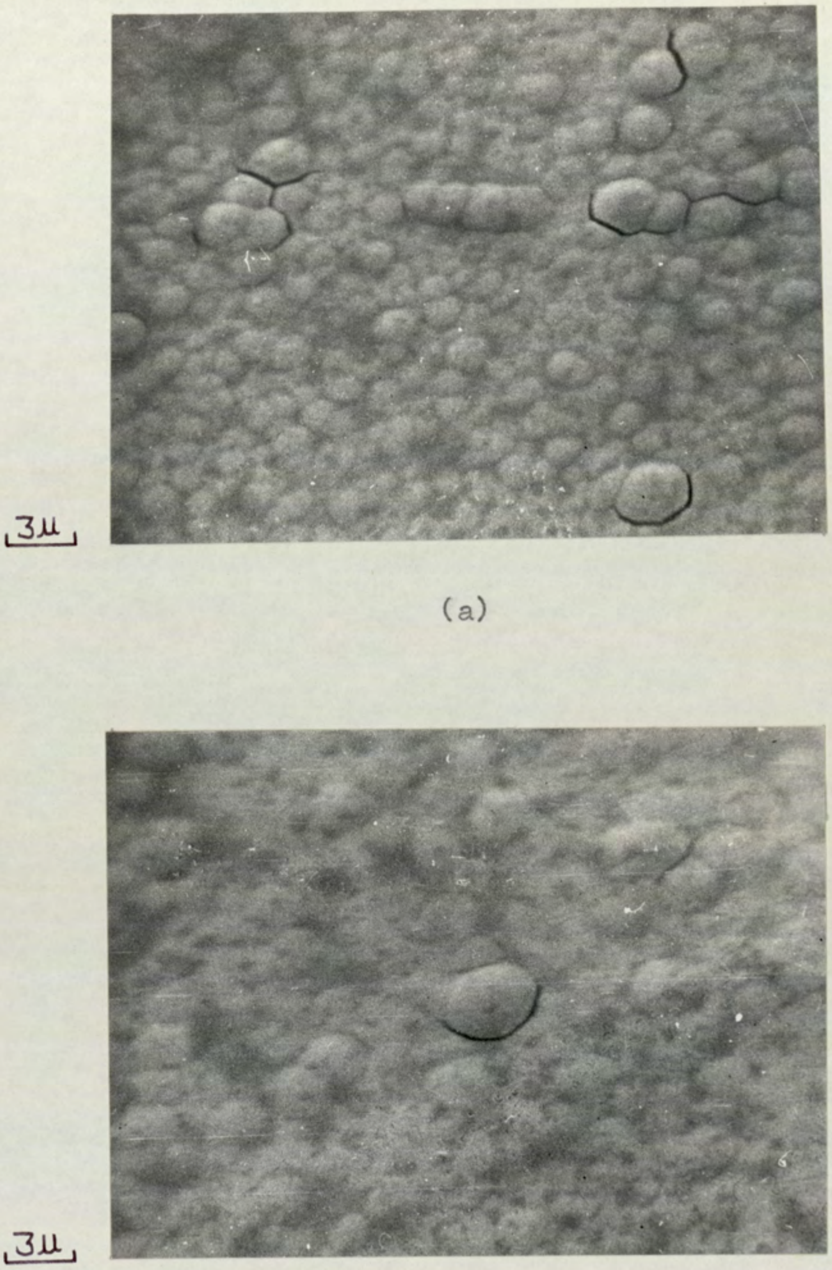
The use of alternating current was found to reduce this stress and the deposit remained coherent after the substrate had been dissolved away. This suggests that the alternating current removed the cause of the high stress. In the case of the higher current density, the use of alternating current led to a decrease in porosity from 44 to 29 pores/cm^2., though the latter figure is still high. In the case of the lower current density the porosity increased slightly from 14 to 16 pores / cm^2.

