# CHEMICAL POLISHING OF ALUMINIUM
# AND SOME ASSOCIATED PHENOMENA

BY

ANDREW WINSLOE CLIFFORD, B.Sc.

A Thesis submitted for the degree of
Doctor of Philosophy of the University
of Aston in Birmingham

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The role of nitric acid in solutions of the phosphoric/sulphuric/nitric acid type used in the chemical polishing of aluminium has been studied, using a number of techniques, including potential/time determinations and scanning electron microscopy.

The nitric acid was found to control the amount and distribution of copper deposited from the solution. In addition, the nitric acid is responsible for the formation and maintenance of a passivating surface film that prevents crystallographic etching.

The effect of increasing the ratio of sulphuric to phosphoric acid in these solutions was also studied. A ratio of phosphoric to sulphuric acid of 1.6:1 was found to produce a highly reflective surface. A ratio of 1:1 did not produce a reflective surface due to the formation of insoluble compounds on the surface. These compounds were also found on the surface of specimens allowed to drain for times in excess of 10 seconds prior to rinsing in water. It was found possible to limit these deposits by the addition of benzotriazole into the solution.

The anodic dissolution characteristics of both aluminium and stainless steel were studied. Pitting produced on both the aluminium and the stainless steel was found to be due to the presence of adherent gas bubbles on the surface preventing dissolution at the points of contact. This could be prevented in the case of the aluminium by a chemical polish for a minimum of 30 seconds prior to electropolishing, and in the case of stainless steel, by the addition of 2g/l of copper into the solution which facilitated polishing in the rapid gas evolution region, thus preventing gas bubbles adhering to the surface.

On electropolishing brass, however, gassing defects occured in the rapid gas evolution region. An explanation for the difference between the behaviour of these metals under these conditions has been proposed in terms of the nature of the surface film present on the surface during polishing.

KEY WORDS : ALUMINIUM
CHEMICAL POLISHING
ELECTROPOLISHING
STAINLESS STEEL
GASSING DEFECTS

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# CHAPTER 1

# INTRODUCTION AND LITERATURE SURVEY

## 1.1 Introduction

A highly reflective surface can be produced on some metals by immersion in mixtures of strong acids or alkalis. Alternatively, this can be achieved by applying an external potential to the work piece whilst in the polishing solution. These processes are known as chemical polishing and electropolishing respectively.

A considerable tonnage of components are polished by these means each year, and the choice of method depends on such factors as the operating costs of the solution for a particular metal or alloy, and the capital outlay for the plant. For example, aluminium is usually chemically polished whilst stainless steel tends to be electropolished due to the instability of the chemical polishing solutions available and their consequent short life. As the processes are similar in operation to anodising and electroplating processes they can be easily installed in a single production line, and mechanical polishing can often be entirely replaced. The process is suitable for bulk treatment with low labour costs and the articles require no further treatment prior to anodising or electroplating.

Industrial processes are generally divided into two types:

a) Processes that replace mechanical polishing and provide a bright, though not highly reflective finish.

b) Processes that produce a highly reflective 'mirror' finish.

A considerable number of processes have been developed for both chemical and electropolishing and have been described in detail by previous authors (1,2,3,4).

Chemical polishing solutions based on a mixture of phosphoric and nitric acid, with other additions, typically sulphuric or acetic acid are widely used, although the solutions containing acetic acid have a relatively short life (5).

The solutions most widely used are the phosphoric/sulphuric/nitric acid based solutions. These are available commercially under the names Alupol IV and V (6) in Germany and Phosbrites 159 and 176 (7,8) in this country. These solutions give a highly reflective surface to a wide range of aluminium alloys.

Another solution used quite widely is the Erftwerk solution, this contains nitric acid and ammonium hydrogen fluoride, and was developed by the Vereinigte Aluminium Werke in Germany (9), but this solution is limited to a few high purity alloys. It is characterised by a high dissolution rate of approximately 25-50μm per minute, and uses short treatment times, typically 40-60 seconds (10).

Electropolishing solutions also use phosphoric-sulphuric acid mixtures with some added nitric acid (2). The nitric acid is very often replaced by chromic acid (11). Other electropolishing solutions used to a greater or lesser extent commercially are the alkaline Brytal solution (12) which is most suitable for super-purity based alloys, and the fluoboric acid based Alzak process (13).

Tegart (3) has distinguished the functions of a polishing process to be:-

a) 'smoothing', where the large scale irregularities, above Iμm in size are removed.

b) 'brightening', where smaller irregularities, down to approximately 0.0Iμm, are removed.

The two are distinct since during etching smoothing may occur but the surface retains a dull matt finish.

Since there is a degree of overlap between the theories relating to chemical and electropolishing, and the majority of the work in the past has been confined to the latter, both will be included in this review.

## 1.2 Electropolishing

The first optical micrographs produced by anodically dissolving a metal, rather than the traditional mechanical polishing method, were published in 1936 by P.Jacquet(14), who also recorded the relationship between the current and anode potential, which has been substantiated by numerous subsequent researchers.

The curve of anode potential against anode current density (Fig.1.1) has been divided into five sections(3):

1) The region A-B where the increase in current is proportional to the increase in potential, and is often referred to as the 'etching' region.

2) The region B-C where the current is unstable and fluctuates.

3) C-D, in this region further increases in potential produce little or no change in the current density and is often referred to as the 'limiting current density region' or the 'polishing plateau'.

4) D-E, an increase in potential above the point D leads to a rise in current density, and slow gas evolution.

5) E-F a further increase in potential leads to a continued rise in the current density, with rapid gas evolution.

Huber(15) associated the reactions occuring at different steps in the curve of the diagram for aluminium to be:

a) $Al \rightarrow Al^{3+} + 3e^-$

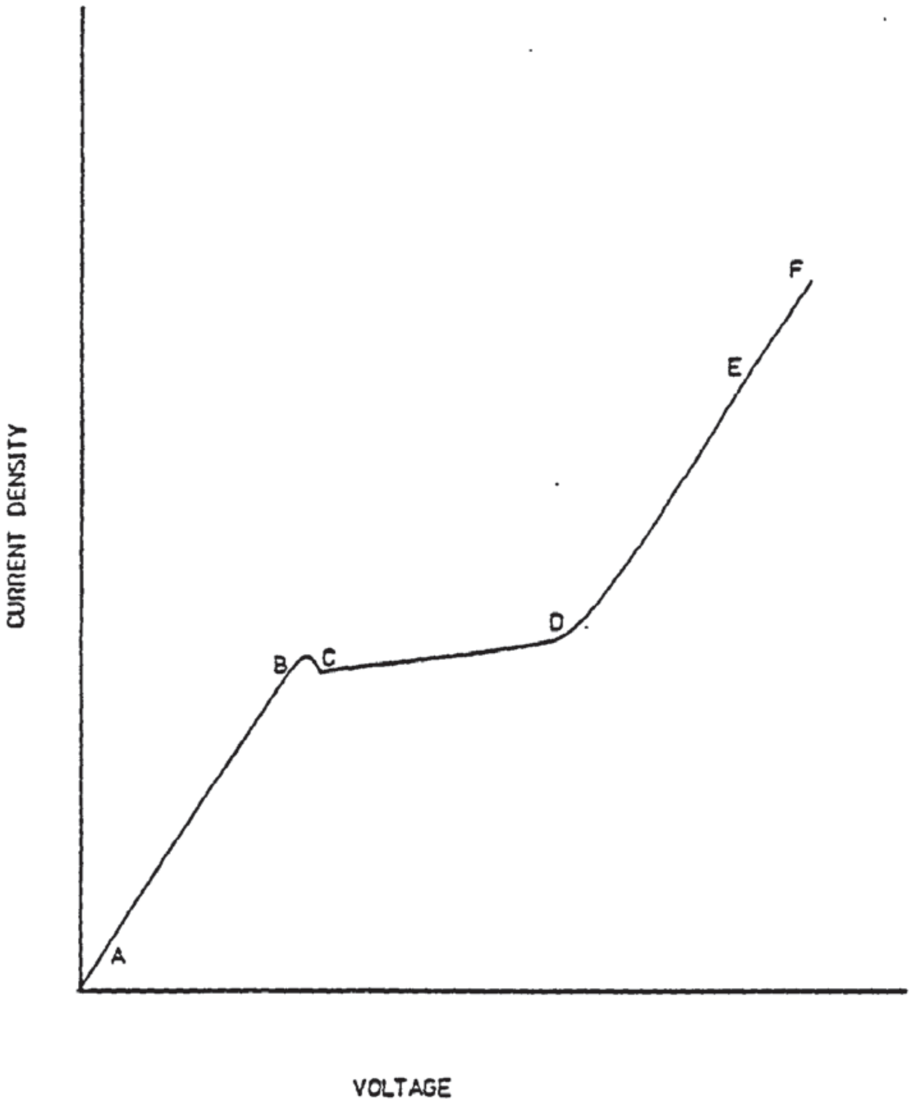


Fig.I.I. Typical Voltage-Current Density relationship for Electropolishing.

b) $2Al + 6OH^- \rightarrow Al_2O_3 + 3H_2O + 6e^-$

c) $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

The first stage represented by A-B, is associated with metal dissolution, determined by concentration and activation polarisation; atoms are dissolved from the surface according to their free energy, as in an anodic etch. In region B-C the conditions are unstable and polishing may or may not occur. Reaction (b) occurs in the region C-D, and is controlled by the rate of film dissolution and is the region where polishing occurs. At anode potentials above the point D of Fig.1.1 reaction (c) occurs and oxygen is evolved.

Jacquet(16) noticed that anodes in the limiting current density region had a layer of electrolyte, of higher viscosity than the bulk solution, streaming down from the surface, and suggested that this layer had a relatively high electrolyte resistivity. Thus the resistance between peaks on the surface was less than that between troughs and the bulk of the solution, and that this would lead to preferential dissolution of the peaks due to a higher current density at the peaks. This view was supported by Hickling and Higgins(17) who found that the diffusion current density at peaks on a composite anode of copper in phosphoric acid was higher than at cavities. Edwards(18) using a laminated copper anode, different from that used by Hickling and Higgins, found that the current density on projecting areas was greater than on recessed areas, but that the ratio did not change on passing from etching to polishing conditions.

Theories on the mechanism by which a metal acquires a polished surface can be categorised into those associated with:

(1) Diffusion; (2) Acceptance of solution cations; (3) Passivation; (4) Ionic adsorption.

### 1.2.1 Diffusion

Elmore(19,20) stated that certain assumptions were necessary to account for electrolytic polishing. (1) When a current is passed through a cell, metal ions leave the anode by diffusion and not by electrolytic migration, and that this requires a concentration gradient that is proportional to the current density. (2) After the current has flowed for time $t_o$ the concentration of metal ions at the anode reaches a maximum, representing the solubility limit of the metal in that electrolyte. (3) After time $t_o$ the current flowing is limited by the concentration gradient of the anode layer. From these assumptions Elmore suggests that metal ions will diffuse more rapidly from asperities than depressions, and thus the surface will be smoothed. Elmore derived from the diffusion equation the following relationship between the applied current $i_o$, and the transition time $t_o$ to establish a saturated anode layer and obtain polishing conditions.

$$i_i t_o^{\frac{1}{2}} = \frac{1}{2} C_m AF(\pi D)^{\frac{1}{2}} = \text{Constant}$$

Where $C_m$ is the solubility limit of the metal in the electrolyte; A is the area of the anode; D the diffusion coefficient of dissolved metal and F is the Faraday.

However, this theoretical formula can be criticised since it does not take into account the fact that as the viscosity of the anode layer increases the rate of diffusion will decrease.

Walton(21) investigated the anode layer of copper polished in phosphoric acid and phosphoric acid/glycerol/ethylene glycol mixtures and found that dissolved copper raised the viscosity considerably (more so in the mixture than in the phosphoric acid alone) and that the anode was highly supersaturated in copper phosphate. He also estimated the effective anode layer thickness to be approximately $1X\ 10^{-3}$cm.

### 1.2.2 Acceptor Theory

Halfawy(22) put forward the theory that it was not the diffusion of metallic ions that controlled the dissolution of a metal, but the distribution of the anions over the asperities and depressions on the anode. The author considered that a phosphate ion of velocity u moves through an electrolyte of viscosity $\eta$, under the influence of a potential gradient f then according to Stokes' law:

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

where b is the radius of the phosphate ion. Due to the relatively high viscosity of the anode layer compared with the bulk solution the anions move more slowly through the viscous layer. In addition, the higher the potential gradient the higher the ionic velocity according to Stokes' Law. Therefore, the ionic velocity of phosphate ions arriving at the viscous layer will be reduced, once in the viscous layer, as projections have a higher potential gradient than depressions the ions will migrate to these regions preferentially and more rapidly.

The accumulation of phosphate ions at the projections will lead to preferential dissolution and smoothing of the surface. Edwards(23) extended the work of Elmore and demonstrated the importance of viscosity, and suggested that the rate of dissolution was due to the diffusion inwards of acceptor anions to combine with metal cations. The author also suggests that crystallographic etching does not occur since the acceptors in the electrolyte arrive at the anode under the influence of diffusion, and possibly convection, but not to any great extent electrolytic migration, so their distribution over the surface will not be affected by slight differences in potential due to crystal structure. However, at anode potentials below those associated with polishing, and before polishing conditions are established, there will be an excess of acceptor ions at the surface, so that crystal structure will determine the rate of dissolution, and etching will result. Wagner$^{(24)}$ carried out a mathematical analysis of an ideal electropolishing process based on the mechanism of diffusion of acceptor ions that agreed with the observations of Edwards.

### 1.2.3 Passivation

Evans$^{(25)}$ put forward an explanation for the polishing process based on the passivation of depressions in the anode surface. This however is incompatable with the fact that these regions are also subject to dissolution.

Hoar and Mowat$^{(26)}$ studied the potential of nickel in a urea/ammonium chloride melt and suggested that the increase in resistance they found was due to a compact solid film which is dissolved at the solution/film interface as fast as it forms at the metal/film interface. The film allows cation transport by diffusion, and the random nature of cation vacancies in the film ensures that the difference in position and energy of lattice cations has no effect on their dissolution. Hoar and Farthing$^{(27)}$ demonstrated the existance of a surface film by dropping mercury on the surface of the metal. Metals undergoing etching were wetted, whereas metals being polished were not. The presence of a surface film on metals during or after polishing has been shown by a number of authors using a variety of techniques; cathodic reduction$^{(28)}$ a-c impedence$^{(29)}$; electron diffraction$^{(30)}$; electron microscopy$^{(31)}$ and electron spectroscopy for chemical analysis combined with ion milling$^{(32)}$.

Gabe$^{(33)}$ studied the polarisation characteristics of copper during electropolishing and suggested that at lower temperatures (11-30°C) electropolishing may be diffusion layer controlled, whilst at higher temperatures (51-75°C) it may be surface film controlled. The author in a later paper$^{(34)}$ noted that the polarisation features for electropolishing mild steel in phosphoric acid and sulphuric acid and copper in phosphoric acid were very similar but in practice copper polishes and mild steel does not. Gabe suggests that there is a clear subtle relationship between the surface film and the diffusion layer, the former dependent on the formation of an insoluble dissolution product, and the latter on the viscosity of the solution.

### 1.2.4 Ionic Adsorption

Darmois et al (35,36,37) put forward a theory of polishing involving the adsorption, on the anode, of anions of the electrolyte. In a fused salt electrolyte under polishing conditions, the anode becomes covered with a thin but compact layer of anions which are capable of setting up an electrostatic field sufficiently intense to detach the metal ions in a random manner.

## 1.3 Chemical Polishing

Marshall (38,39) noted that the surface of steel immersed in a mixture of oxalic acid/hydrogen peroxide and sulphuric acid, without an applied potential, developed a bright surface. Pinner (40) considered the mechanism of chemical polishing of aluminium to be one of controlled corrosion, the reactions to be electrochemical in nature and not purely chemical. Pinner suggested that in the absence of an external applied potential local anodic and cathodic areas existed in different areas on the surface. These could be impurities, grain boundaries, alloying constituents or other dissolved constituents in the solution. The anodic reaction according to Pinner was the dissolution of the aluminium:

$$Al \rightarrow Al^{3+} + 3e^-$$

Brace and Kape (41) supported this view and suggested that the aluminium initially forms a complex film containing aluminium phosphate, but continuation of dissolution results from further aluminium ions diffusing through the film and dissolving in the polishing bath.

General agreement exists on the nature of the cathodic reaction which is partially the evolution of hydrogen according to the equation:

$$3H^{+} + 3e^{-} \rightarrow \frac{3}{2} H_2$$

According to Fischer and Koch(42) the polishing mechanism operates due to the local cell:

Al / acid / redox system / noble metal

The function of the noble metal is stated to be to catalyse the reduction of the oxidising agent. However, this presupposes the presence of a noble metal in the solution which is not always the case.

### 1.3.1 Heavy Metal Additions

A number of authors(2,4,41,43,44) have reported the presence of heavy metal additives to chemical polishing solutions (e.g. Cu,Ni,Fe,Co, Cd,Ag) although no theoretical justification is given for addition of one in preference to others. Fischer and Koch(42) suggested that the function of the heavy metal was to catalyse the reduction of the oxidising agent. Brace and Kape(41) stated that when a chemical polishing solution contains the soluble salt of a heavy metal (e.g. Cu) the metal is precipitated on the surface by a simple replacement reaction:

$$3CuSO_4 + 2Al \rightarrow Al_2(SO_4)_3 + 3Cu$$

The authors believed that the deposited copper provided local galvanic cells due to the potential difference between the two metals, and that deposition first occurred at defect sites in the oxide film, and proceeds until the surface is covered with copper to a thickness of several atomic layers, thus reducing the rate of dissolution of the underlying aluminium but resulting in micro-smoothing. The authors also believed that if the optimum copper content of the solution was exceeded, the number of copper atoms arriving at an active site was increased, leading to a build up of massive loose deposits that cause appreciable local currents and etching of the aluminium in the vicinity, but this soon causes undercutting of the copper which falls off and is re-dissolved. The process continues as further dissolution creates new active sites at which etching predominates. Thus the rate of dissolution is greater and the brightness less. In addition if a redox system operates, the heavy metal itself may be partly oxidised to form cuprous or cupric oxide, and this suggestion was supported by the observation that the copper smudge found on the surface after chemical polishing was difficult to remove in a nitric acid solution which would not be the case if pure copper were deposited. However, Pinner(45) stated that it was most unlikely that copper would be oxidised in a local cell in which it formed the cathode.

### 1.3.2 The Role of Nitric Acid

Lattey(46) proposed that the presence of nitric acid in chemical polishing solutions reduces the overpotential of hydrogen discharge and thus allows the reaction to proceed more smoothly, and that more or less solid passivating layers and films must be expected according to the composition of the bath. Brace and Kape(41) have shown that there is an optimum nitric acid content for maximum reflectivity, in phosphoric/sulphuric/nitric acid solutions, and that the weight loss of aluminium polished in baths containing nitric acid has a minimum at approximately 6% which corresponds to maximum brightness. Fischer and Koch(42) have shown by the analysis of the gases evolved from the chemical polishing of aluminium that the nitric acid is reduced to release oxygen, and oxides of nitrogen. Brace and Kape(41) further suggested that this reduction leads to the formation of a relatively stable oxide film which is in a state of dynamic equilibrium, being continuously reformed as dissolution proceeds. Below the optimum nitric acid concentration etching occurs because too few oxygen ions reach the surface to maintain a stable film, and above the optimum concentration the film appears to gradually break up, since an etch pattern develops progressively.

Wernick and Pinner(2) considered two possibilities:

1) that the nitric acid reacts with the metal in the undissociated state and results in the formation of oxides of the metal, and oxides of nitrogen. The cathodic reaction may then be the reduction of the nitric acid to the hydroxyl (or oxygen) ion plus nitrous acid, the net reaction being:

$$2Al + 3OH.NO_2 \rightarrow Al_2O_3 + 3HNO_2$$

2) the nitric acid may react with the aluminium in the dissociated state: $H^+ + NO_3^-$. The latter seems unlikely however, since the polishing solutions in question (concentrated phosphoric/sulphuric and nitric acid) contain insufficient water to allow for any significant dissociation. Dmitriev(47) studied the changes in potential with time of aluminium in a phosphoric/sulphuric/nitric acid mixture and found periodic oscillations in the potential. These he attributed to changes at the aluminium/solution interface and changes in the conditions for dissolution of the oxide film. The author also noted that copper deposition was greatest after the termination of an oscillation.

Turashev and Belyaeva(48) studied the potentiostatic polarisation of aluminium in phosphoric/sulphuric and phosphoric/sulphuric/nitric acid solutions and found that the applied potential, to give the best electropolished finish corresponded closely with the natural potential (with respect to a saturated calomel electrode) of aluminium in the solution containing 5g-eq/litre of nitric acid. However, the solutions that the authors used did not contain any dissolved copper, which is widely known to considerably improve the finish achieved, and also to alter the potential of the aluminium(47).

### 1.3.3 Surface Structures

Electron microscope studies by Bucknell and Geach(49) and Brown(50) led to the discovery of fine line markings on replicas taken from anodically polished aluminium. These were interpreted as shallow steps or grooves in the metal surface, which were equispaced at intervals of about 1000 Å. They frequently resembled furrows in their parallel alignment, and changed direction from grain to grain. Brown and later Bussy(51) suggested that the surface markings they observed represented some imperfections in the grain structure of the metal. Welsh(52) refuted this suggestion and found that the conditions of electrolysis influenced the spacing of the markings and suggested that the markings were associated with the electrode process. Hollow(53) also refuted the suggestions of Bussy and Brown.

Hunter and Robinson(54) studied the markings produced by the chemical polishing of super purity aluminium and considered that each grain contained many thousands of subgrains which were defined by preferential attack of their boundaries. Hirsch(55) expressed doubt at this and stated that the network was due to the orientation dependence of the etching characteristics of the electrolyte.

Phillips and Welsh(56) using electron microscopy to study thin foils, found no correlation between the surface markings and the underlying, much larger, normal subgrain structure of the metal. The authors attributed the surface markings to the etching process.

Cuff and Grant(57) using electron microscopy of shadowed replicas found that the markings, previously thought to be furrows were in fact ridges, which the authors believed represented a surface manifestation of a three dimensional network of segregated impurity atoms. The authors proposed that the areas which the impurity atoms had segregated to, which were cathodic relative to aluminium, became cathodic regions and according to the acceptor theory, phosphate atoms would be repelled from the ridges to the areas between, which would therefore dissolve preferentially. Bichsel(58) supported the observations of Phillips and Welsh(56) that the surface markings were not related to the underlying subgrain structure, and the observations of Cuff and Grant(57) that the markings were ridges and not furrows. Bichsel attributed the surface markings to local attack at points with lattice dislocations which may contain traces of impurity elements. Isolated flat etch pits develop which increase in size and finally meet, thus producing raised cell ridges. The author also observed 'corrosion products' on the cell ridges and assumed that these deposits represented the anodic part of a local galvanic cell whereas the cell centre is cathodic in relation to the cell rib. This, however, is inconsistent with the proposals of Cuff and Grant.

### 1.3.4 Existence of a Surface Film

The presence of a surface film during electropolishing has been demonstrated by Hoar and Farthing(27) by a mercury wetting test. Francis and Colner(59) observed cyclic phenomena when electropolishing silver in a cyanide solution and attributed this to the successive growth and dissolution of a surface film of silver cyanide. Hoar and Mowat(26) also assumed that the periodic oscillations in current and voltage that they found before polishing conditions were established were due to alternative passivation and dissolution of a surface film. Fujimura(60) studied the film produced by the electropolishing of aluminium in various solutions. Some solutions produced a polishing film which the author believed had a structure similar to that of an anodised film, consisting of a thin (20-200 Å) barrier layer under a thicker (up to 5μm) porous layer. The author did not find a film on the surface of aluminium after polishing in a perchloric acid based solution and concluded that polishing could occur with or without a surface film.

Williams and Barret(30) supported the acceptor theory of Elmore, and suggested that the surface film they found from electron diffraction to be rich in copper phosphate, was a secondary phenomena merely indicating the attainment of a solubility limit.

Hoar, Mears and Rothwell(61) pointed out that the anodic behaviour of an anode in the presence of a surface film will depend on the electrical characteristics of the film. If its electron conductivity is low, film growth by ion transport may occur, particularly at high positive potentials. If the electron conductivity is high, electroreduction of solution species occurs at the film/solution interface at quite low anode potentials, too low to produce substantial ion transport and so the metal will be passive. Therefore, for anodic brightening the film must have a relatively high cation conductivity and allow easy passage of cations through the film to the solution. The authors suggest that the film is not a simple oxide but a contaminated oxide with significant amounts of the anion from the solution.

Neufeld and Southall(31) studied the films produced by electropolishing and chemical polishing, directly by electron microscopy, by growing a supporting barrier layer type film which they assumed did not affect the stucture of the existing film. They stated that the films produced had no common structure for the electrolytes used and suggested that the electrolyte need only be able to induce adequate ionic conductivity in the surface film for the production of a bright surface.

Olefjord(32) used electron spectroscopy for chemical analysis combined with argon ion milling to study the films produced by electropolishing stainless steel. The author found that the top layer consisted of sulphates and phosphates and after the first ion milling operation only oxygen, chromium and ion were present. Further ion milling and subsequent analysis produced no change in the percentage of chromium or oxygen, but increased amounts of nickel and manganese were found.

### 1.3.5 The Influence of Impurity and Alloying Elements

It is widely known that some chemical and electropolishing processes, notably the Brytal and the Erftwerk, cannot normally be used on low grade material. In these processes an iron content of as little as 0.032% (by weight) in aluminium is sufficient to cause a considerable drop in reflectivity. A lowering of reflectivity is also found on aluminium containing relatively small amounts of: copper (0.06%) and silicon (0.04%)(2). Phosphoric/nitric based solutions on the other hand will produce good results on a wide range of aluminium alloys. Brace(62) suggested that in phosphoric acid based chemical polishing solutions the effect of impurities and alloying elements depends on their metallographic state. Elements in solid solution have little effect, and the author claims that small amounts of copper are in fact beneficial. Elements that dissolve in the solution may actually leave behind a surface with a lower impurity content than the original surface.

Cooke and Spooner(63) studied the effect of alloying elements and impurities on the chemical polishing characteristics of an aluminium - 1% Mg.alloy. They found no detrimental effect from copper up to a concentration of 1.5%, but at the next concentration (6%) a low reflectivity was produced, which the authors attributed to preferential dissolution of the $CuAl_2$ constituent. The addition of copper to the polishing solution suppressed pitting caused by iron impurities up to a level of 0.008%. In addition certain other elements could be tolerated up to certain levels without loss in specular reflectivity. In particular magnesium (up to 2%), silicon (up to 0.1%), and titanium (up to 0.29%).

Guminski, Sheasby and Lamb$^{(64)}$ investigated the reaction rates of certain second phase constituents in aluminium during etching, chemical polishing and anodising. After chemical polishing they found that the iron rich impurities (present at a concentration of 1.5%) dissolved at an equal rate to the matrix. Silicon (11%) and titanium dissolved at a much slower rate. Copper however, dissolved at the same rate as the matrix. The authors concluded that constituents that react at a different rate to the matrix are generally detrimental. The authors do not however comment on the effect, if any, of the impurities on the aluminium in their vicinity.