The microstructures of the alternating current, deposits figs. 4.48 and 4.49, were also of interest. Plating with this solution was carried out at the recommended temperature of 20°C, and the structure produced was similar to that from the simple acid citrate colution with direct



Direct current deposits from 'Autronex CI' solution used at 20°C and 2.5 amps/ft.^{2} Thickness (a) 1.25μM ; (b) 2.5μM ; (c) 5.0μM

Fig. 4.46

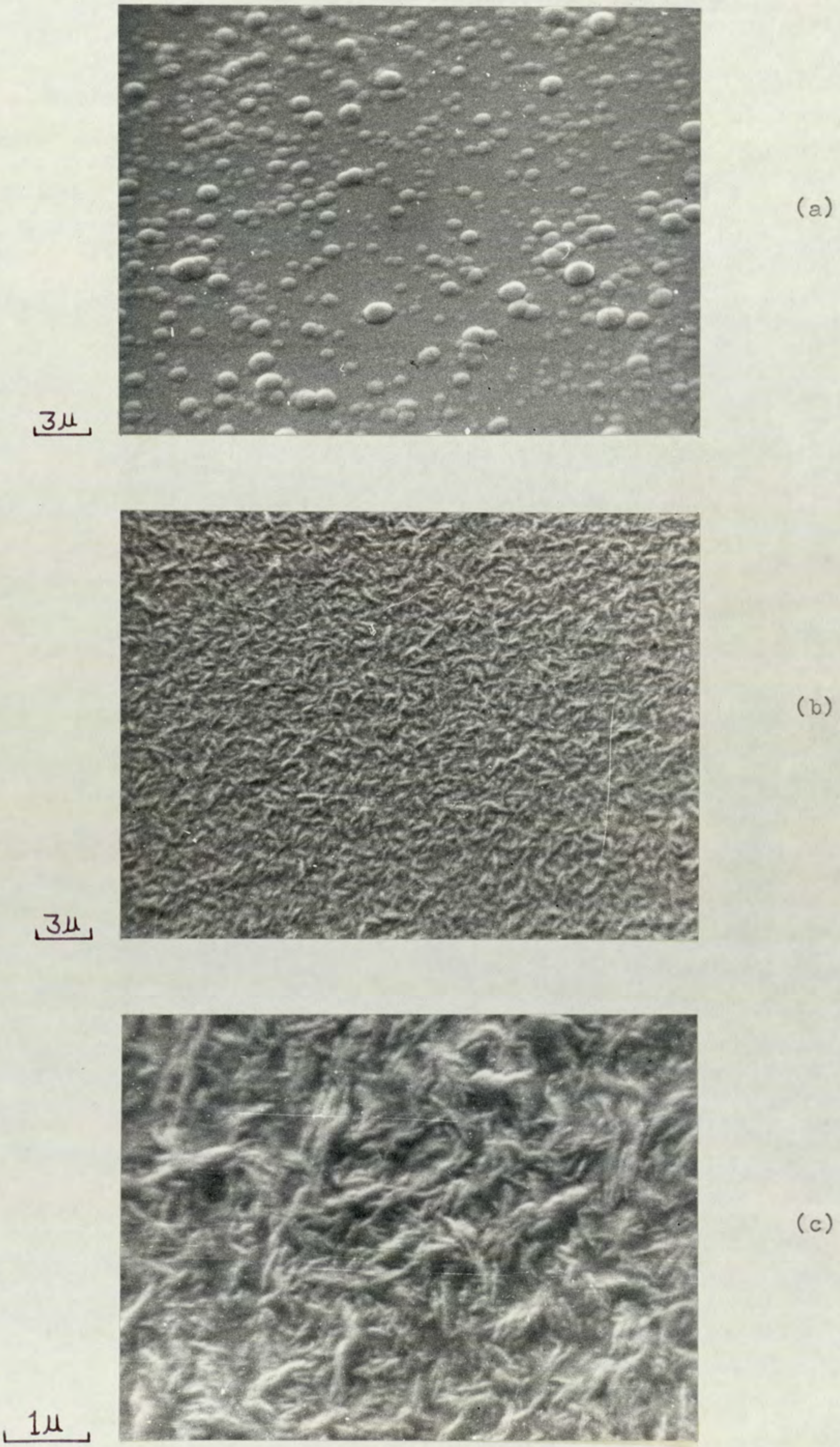


(a)

(b)