Chatterjee and Thomas$^{(65)}$ considered that the etching mechanism of aluminium in caustic soda was largely under electrochemical control. The intermetallic constituents forming the cathodes of local cells with the surrounding aluminium in the anode. During dissolution, aluminium goes into solution from the anodic areas, while an equivalent quantity of hydrogen is evolved from the cathode sites, according to the reaction:

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

At the cathodic sites the hydrogen ions yield their charge to become gaseous molecules and thus disperse. The energy requirement of this stage in this system is determined by the hydrogen overvoltage since the only process operating is hydrogen ion reduction. This in turn depends on the nature of the cathode material. West$^{(66)}$ recorded the exchange current densities for hydrogen evolution for various metals, in particular:

| | | | |
|---|---|---|---|
| Aluminium | approx | $10^{-10}$ | A/cm$^2$ |
| Copper | " | $10^{-7}$ | A/cm$^2$ |
| Iron | " | $10^{-6}$ | A/cm$^2$ |
| Silicon | " | $10^{-12}$ | A/cm$^2$ |

Chatterjee and Thomas$^{(65)}$ suggested that the relatively high value for iron allows a high cathode reaction and is very effective in promoting active corrosion dissolution. The authors also found that iron intermetallics increased the rate of etching of aluminium in caustic soda solutions(67).

## 1.4 The role of Benzotriazole

Although the use of benzotriazole (B.T.A.) in hot mixed concentrated acids has not been previously reported, it is important to consider the mechanism by which B.T.A. acts as a corrosion inhibitor in neutral and dilute acid solutions, as the mode of action in the concentrated acids may be similar. Cotton(68) suggested that B.T.A. forms an insoluble complex film of a polymeric nature. The bond between the metal surface and the B.T.A. being a true chemical combination. The real function of the B.T.A. is to reinforce the protection usually afforded to the oxide film, particularly at defect sites, rather than by direct combination with the bare metal.

Dugdale and Cotton(69) further suggested that B.T.A. prevents staining of copper by the formation of a copper/B.T.A. compound that acts as a cathodic inhibitor for the oxygen reduction reaction, and is assisted to a lesser extent by the physical barrier effect of the copper/B.T.A. compound on the surface.

Mansfield, Smith and Parry(70) used potentiostatic polarisation, a-c impedence and ellipsometry techniques to study the effect of B.T.A. on copper in a sodium chloride solution and supported the view of Cotton et al(68,69) that B.T.A. is chemisorbed onto the surface and prevents the adsorption of oxygen and the consequential oxidation of the copper. However, the authors found, contrary to Cotton, that the B.T.A. adsorbed onto the surface after dipping in a solution containing B.T.A. could be dislodged from the surface by rinsing, and allow dissolution of the copper, although tarnishing did not occur.

Walker(71) found the pitting of aluminium in water containing copper ions could be prevented by the addition of B.T.A. to the water.

Mayanna and Setty(72) studied the effect of the addition of B.T.A. to a dilute (0.1N $H_2SO_4$) acid solution and found that B.T.A. acts as a cathodic inhibitor at low concentrations and an anodic inhibitor at high concentrations. The authors considered that since B.T.A. forms complexes with $Cu^+$ and $Cu^{++}$ ions, B.T.A. in the acidic solution may affect the kinetics of each step and, therefore, the overall reaction.

X-ray photon spectroscopy was used by Chadwick and Hashemi(73) to study the adsorption of B.T.A. on copper and copper alloys. The authors found that on pure copper, copper oxides are the substrate for B.T.A. adsorption, but expressed doubt as to the importance of the surface oxide to the chemisorption process. In addition, they found that B.T.A. does adsorb onto an oxide free copper surface, but that the film thickness was low, whereas when cuprous oxide was present adsorption was rapid and the film produced was relatively thick, especially in acid solutions.

## 1.5 Gassing Defects produced by Chemical and Electropolishing

To achieve a highly reflective surface when either electropolishing or chemically polishing aluminium it is necessary for the operating conditions of a particular system to be adjusted to the optimum for that system. If the optimum conditions are not maintained then defects can be produced on the surface. Some defects can be attributed to the material (e.g. impurity elements), however, some defects are a direct result of breakdown of the polishing conditions and are not due to poor material or contaminated solutions etc.

Jacquet(14) in his early work noted that in the region of slow gas evolution gas bubbles adhered tenaciously to the surface and prevented dissolution at the points of contact, and gave rise to protusions on the surface, and violet agitation prevented this.

This view was supported by Tegart$^{(3)}$ who produced optical micrographs of brass polished in the slow and rapid gas evolution region showing pits with central light mounds. The author suggested that there could be two different forms of defects characterised by adherent and non-adherent gas bubbles. The presence of adherent gas bubbles has also been noted to cause surface defects in the alkaline Brytal solution$^{(2)}$.

Neufeld and Southall$^{(74)}$ however, refuted this idea and produced optical micrographs of pitted stainless steel with a central light region, but failed to find a central mound using scanning electron microscopy and considered that the light region of the optical micrographs were artifacts caused by reflection of light within the pits, although in the discussion that followed the presentation of the paper$^{(75)}$ realised that this idea was open to question. The authors proposed that the pits represented locations where a stream of gas bubbles was being evolved. The increased stirring at these points will reduce the thickness of the anode layer and lead to increased dissolution at these points.

Henley$^{(76)}$ drew attention to the similarity in appearance of some of the pits obtained by Neufeld and Southall to pits sometimes produced during the chemical polishing of aluminium, particularly the presence of a small bright region in the centre of the pit.

Thomas$^{(77)}$ studied similar defects and associated the central prominence with some material masking the surface, but attempts to reproduce the defects in experiments using various oils, greases, paints etc. proved unsuccessful.

Generally only a few passing references to gassing defects could be found in the literature, apart from the preceeding references. Pullen and Scott(78) reported gas flow marks in alkaline electro-brightening of aluminium, and emphasised that the solution should not be stirred during polishing if defects were to be avoided. They also noticed that slight gassing enhanced brightening, but excessive gas flow produced white streaks.

# CHAPTER 2

## EXPERIMENTAL PROCEDURE AND TECHNIQUES

### 2.1 Materials used

Super-purity (99.99%) aluminium and 99.5% Anodizing Quality aluminium, as supplied by the British Aluminium Company Ltd., in the form of bright rolled annealed sheet 0.9mm. thick, with the following composition (wt%):

| | SUPER-PURITY(99.99%) | ANODIZING QUALITY(99.5%) |
|---|---|---|
| Mg...... | 0.0005% | 0.06% |
| Cu...... | 0.002 | 0.015 |
| Si...... | 0.0055 | 0.15 |
| Fe...... | 0.006 | 0.19 |
| Mn...... | 0.0015 | - |
| Ti....... | - | 0.025 |

### 2.2 Specimen size

Two specimen sizes were used. Specimens 5cm. by 1cm. were used for the electrode potential determinations, and specimens 10cm. by 5cm were used for determining the specular reflectivity.

### 2.3 Solutions

Analar grade reagents were used throughout, except where otherwise stated.

### 2.3.1. Chemical polishing solutions

TABLE 2.1

| Solution | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| Phosphoric acid (SG 1.75) Vol % | 82.5% | 77.5% | 65.9% | 82.5% | 77.5% | 65.9% |
| Sulphuric acid (SG 1.84) Vol % | 17.5% | 16.5% | 14.1% | 17.5% | 16.5% | 14.1% |
| Nitric acid (SG 1.5) Vol % | - | 6% | 20% | - | 6% | 20% |
| Phosphoric: Sulphuric acid ratio | 4.7:1 | 4.7:1 | 4.7:1 | 4.7:1 | 4.7:1 | 4.7:1 |
| Copper content g/l | - | - | - | 1.0 | 1.0 | 1.0 |
| Solution operating specific gravity (at 15°C) | 1.75 to 1.78 | | | | | |

TABLE 2.2

| Solution | G | H | J | K |
|---|---|---|---|---|
| Phosphoric acid (SG 1.75) Vol % | 58.2% | 58.2% | 47.0% | 47.0% |
| Sulphuric acid (SG 1.84) Vol % | 35.8% | 35.8% | 47.0% | 47.0% |
| Nitric acid (SG 1.5) Vol % | 6% | 6% | 6% | 6% |
| Phosphoric: Sulphuric acid ratio | 1.6:1 | 1.6:1 | 1:1 | 1:1 |
| Copper Content g/l | 1.0 | 1.0 | 1.0 | 1.0 |
| B.T.A. content g/l | - | 2.8 | - | 10.0 |
| Solution operating specific gravity (at 15°C) | 1.79 to 1.82 | | | |

The ratio of phosphoric acid to sulphuric acid for the solutions listed in table 2.1 is 4.7:1. The water content was kept approximately the same by maintaining a specific gravity of 1.77 (measured at 15°C). The solutions were changed before the aluminium content rose above 1g/l.

All the solutions listed in table 2.2 contain 1g/l of dissolved copper. In addition these solutions were prepared from commercial grade reagents. Benzotriazole (B.T.A.) was added as a crystalline solid. The copper additions were made in the form of copper sulphate crystals, $CuSO_4.5H_2O$. (3.93gms $CuSO_4.5H_2O \equiv$ 1gmCu metal). The ratio of phosphoric acid to sulphuric acid in solutions G and H is 1.6:1, and in solutions J and K the ratio is I:I.

## 2.4 Specimen Preparation

Since the aluminium sheets supplied had an excellent finish no pre-treatment was used. The specimens were guillotined to the appropriate size, degreased in acetone, dried in air, and stored in a desiccator until used.

## 2.5 Polishing apparatus

### 2.5.1. Specular Reflectivity

Polishing for specular reflectivity was carried out in three litre glass beakers. The solution was held at a constant temperature of 100°C ± 1°C by a controlled electrical hotplate. This temperature was chosen as it is the one most commonly used commercially and gives an excellent finish when the conditions are set at the optimum. Moderate agitation of the solution was provided by a magnetic stirrer. Preliminary experiments showed that the precise amount of agitation was not critical, and only slight agitation was necessary to prevent gas streaking.

The specimens were held in the solution by a glass holder (fig.2.1), except for solution A where the sample floated out of the holder. In this solution an aluminium jig was used (fig.2.2). Samples for Scanning Electron Microscopy were held in a Polypropylene jig which was not attacked by the polishing solution.

### 2.5.2 Electrode Potential Determination

The solution was contained in a 1 litre glass beaker, maintained at a temperature of 100°C ± 1°C by a controlled electrical hotplate. Moderate agitation was provided by a magnetic stirrer. The amount of agitation was found to affect the potential to a small extent and the amount of agitation was therefore, kept constant throughout.

As the solution temperature was 100°C the saturated calomel

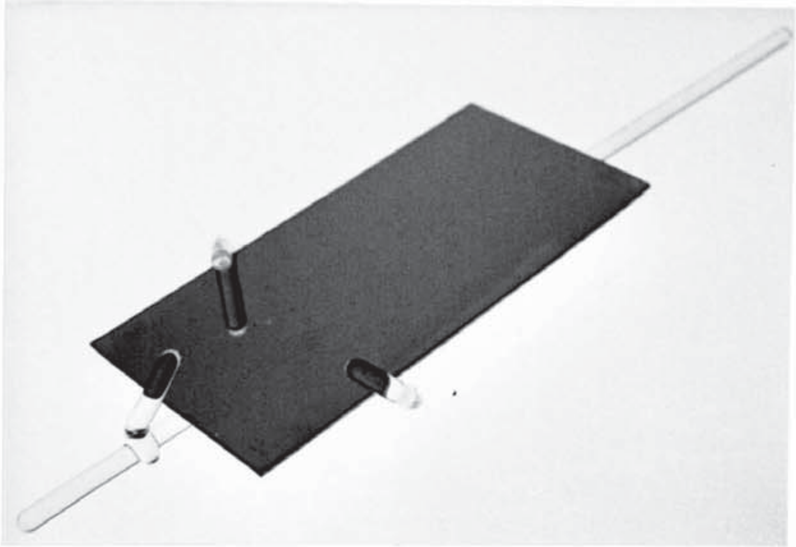


Fig.2.I. Photograph of 5 X IOcm. specimen and glass holder.

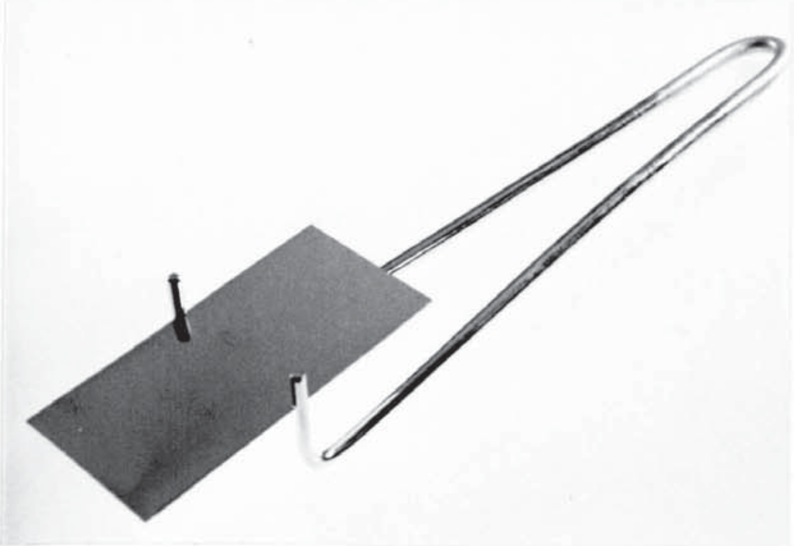


Fig.2.2. Photograph of 5 X IOcm. specimen and aluminium holder.

reference electrode was separated from the rest of the solution by a means of a capillary salt bridge arrangement. The length of the salt bridge was kept to a minimum to reduce any IR drop. Preliminary experiments showed that it was necessary for a syphon to operate in the first salt bridge, in such a way as to prevent gas bubbles collecting in the capillary tube and breaking the electrical contact. Fig.2.3 shows a diagramatic representation of the apparatus used. The potential difference between the aluminium electrode and the saturated calomel reference electrode was continuously monitored on a high impedence chart recorder, set at a maximum deflection of 1 volt, and using a chart speed of 30mm. per minute.

## 2.6. Experimental Techniques

### 2.6.1 Specular Reflectivity

Aluminium specimens (5cm. by 10cm.) were chemically polished for times ranging from 5 seconds to 5 minutes.with 5 second intervals in the first minute and 30 second intervals thereafter. After polishing the samples were rapidly transferred to a de-ionised water swill, to stop the polishing reaction and remove the acid on the surface. The aluminium was then transferred to a 50% (by volume) nitric acid solution to remove the copper deposited on the surface during polishing. The nitric acid itself was then removed in a further de-ionised water swill. The sample was finally rinsed in acetone and dried in air.

Preliminary experiments showed that the polishing of five panels for three minutes altered the nitric acid content by 0.5%, consequently, the nitric acid was frequently checked by volumetric analysis using ferrous sulphate, and additions were made accordingly so that the nitric acid did not vary significantly for a given panel. To eliminate the effect of dissolved aluminium, in the unaged solutions the solutions

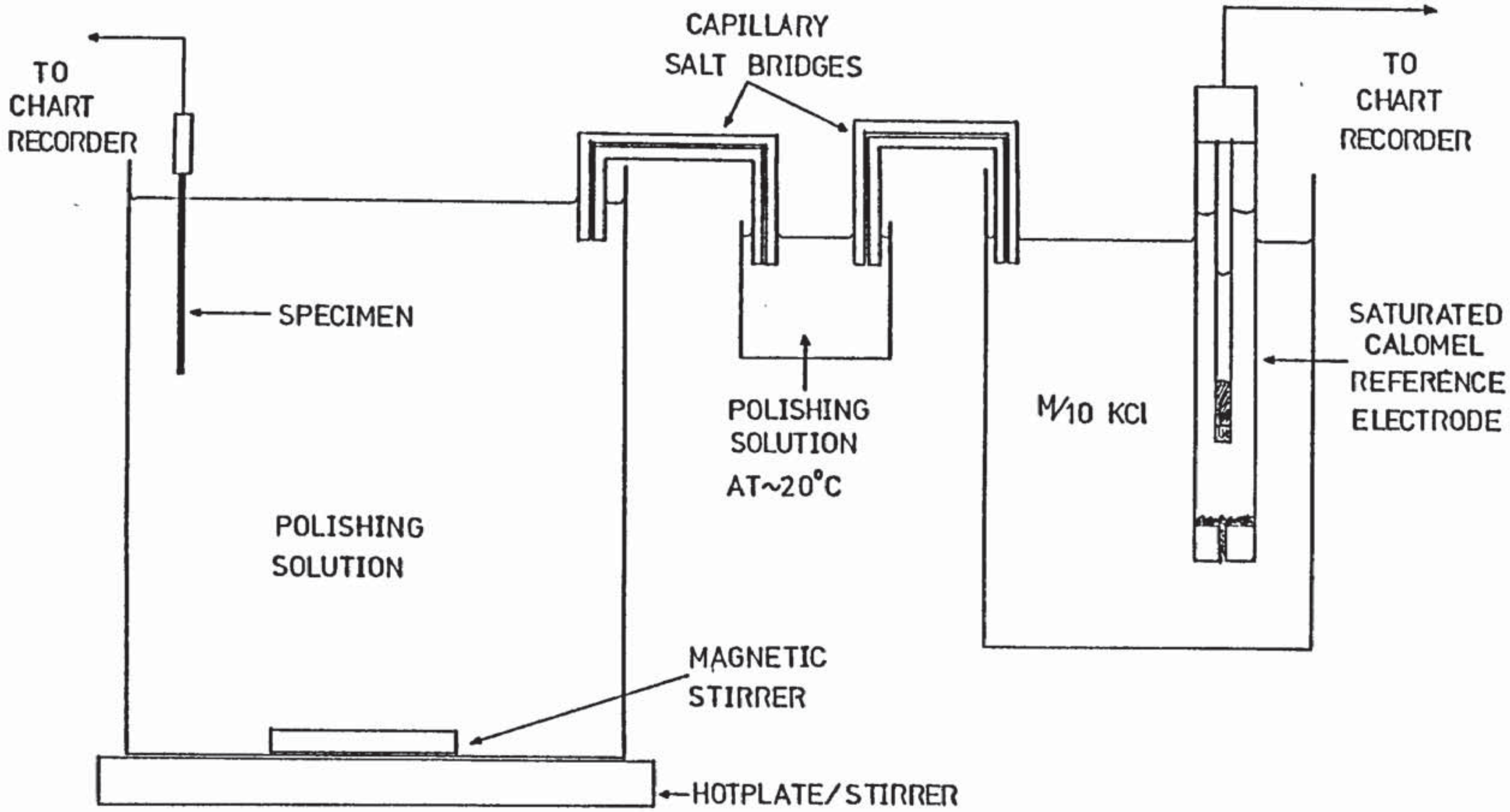


Fig.2.3. Cross section view of the apparatus used for the electrode potential determinations.

were changed as the aluminium content approached 1g/1 (estimated by weight loss measurements, and later by volumetric analysis using Diaminoethanetetra-disodium salt ($C_{10}H_{14}O_8N_2Na_2.2H_2O$)).

### 2.6.2 Estimation of Surface Finish

Visual observation is very often used as an assessment of surface finish, however, due to individual differences and the need for a more quantitative assessment, a more objective test is necessary. One method of enhancing the visual test is by using the Gardam grid. This consists of an illuminated screen with a grid of crossed lines on the surface of the screen. An order of image clarity is established by noting the point at which the image of the grid on the specimen becomes indistinct. However, a more useful method and the one used in this investigation, is the measurement of Specular Reflectivity. Scott$^{(79)}$ suggested that the ratio of specular reflectivity to the total reflectivity gives a basis for comparison that is in close agreement with visual observation. He also stated that total reflectivity is a constant for a given metal or alloy. Instruments for measuring specular reflectivity directly must be calibrated against a suitable standard (e.g. a silver mirror or a 45° prism). The instrument used in this investigation was an Evans Electroselenium Co. "Metspec" Specular Reflectivity meter. Light from a 6 volt 3 watt lamp, frosted to eliminate the filament characteristics, is directed through a circular aperture and a condenser lens to fall on the sample surface at an angle of 45° in the form of a parallel beam of light. The reflected light passes through a corresponding lens/aperture system to energise a photo-electric cell. Readings are presented on the 0-100 scale of an "EEL" UNigalvo Type 20. The galvanometer is allowed to stabilize for 30 minutes and is then set to zero. The prism used in this instance was then placed on the surface of a black tile, provided for the standardisation, with it's hypotenuse face downwards.

this forms an unvarying standard for maximum reflectivity (100%). The galvanometer reading is then expressed as a percentage of the specular reflectivity.

### 2.6.3 Electrode Potential Determinations

Specimens 5cm. by 1cm. by 0.9mm. were used for these determinations. The specimens were connected to the apparatus described in section 2.5.2. The aluminium was then allowed to dissolve for ten minutes, whilst the changes in potential, with respect to the saturated calomel reference electrode, were continuously monitored. The amount of nitric acid consumed in these experiments was checked, but it was found that the relatively small samples used an insignificant amount. The effect of possible variations in the precise surface area was also checked.and the variations in surface area produced differences well below 5%.

The following solutions were used for the potential time determinations:

## TABLE 2.3

| Solution | Phosphoric acid (S.G.1.75) | Sulphuric acid (S.G.1.84) | Nitric acid (S.G.1.5) | COPPER |
|---|---|---|---|---|
| 1 | 82.5% | 17.5% | 0 | - |
| 2 | 80.8% | 17.2% | 2% | - |
| 3 | 79.2% | 16.8% | 4% | - |
| 4 | 77.5% | 16.5% | 6% | - |
| 5 | 75.8% | 16.2% | 8% | - |
| 6 | 74.2% | 15.8% | 10% | - |
| 7 | 72.5% | 15.5% | 12% | - |
| 8 | 70.1% | 14.9% | 15% | - |
| 9 | 65.9% | 14.1% | 20% | - |
| 10 | 82.5% | 17.5% | 0 | 1g/1 |
| 11 | 80.8% | 17.2% | 2% | " |
| 12 | 79.2% | 16.8% | 4% | " |
| 13 | 77.5% | 16.5% | 6% | " |
| 14 | 75.8% | 16.2% | 8% | " |
| 15 | 74.2% | 15.8% | 10% | " |
| 16 | 72.5% | 15.5% | 12% | ' |
| 17 | 70.1% | 14.9% | 15% | " |
| 18 | 65.9% | 14.1% | 20% | " |

The phosphoric acid to sulphuric acid ratio in these solutions is 4.7.:1. All percentages are by volume percent.

### 2.6.4 Scanning Electron Microscopy

A Cambridge Instrument Co. 'Stereoscan Mk.2' scanning electron microscope fitted with a 'Kevex' energy dispersive x-ray micro analyser, was used almost exclusively in this investigation for the examination of the aluminium surfaces. This enabled direct examination of the surface, with useful magnification up to 30,000X, with the capacity for accurate qualitative analysis of any surface features observed. Samples $1cm^2$ were carefully cut from the specimens after polishing.

Electron emission from specimens is greatest when the surface is inclined to the electron beam at an angle of 45°, and the best signal to noise ratio is obtained at this angle. However, when examining mirror bright surfaces where the height or depth of defects above or below the surface is very small, it is difficult to obtain sufficient contrast to see the defects at 45°. By mounting the specimens at about 10° to the electron beam (80° tilt) the oblique angle exaggerates the height and depth of the surface defects and by careful adjustment of the operating conditions at this angle it is possible to improve the signal to noise ratio considerably. However, this means that care must be taken to remember the viewing angle when interpreting the resulting micrographs.

Analysis of the surface of the specimens at this angle also increases the percentage of the surface film included in the analysis.

# CHAPTER 3

# THE INFLUENCE OF NITRIC ACID

## 3.1 Introduction

The nitric acid in a chemical polishing solution of the type listed in table 2.1 and 2.2, is consumed by the chemical polishing process. As the aluminium is dissolved the hydrogen produced reduces the nitric acid to its various oxides, and these are evolved as 'nitrous fumes'. In addition some of the nitric acid is lost by evaporation (the boiling point of nitric acid is 86°C). Consequently, the amount of nitric acid in a large industrial scale polishing bath, will be below the optimum concentration after a period of use. In addition, when the nitric acid content of a large tank has been adjusted there may be an excess of nitric acid, particularly if there has been insufficient time allowed for mixing. These conditions may give rise to a poor finish for a period of time.

The object of the work in this chapter is to establish the influence of different nitric acid concentrations on the polishing mechanism.

It has also been noticed from shop floor practise, that the amount of copper, (often referred to as 'smut') on the surface of the aluminium after polishing, was least, immediately after a nitric acid addition, which would tend to indicate that the nitric acid was in some way reducing the amount of copper being deposited on the surface of the aluminium. Consequently, solutions not containing copper were first studied, and then copper additions were made to establish the precise role of both the nitric acid and the copper in these solutions.

The compositions of the solutions used in this chapter are listed in tables 2.1 and 2.2.

### 3.2 Specular Reflectivity Results

The polishing times used in this section were 5,10,15,20,25,30,40, 50,60,90,120,150,180 and 240 seconds. The time taken for the specimen to be transferred from the polishing solution to the water rinse (approximately 1 second) was included in the polishing time since the reaction was still occurring. The experimental error, found from duplicate samples, was found to be within 5%.

#### 3.2.1 Solutions not containing copper

The results show the marked dependence of the specular reflectivity on the polishing time. In solution A (no nitric acid) (fig.3.1) both the 99.99% aluminium and the 99.5% aluminium showed a rapid fall in reflectivity in the first 30 to 60 seconds of polishing (as we found to be the case in all of the solutions). In solution A only the 99.99% aluminium displayed any increase in the reflectivity after the initial drop, and this was only to 33%. The 99.5% aluminium showed no increase in reflectivity. Similar results were obtained from solution B (6% nitric acid) (Fig.3.2) with the exception that the 99.99% aluminium exhibited a significantly greater increase, to 68%. The 99.5% aluminium again showed no increase in reflectivity. The addition of 20% nitric acid to the solution (solution C), produced a very low reflectivity on both the 99.99% and 99.5% aluminium (fig.3.3).