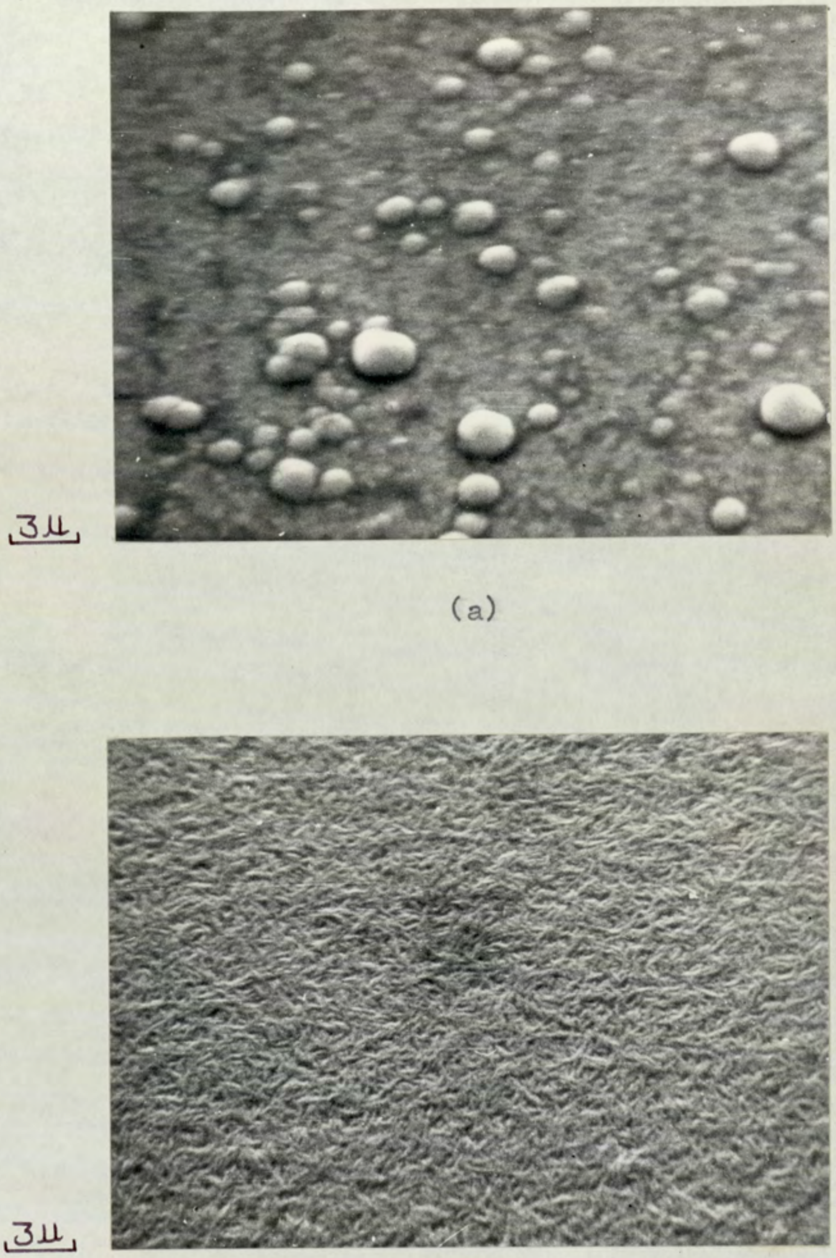
Direct current deposits from 'Autronex CI' solution used at 20°C and 5.0 amps/ft^2. Thickness (a) 2.5μM ; (b) 5.0μM

Fig. 4.47



Alternating current deposits from 'Autronex CI' solution used at 20°C and 4.5/1.5 amps/ft.^{2} a.c. Thickness (a) 1.25μM ; (b) 2.5μM ; (c) 5.0μM

Fig. 4.48



(a)

(b)

Alternating current deposits from 'Autronex CI' solution used at 20°C and 7.5/2.5 amps/ft.^{2} a.c. Thickness (a) 2.5μM ; (b) 5.0μM

Fig. 4.49

current at 20°C, i.e. tangled laths. The structure at low (fig. 4.48) and high (fig. 4.49) current densities were less well defined versions of the tangled laths. Hence the alternating current appears to have removed the effect of the alloying element which with direct current only led to a smooth flat surface. The lath type structure is typical of very porous deposits and thus the porosity of alloy deposits is high when alternating current is used.

To verify that the alternating current had an effect on the alloying elements and addition agents, an alloy gold solution was made up in the laboratory by adding 1gn./1. of nickel as citrate to the basic acid citrate solution. In this way a solution of known composition was produced and it was possible to analyse the resultant electrodeposit for a known alloying element. Nickel was chosen since it can conveniently be detected in small quantities by the electron probe microanalyser, whereas other common alloying elements such as cobalt cannot. The solution made up was known to produce an alloy containing 0.5% nickel approximately. (12)

Deposits plated from this solution were analysed on the electron probe microanalyser. While this instrument does not give an accurate measure of the overall alloy content, it does give an accurate assessment at the point at which the test is carried out. Tests were therefore carried out at several points on the surface and the range of nickel content of the alloy is quoted. Results were as follows :-

direct current deposits	0.37 - 0.59% Ni
alternating current deposits	0.18 - 0.24% Ni