#### 3.2.2 Solutions containing 1g/1 copper

In solution D (no nitric acid) (Fig.3.4), after the initial drop in reflectivity there was an increase in reflectivity for 5 to 30 seconds in the first minute of polishing, but this was followed by a rapid drop to below 20%, for both the 99.99% and the 99.5% aluminium The addition of 6% nitric acid to the solution (solution E) produced a significant

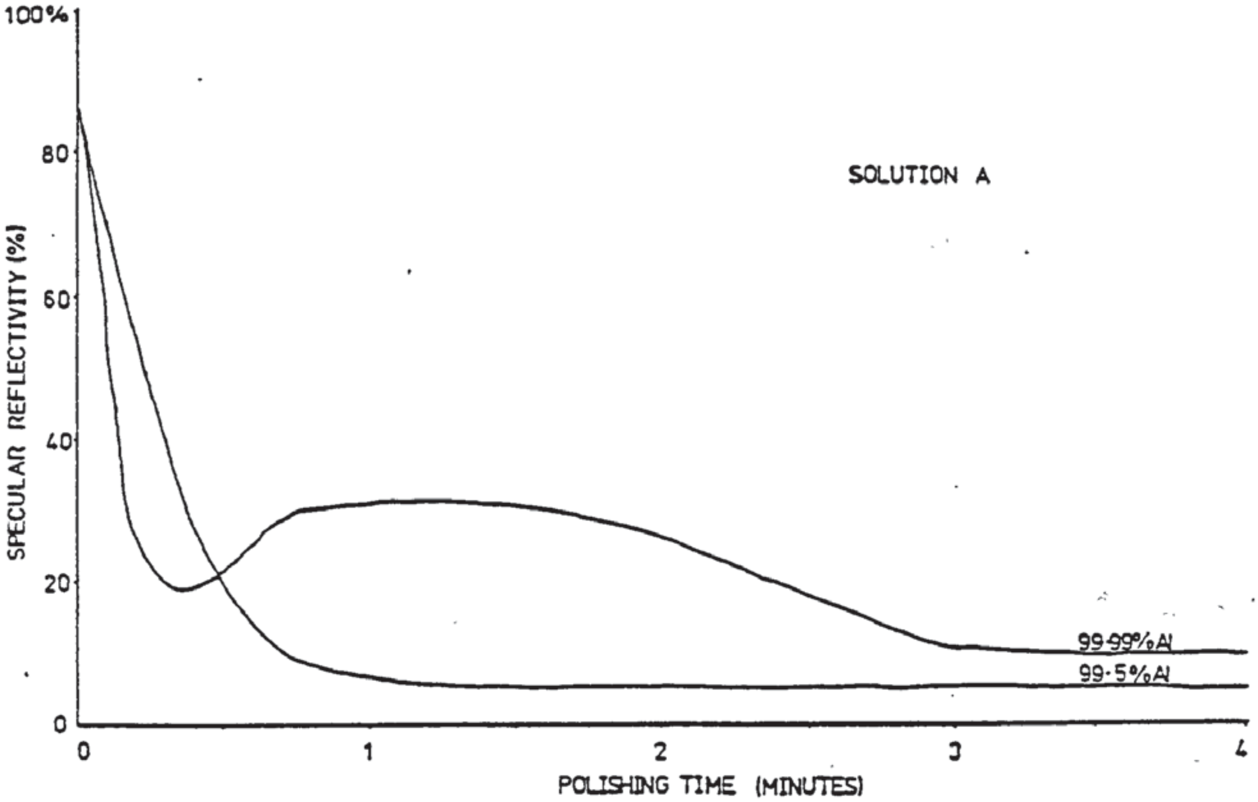


Fig.3.I. Specular Reflectivity vs. Polishing Time

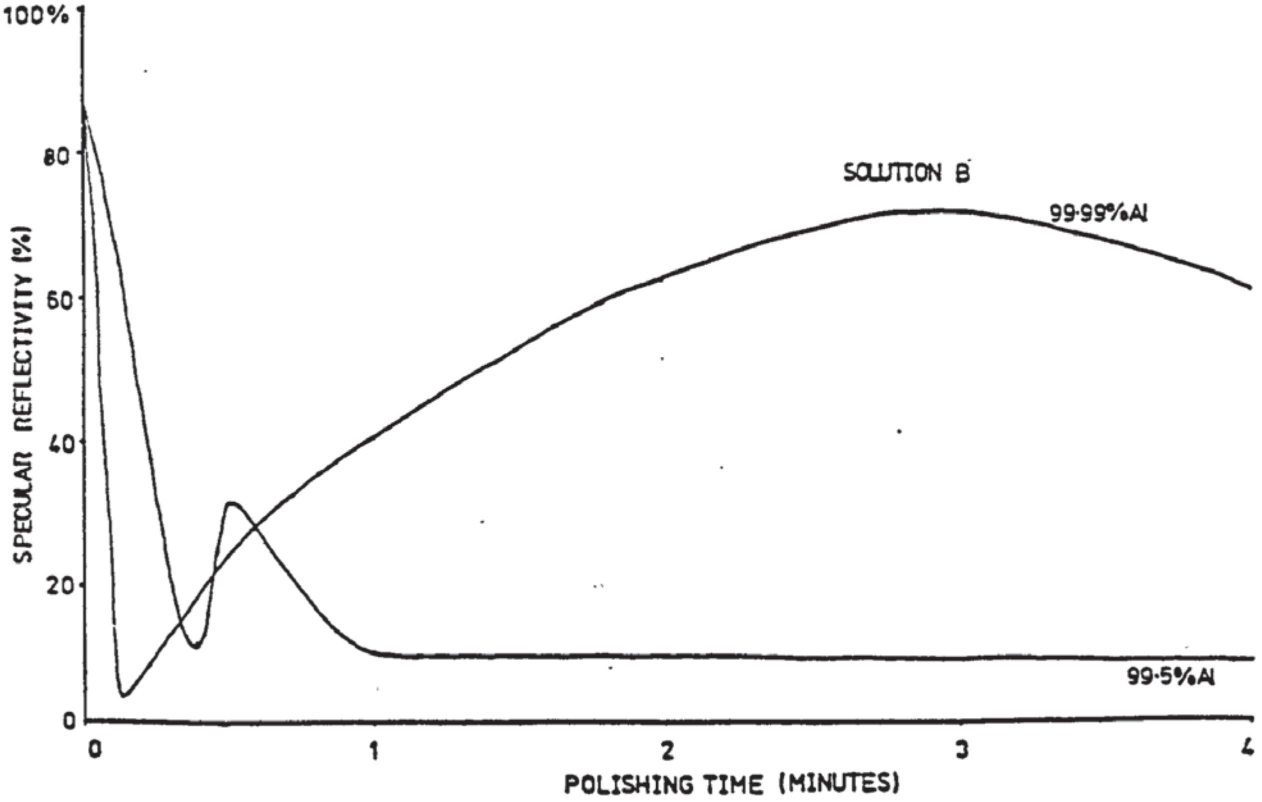


Fig.3.2. Specular Reflectivity vs. Polishing Time

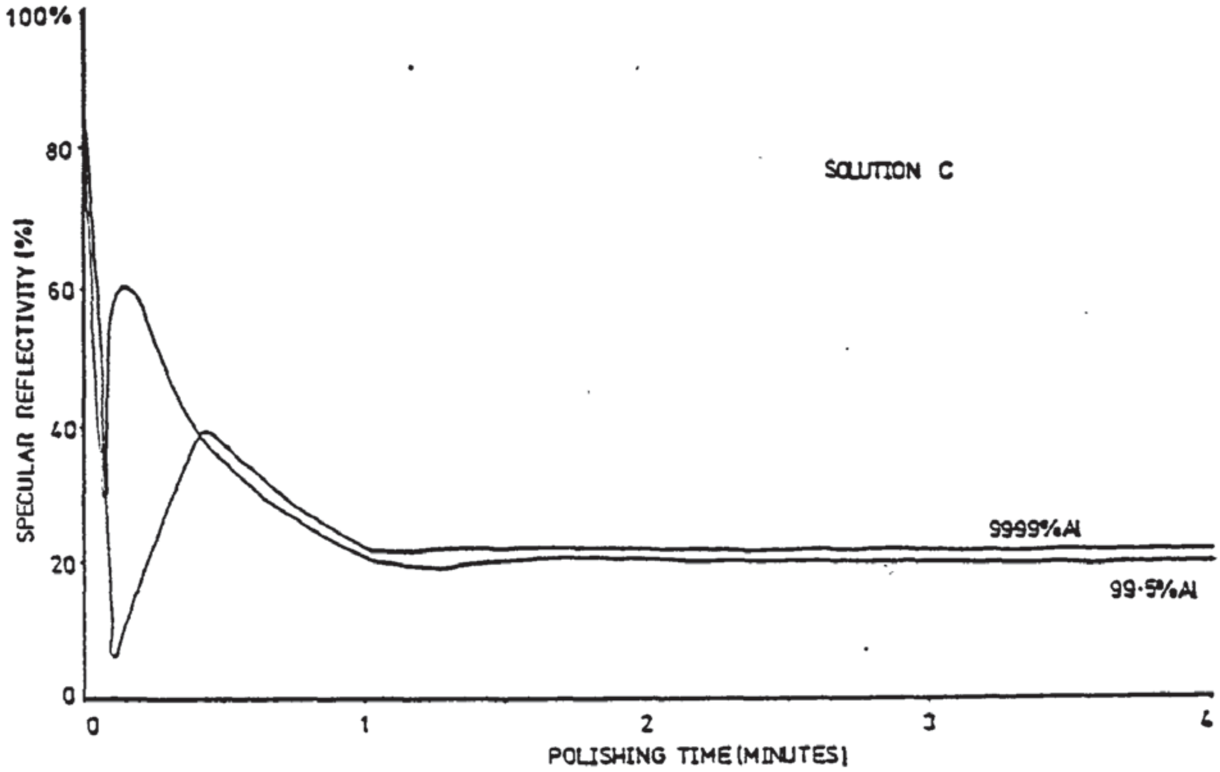


Fig.3.3. Specular Reflectivity vs. Polishing Time

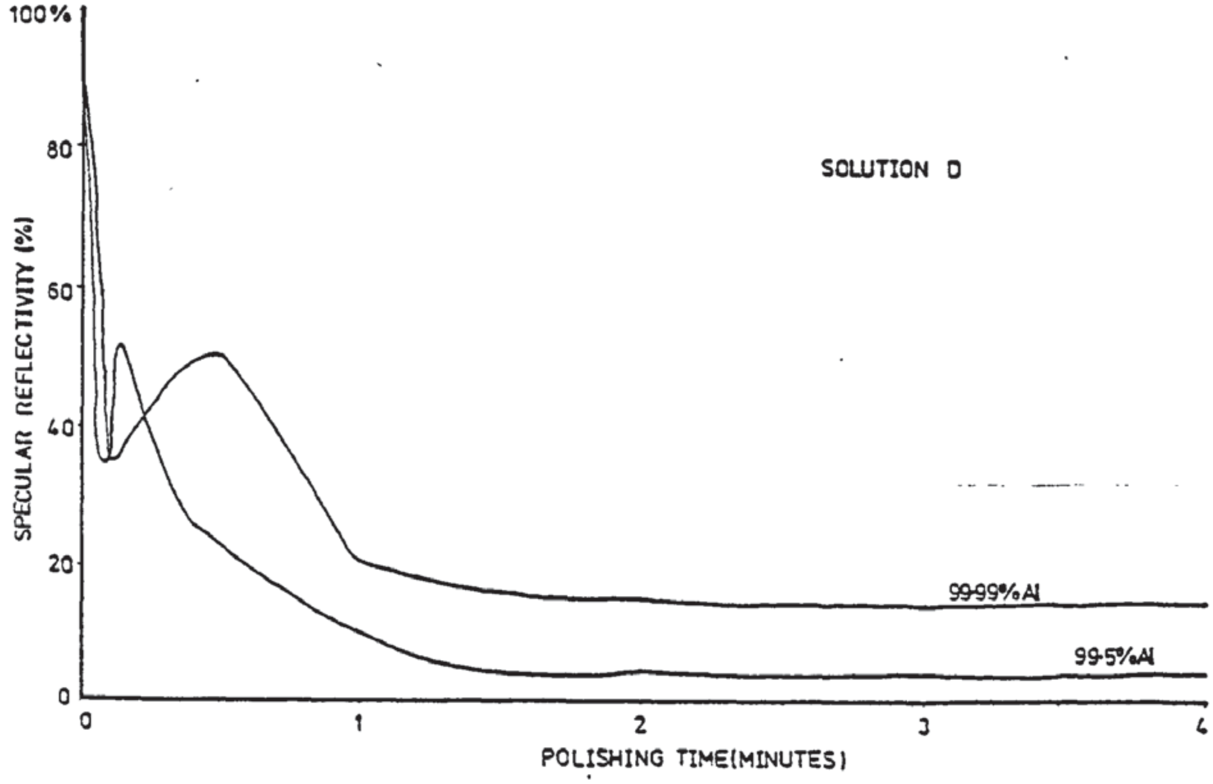


Fig.3.4. Specular Reflectivity vs. Polishing Time

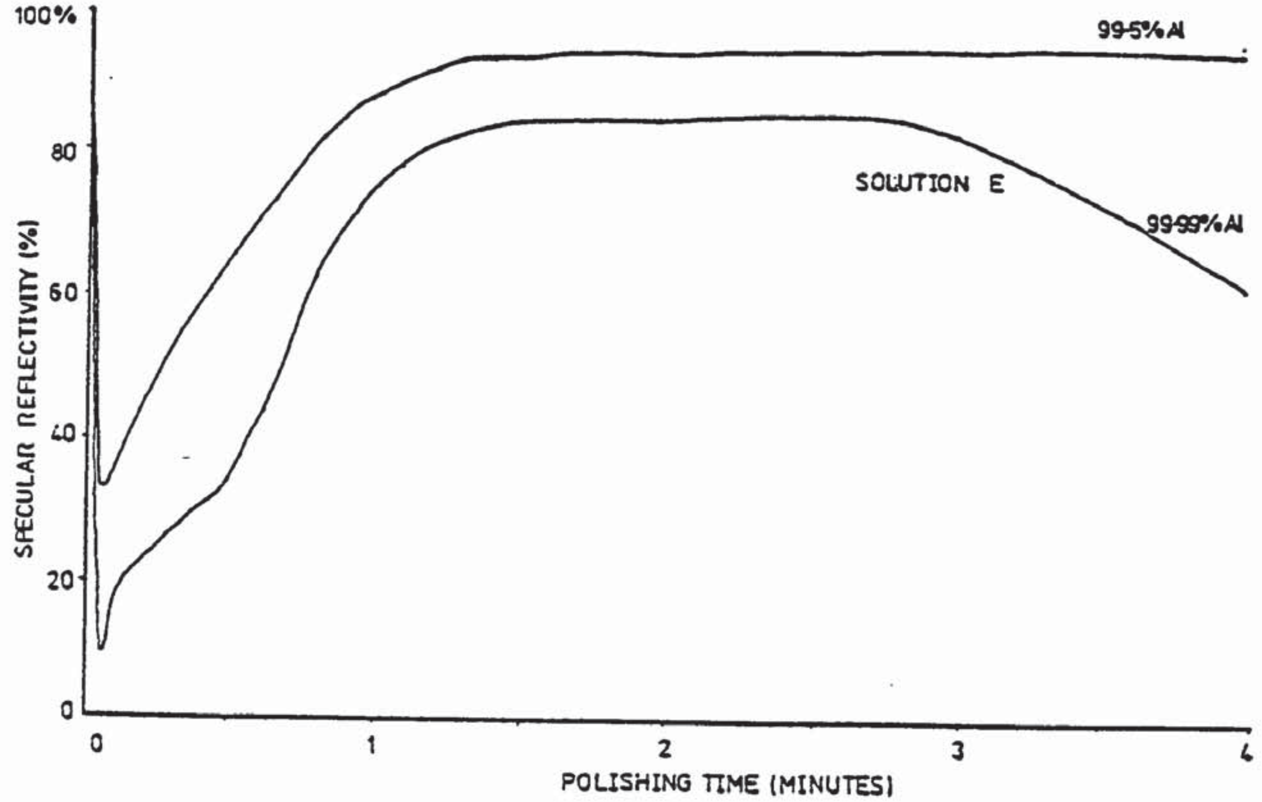


Fig.3.5. Specular Reflectivity vs. Polishing Time

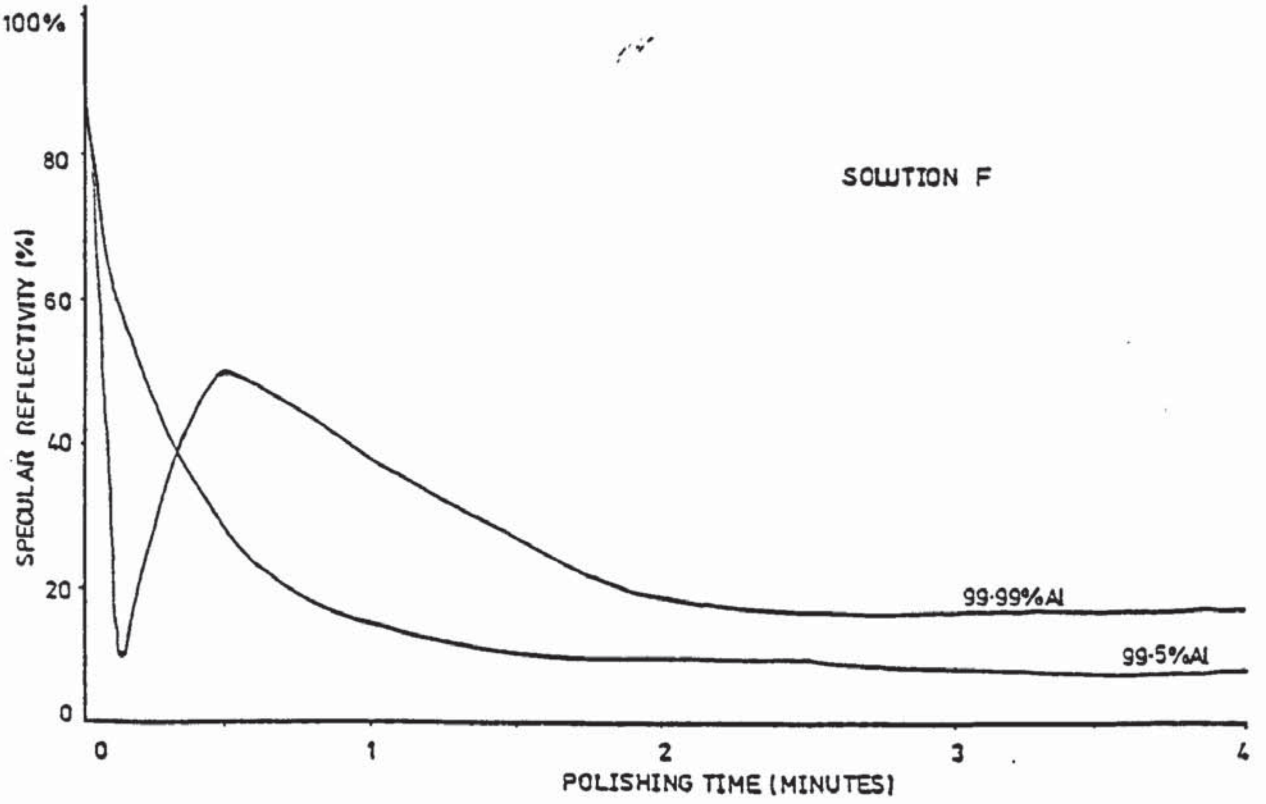


Fig.3.6. Specular Reflectivity vs. Polishing Time

increase in the reflectivity (Fig.3.5). Both the 99.99% and the 99.5% aluminium showing highly reflective surfaces. The 99.5% aluminium was slightly higher than the 99.99% aluminium. The 99.99% Al also showed a slight drop in reflectivity after 3 minutes polishing. However, in solution F (20% nitric acid), although the 99.99% aluminium showed an increase in reflectivity for a few seconds after 30 seconds polishing, the reflectivity after a useful time of polishing, (i.e. that necessary to remove surface defects) was very low (Fig.3.6).

## 3.3 Scanning Electron Microscopy

### 3.3.1 The influence of Nitric Acid in the absence of Copper

### 3.3.1.1. Solution A (no nitric acid), 99.99% aluminium.

Representative samples, where significant changes in surface morphology had occurred, have been selected to avoid unnecessary duplication.

After 5 secs. polishing (fig. 3.7), the surface of the aluminium had been attacked to form spherical etch pits at random sites on the surface. These etch pits grew laterally, and became more extensive after 10 secs. polishing (fig.3.8), with preferential etching at defect sites in the air formed oxide due to rolling and surface scratches. With 20 secs. polishing the etch pits had merged to cover the entire surface (fig.3.9). After 30 secs. polishing the depth of the etch pits had been considerably reduced by the levelling of the ridges of the pits (fig.3.10). 60 seconds polishing further increased the extent of this smoothing (fig.3.11). Certain other features on the surface were apparent at this time of polishing. 'Peaks' of aluminium were visible, standing proud from the surface (fig.3.12). Energy dispersive x-ray micro analysis of these peaks did not reveal the presence of any other elements (not including elements lighter than sodium which cannot be detected by the

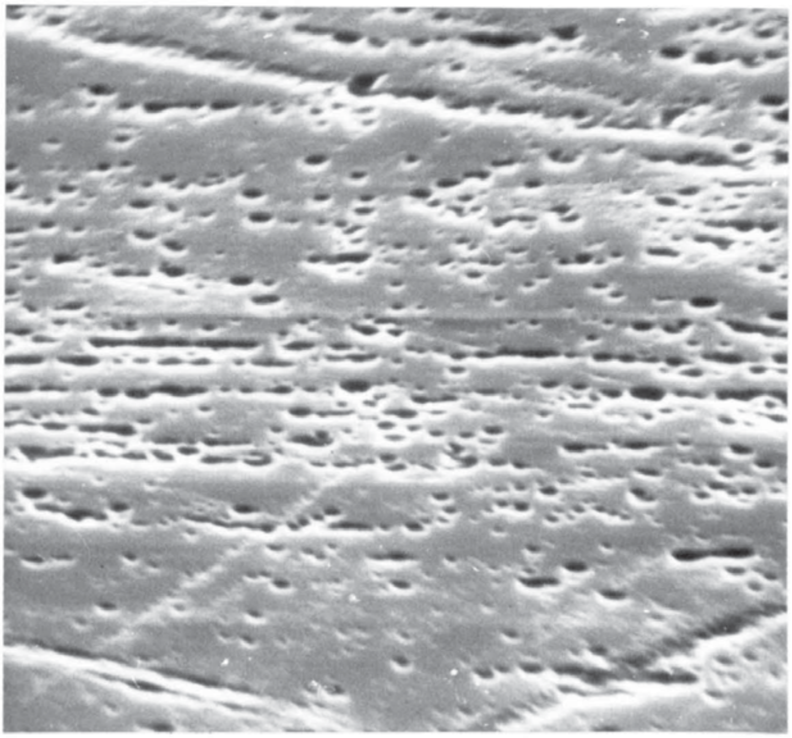


Fig.3.7. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution A (no Nitric acid) for 5 seconds. X 5000.

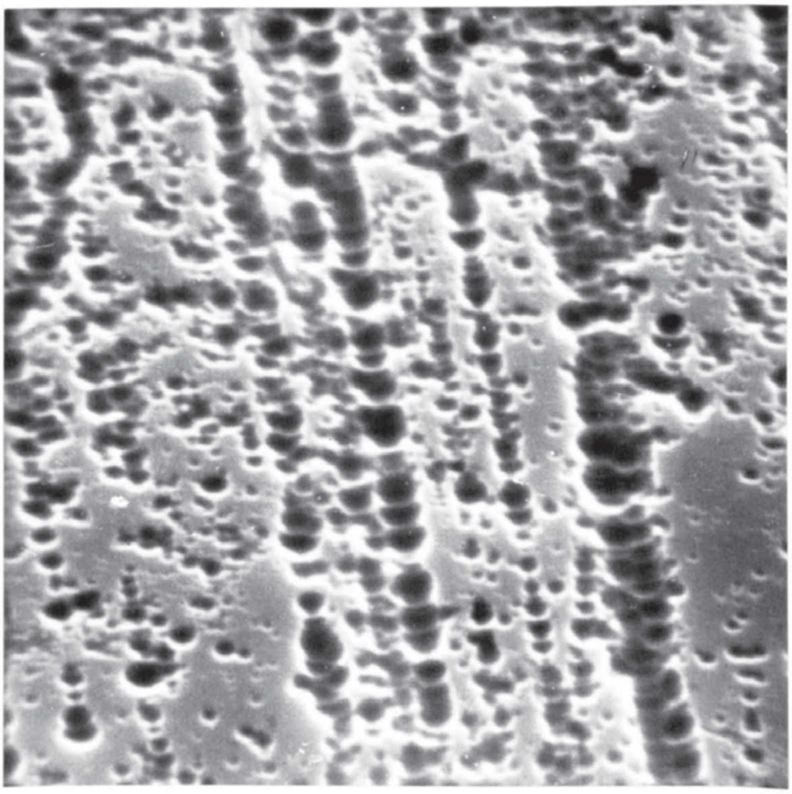


Fig.3.8. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution A (no Nitric acid) for IO seconds. X 5000.

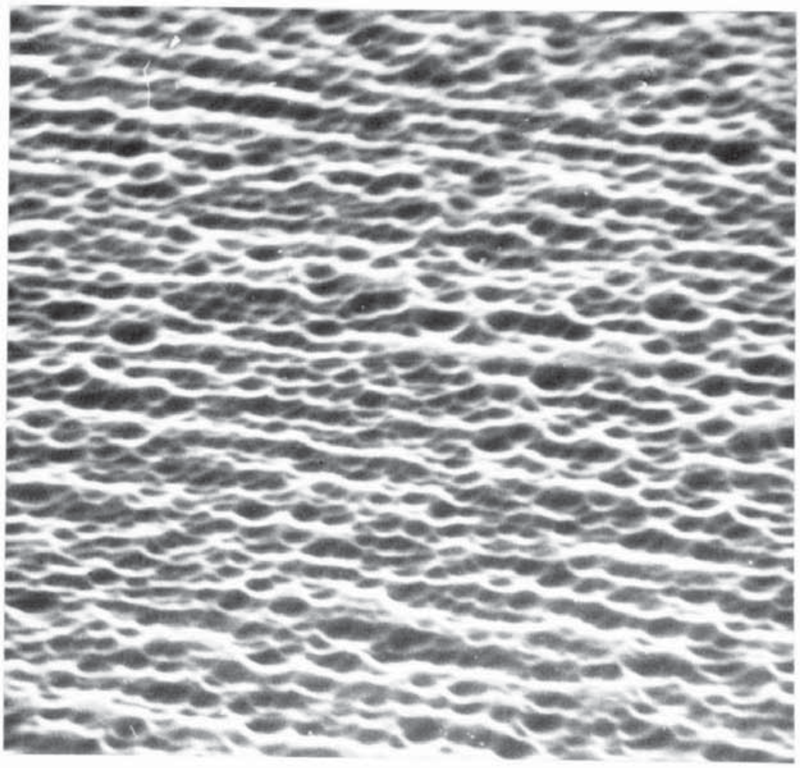


Fig.3.9. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution A (no Nitric acid) for 20 seconds. X 5000.

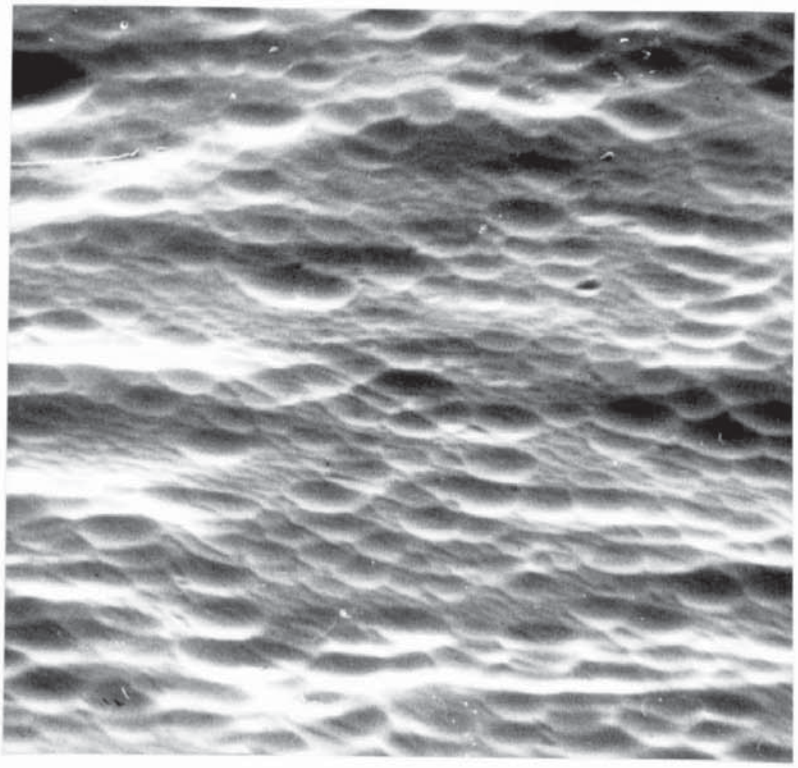


Fig.3.10. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution A (no Nitric acid) for 30 seconds. X 5000.