These results suggest that nickel is removed preferentially during the anodic part of the cycle, and the removal of the alloy from the lattice results in the reduction in stress which was brought about by the introduction of alternating current. Although this will result in an increase in the proportion of nickel in the cathode layer, energetically, it is easier for gold to be deposited, and deposition proceeds during the cathodic period with the same proportion of nickel. The major effect of alternating current is to remove the nickel. Thus there is not the same degree of rearrangement of gold ions as with alternating current on the simple solutions and the modification of the structure brought about by the alloying element is lost. The resultant structure is similar to that from the simple solution with direct current. This increases the porosity of the deposits since the structure reverts from a compact form to a lath type. It appears that alternating currents may not be used on existing commercial solutions with any beneficial effect.

5. FURTHER DISCUSSION AND CONCLUSIONS.

5. 1. Porosity.

The use of the scanning microscope has revealed pores present in the gold electrodeposits. Leeds (4) has classified pores into two types, crystallographic porosity and porosity arising from substrate defects and inclusions. The present work supports this type of division, and the pores observed in the electron microscope fall into two categories :-

a) Large pores up to 2uM in diameter usually associated with some form of substrate defect such as a pit or an embedded particle of polishing grit.

b) Small pores which were detected only after a corrosion test. Often only a film of corrosion product could be seen covering an apparently uniform and continuous deposit structure. Such pores are therefore very small and do not necessarily travel directly to the substrate but may follow a tortuous path. This type of porosity would be expected to include the crystallographic pores.

The type of substrate defect which gives rise fo porosity of type (a) must be considered. It has already been shown (section 4. 1. 1.) that in certain cases nucleation takes place on substrate inclusions so it is unlikely that pores will form on these inclusions. The reason is that they are copper oxide, a conductor of electricity. The difficulty arises with non-conducting inclusions or embedded particles of polishing compounds such as silicon carbide. No deposition takes place on these particles, as can be seen in fig. 4.38 and hence pores are formed. Cooksey and Campbell have also demonstrated this type of porosity. (5)

Evidence for the existence of crystallographic pores of type (b) arises from the reduction in porosity brought about by increasing the gold ion concentration in the electrolyte. Pores of type (a) would be expected to be independent of plating conditions apart from a certain amount of bridging which might take place. The fall in porosity when the gold concentration was increased was very marked and must be attributed to a fall in the number of pores of type (b). Since these pores are very small they would be easily bridged over. The crystallographic pores probably originate in the initial stages of deposition from the failure of adjoining grains to coalesce fully leaving paths open to the substrate. One reason for the failure to coalesce may be a simple shortage of gold ions available for discharge at the appropriate points. This shortage is more noticeable in cyanide solutions where the gold ions are part of a negatively charged ion and concentration polarisation is high. If the growing grains 'rob' the surrounding solution then the area between two growing crystals may be left uncovered. The reduction brought about by an increase in gold ion concentration supports this theory. Leeds suggests two other reasons for the failure of grains to coalesce. (4) He points out that two adjoining growth steps could be orientated in such a way that they could not fit together properly. However, such mis-orientation would only lead to very small gaps in the coating, of the order of the lattice parameter of gold. He also suggests that impurities may be adsorbed onto the surface preventing lateral growth and giving rise to pores.

5. 2. Practical Significance of the Results.

5. 2. 1. Economic Aspects.

It has been stated that the cost of the gold metal used in an electrical contact forms a considerable part of the total cost of the contact. It is therefore important to keep to a minimum the thickness of the gold deposit in order to cut the cost of the connector. To appreciate how the thickness necessary to give adequate protection can be reduced, the way in which the required thickness is determined must first be considered.

Standard specifications such as B.S. 4292 exist to define the quality of gold coatings, but the thickness required is often decided by agreement between the customer and the plater. The customer normally demands a coating which will provide a certain level of corrosion resistance, and a corrosion test may be specified which the gold plated components must pass. In some cases, wear tests may be called for prior to corrosion testing in order to simulate operating conditions more exactly. The electroplater knows from experience what thickness of gold plate is required to meet each specification, and hence the thickness is determined. 5µM is found to be adequate for most applications in this country. If the porosity of the electrodeposit could be reduced then a thinner coating might provide adequate protection with a consequent saving of gold and a lower priced connector. The ways in which porosity can be reduced will be discussed later in section 5. 2. 2.