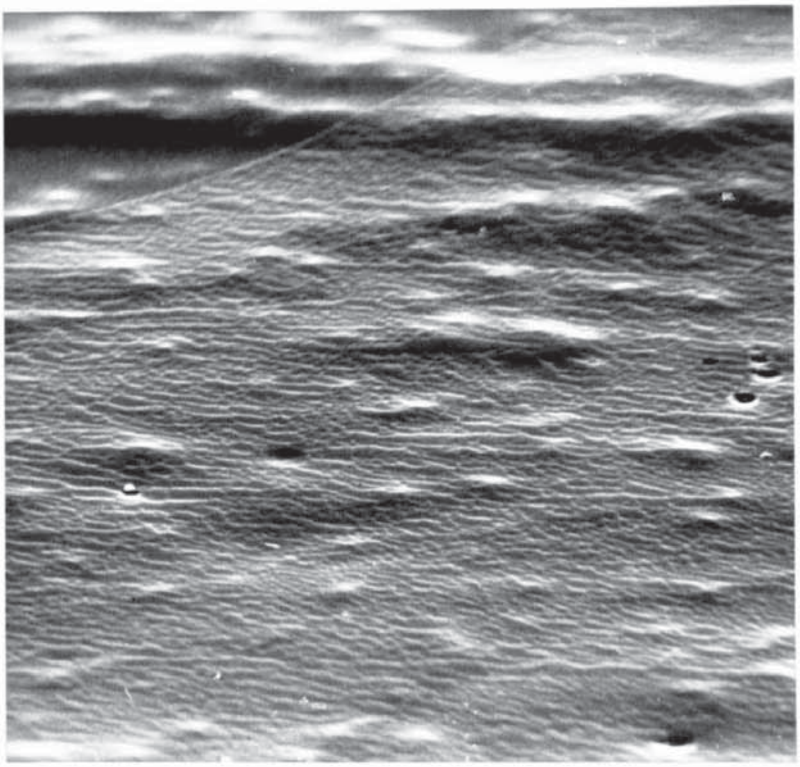


Fig.3.II. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution A (no Nitric acid) for 60 seconds. X 2000.

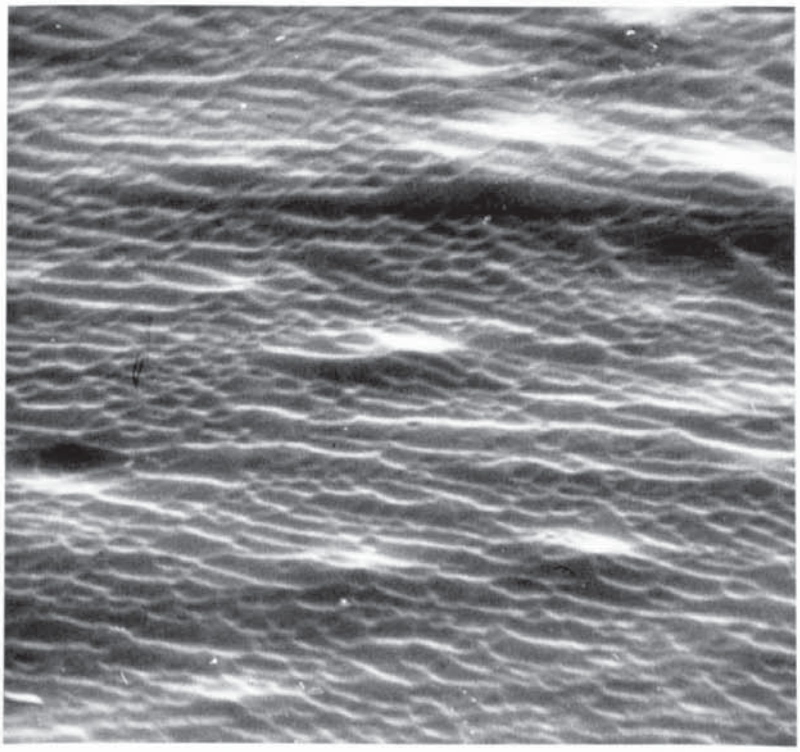


Fig.3.I2. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution A (no Nitric acid) for 60 seconds. X 5000.

apparatus used). In addition there was a grain orientation dependence of the surface features (fig.3.13), which bear a close relationship with the sub-micro patterns found by previous authors(57,58). Following 120 secs. polishing time (fig.3.14) the number of peaks had greatly increased. Higher magnification of these peaks (fig.3.15) revealed that they consist of a central protrusion, or 'peak', surrounded by an annular groove of aluminium that has dissolved at a more rapid rate than either the peak or the rest of the aluminium. Polishing of the aluminium for 300 secs. (fig.3.16), produced a further defect on the surface where certain grains of the aluminium were dissolving at different rates to others.

### 3.3.1.2 Solution A (No nitric acid), 99.5% Aluminium

The 99.5% aluminium did not show the same pattern of etching found on the 99.99% aluminium in this solution. The pits were considerably shallower, and they covered the entire surface after only 5 seconds polishing (fig.3.17). A number of inclusions were visible, and were associated with surrounding pitting (fig.3.18). The majority of these inclusions were found to be iron rich (fig.3.19 & 3.20). Some silicon rich inclusions were also found, (fig.3.21 & 3.22), but these did not show the same associated pitting found around the iron rich inclusions. After 30 secs. polishing (fig.3.23) some of the inclusions were no longer present on the surface, either due to direct dissolution or by undercutting of the aluminium. The extent of the pitting at this time had increased however, and further polishing of the surface for 120 secs. increased the pitting still further (fig.3.24).

At polishing times of 120 secs. and longer, the surface had distinct regions showing the sub-micro patterns found by previous authors. On this occasion the patterns were coarser than found on the 99.99% aluminium. Grains of different orientation showed different patterns,

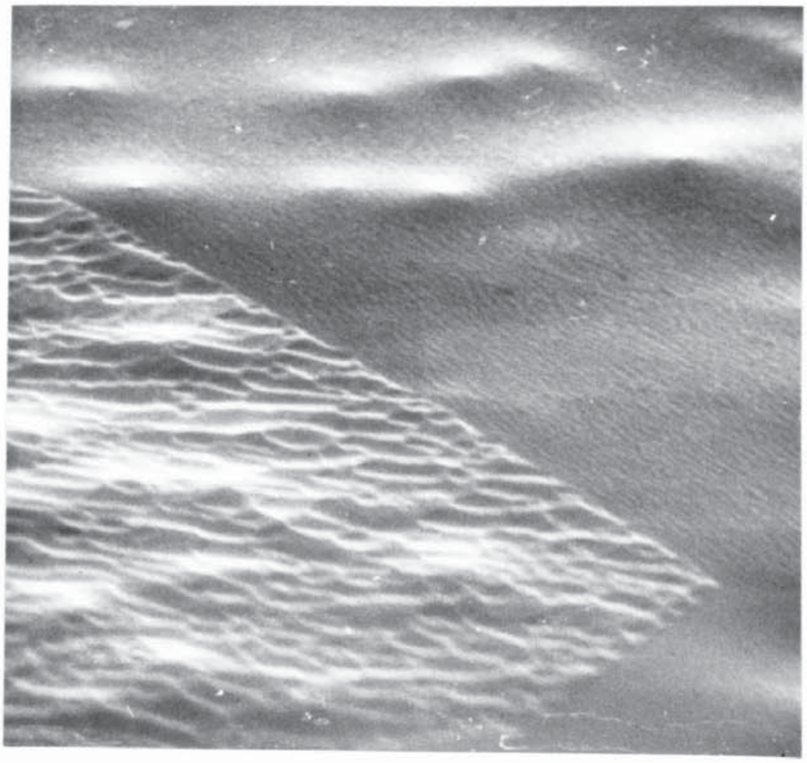


Fig.3.13. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution A (no Nitric acid) for 60 seconds. X 5000.

Fig.3.14. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution A (no Nitric acid) for 120 seconds. X 1000.

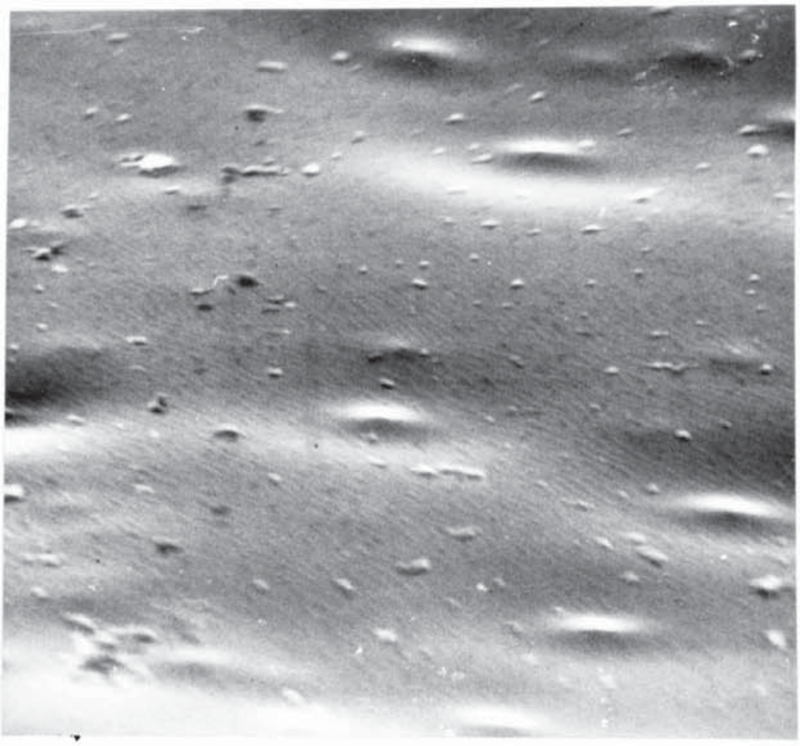


Fig.3.15. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution A (no Nitric acid) for 120 seconds. X 5000.

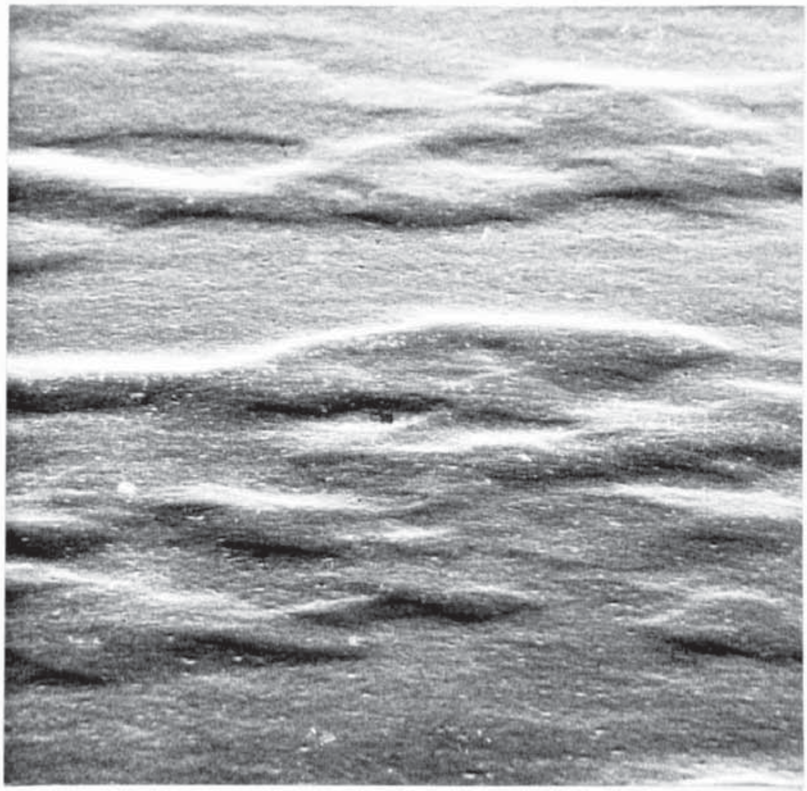


Fig.3.16. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution A (no Nitric acid) for 300 seconds. X 100.

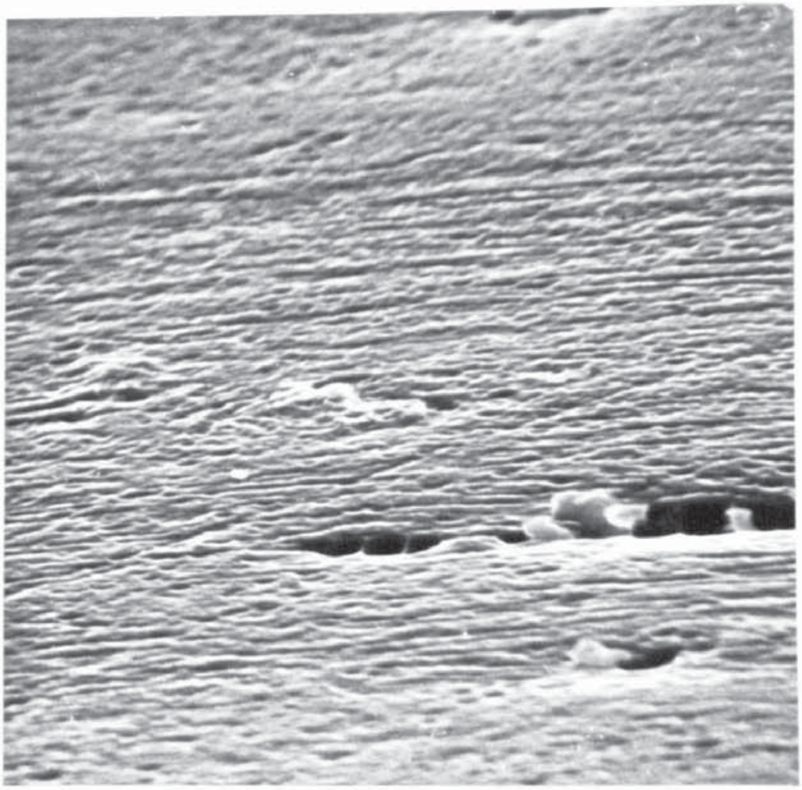


Fig.3.I7. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution A (no Nitric acid) for 5 seconds. X 2,400.