The type of corrosion test specified is also an important factor in determining the thickness of gold necessary, since a less severe test would permit a thinner coating to be used while porosity remained at the same level. An example of this is the different tests used in Britain and America to assess gold coatings used for the same applications. In America, where nickel undercoats are commonly used, a salt spray type corrosion test is used which is much less severe than the gas tests used in this country. As a result, coatings used in America are often only half as thick as their counterparts doing exactly the same job in Britain. Since their performance is satisfactory, this is one way in which gold thickness could be reduced while still using existing solutions and practice.

5. 2. 2. Plating Conditions.

The results obtained have shown that the porosity of gold electrodeposits can be reduced by increasing the activity of the gold metal ions in the electrolyte. This conclusion is supported by the work of Leeds and Clarke on the effect of plating parameters on porosity. Their results have been summarised by Leeds (4) who states that increases in current density and reductions in agitation, gold content of the electrolyte, and plating bath temperature all lead to increases in porosity. The ways in which increases in the activity of the gold ions can be achieved in practice may be summarised as follows :-

a) Increasing the concentration of gold salts in the plating solution. This produced the largest fall in porosity and could easily be achieved in practice. The main disadvantage of this technique is that increased drag out losses would result, but modern methods of recovering gold from rinsing solutions should offset this.

b) Increasing the bath temperature, a technique already used in many instances.

c) Vigorous agitation which is essential to ensure an adequate supply of gold ions to the cathode surface.

A further factor which could be improved on while retaining existing solutions is the quality of the substrate surface. This surface should be as free from pits and inclusions as possible. Mechanical polishing should be avoided where possible since these operations will leave particles of polishing compound embedded in the substrate surface which will form the basis of pores. Such particles are not removed by electrolytic degreasing, and the most desirable pre-treatments which can be used either alone or after mechanical polishing are chemical or electropolishing. These processes remove some of the surface layers allowing embedded particles to fall away. Undercoats may also reduce the porosity of deposits provided that they cover up any defects in the substrate surface and produce a leveller surface which means that the effective area to be covered by gold is reduced.

5. 2. 3. The Use of Alternating Current.

It has been shown that the use of an asymmetric square wave alternating current can lead to a reduction in porosity when applied to simple solutions free from addition agents. The same effect was not produced when alternating current was applied to commercial solutions. In this case, the beneficial effects of the alloying elements and addition agents were lost. The evidence suggests that the alloying elements were preferentially removed during the anodic deplating period. Thus the smooth uniform deposit brought about by the co-deposition of an alloy was lost and the structure reverted to a less compact and more porous form. Clearly if alternating current were to be used in commercial practice, a solution would have to be specially developed for it. Such a solution would probably be free from addition agents. The effect of alternating current was most pronounced at 20°C and its use might enable simple solutions to be used at room temperature.

One advantage of alternating current when applied to alloy solutions was the reduction in the stress of the deposit. At the higher current density this reduction in stress led to a reduction in the cracking which gave rise to an exceptionally high level of porosity when direct current was used for deposition. Alternating current might therefore be used to allow a faster plating rate when using alloy solutions susceptible to cracking.

5. 3. Conclusions.

1. The structure of gold deposited by direct current was altered from tangled laths to a more uniform compact form by increasing the deposition temperature from 20°C to 50°C. There was also a marked fall in porosity such that 50°C deposits were less porous than 20°C deposits which were twice as thick.
2. The use of electrolytes with higher gold contents brought about a substantial fall in porosity whatever plating conditions were employed and whether or not alternating current was used.
3. The use of alternating current led to a fall in porosity under all plating conditions. The effect was most marked at 20°C when the alternating current modified the structure of the electrodeposit in much the same way as raising the temperature. The effect of alternating current at 50°C was to refine the grain structure

All these conclusions 1-3 may be summarised by saying that the porosity of gold electrodeposits is reduced by factors which increase the activity of the gold ions in the solution. Alternating current maintains the gold ion concentration in the solution more effectively but also allows time for diffusion of the adatoms to stable low energy sites.

4. The porosity of alloy and commercial pure gold electrodeposits was increased by the use of alternating current. The structures formed were rougher and tended to revert to the type of structure produced by direct current on simple solutions free from any alloying elements or addition agents.

5. Porosity can be caused by substrate defects, although not all porosity can be attributed to this cause. Large pores were formed around non-conducting particles embedded in the substrate surface. Smaller pores were detected which would not be resolved by the scanning electron microscope. These pores probably arose from the failure to coalesce of the grains growing in the early stages of deposition. They may be termed crystallographic pores and it is this type which may be reduced by varying the operating conditions to increase the activity of the gold ions in the electrolyte.

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