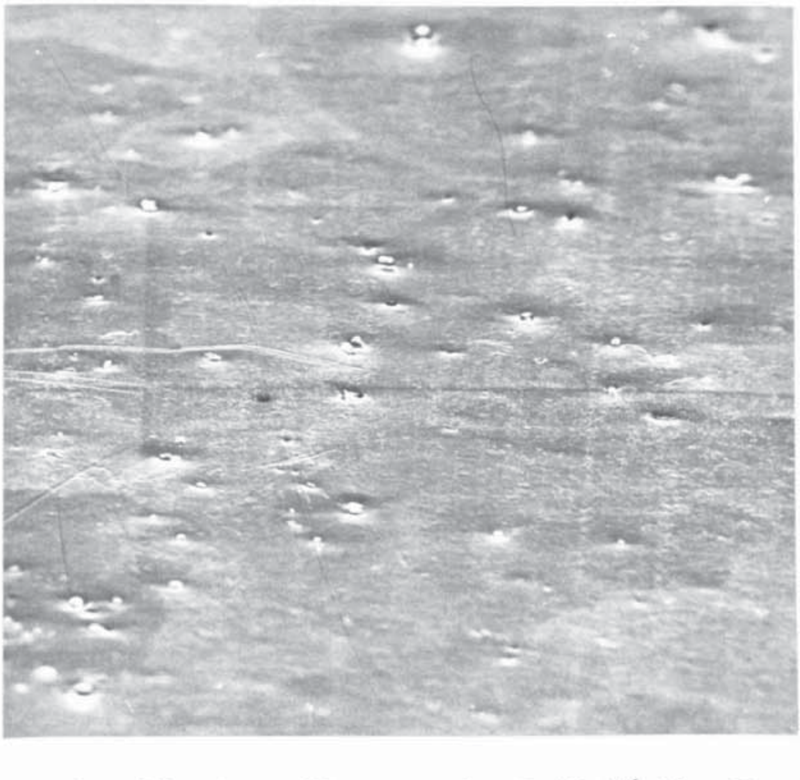


Fig.3.I8. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution A (no Nitric acid) for 5 seconds. X 500.

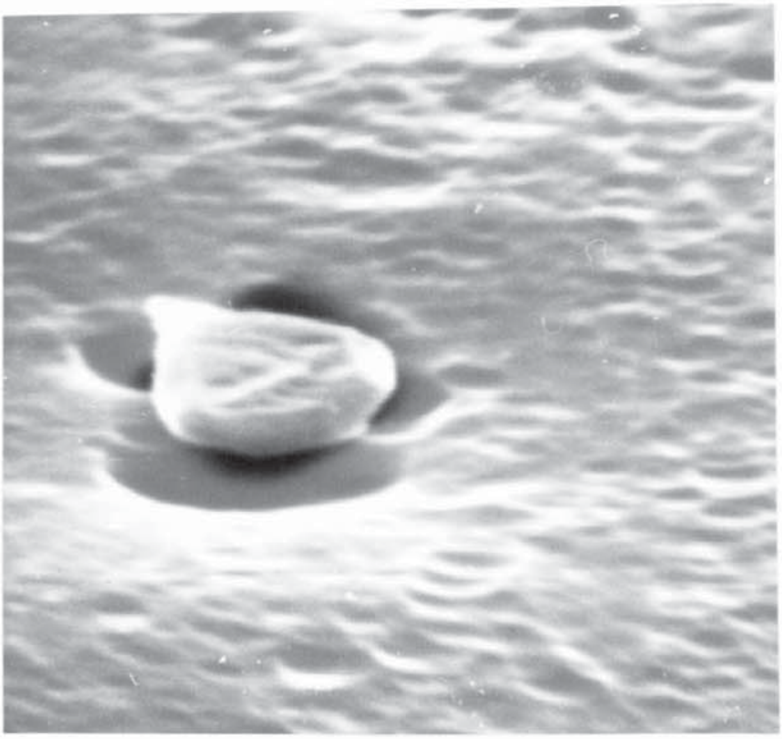


Fig.3.I9. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution A (no Nitric acid) for 5 seconds. X IO,000.

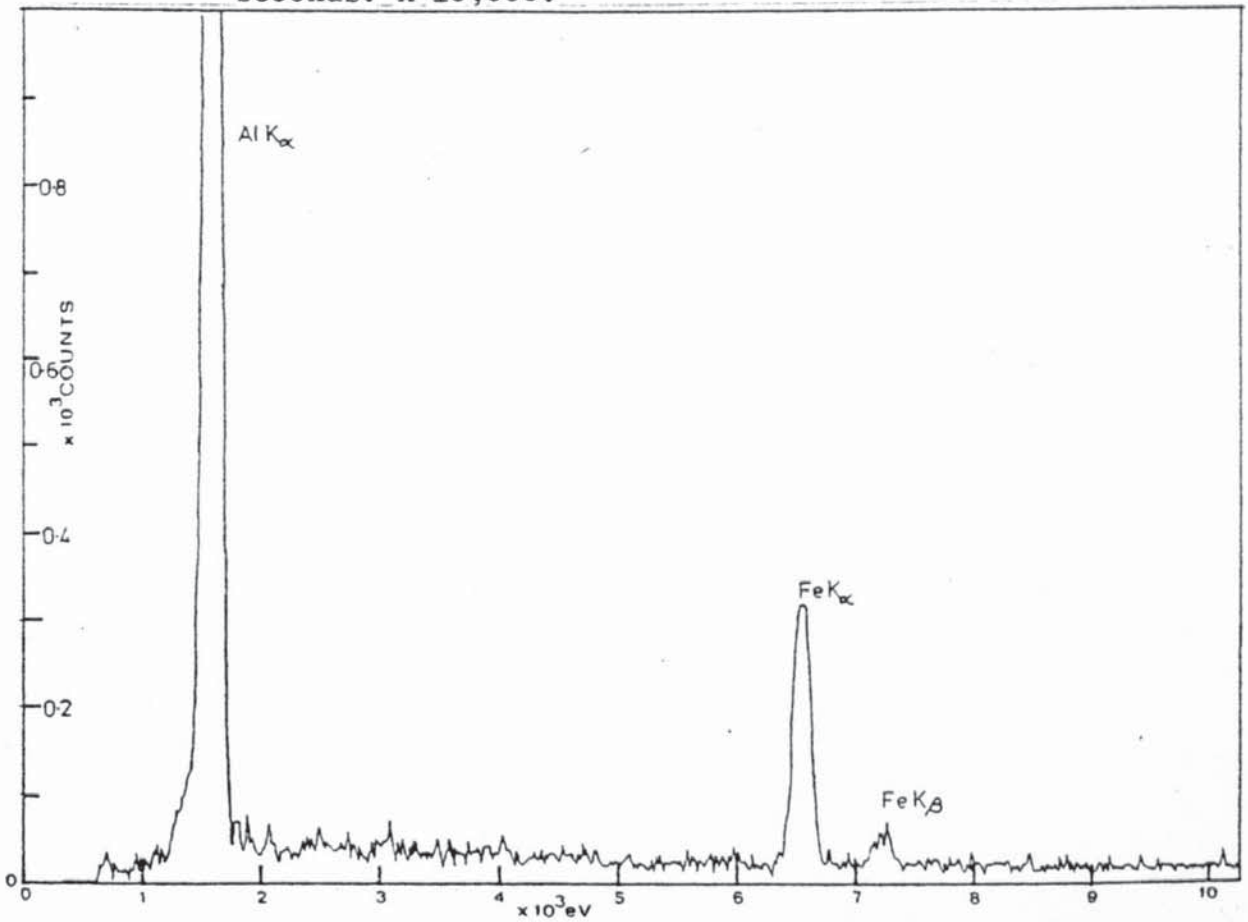


Fig.3.20. 'Kevex' x-ray analysis of the particle in Fig.3.I9. above.

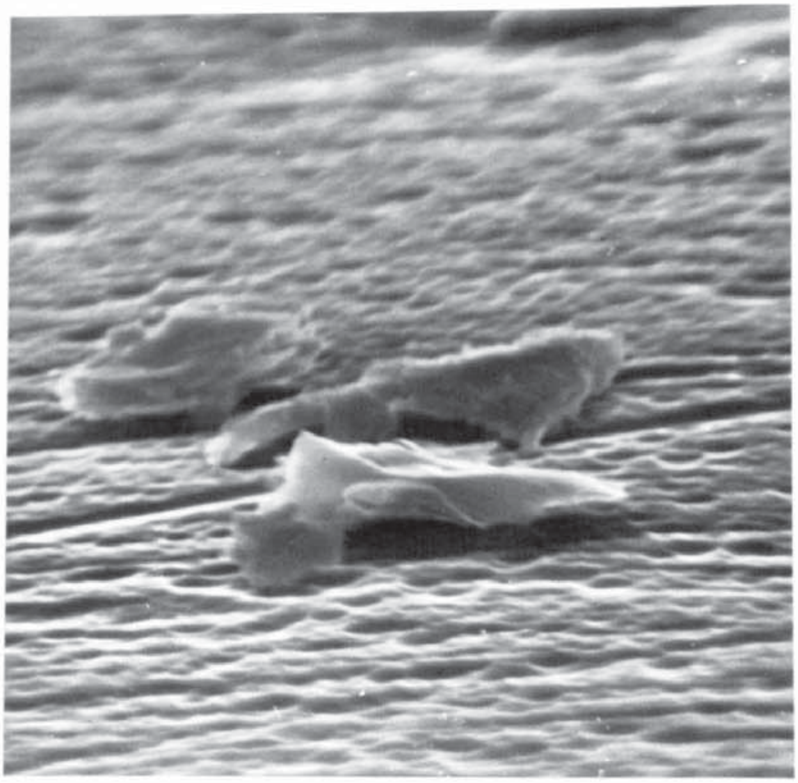


Fig.3.2I. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution A(no Nitric acid) for 5. seconds. X 6000.

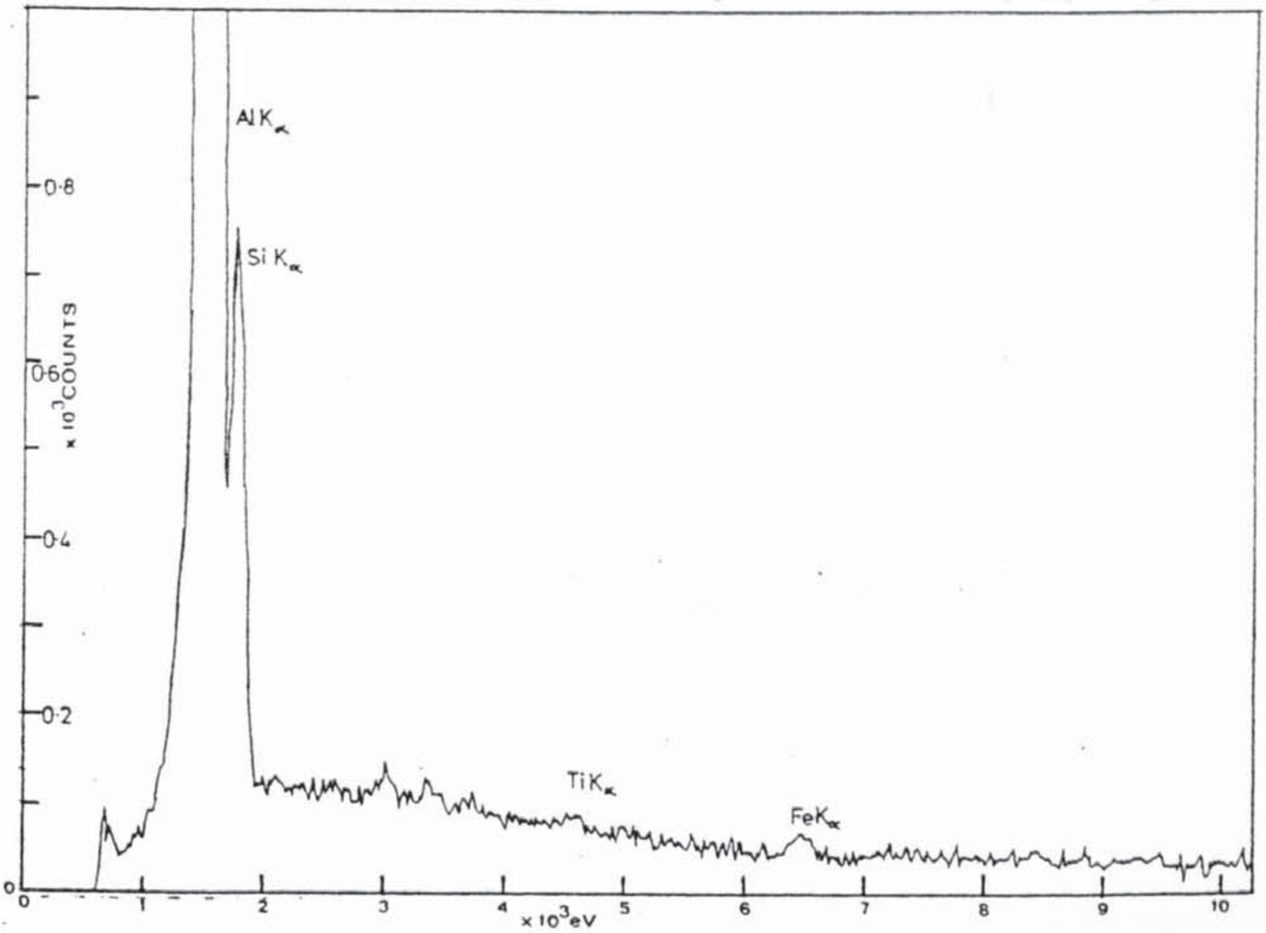


Fig.3.22. 'Kevex' x-ray analysis of the particle in Fig.3.2I. above.

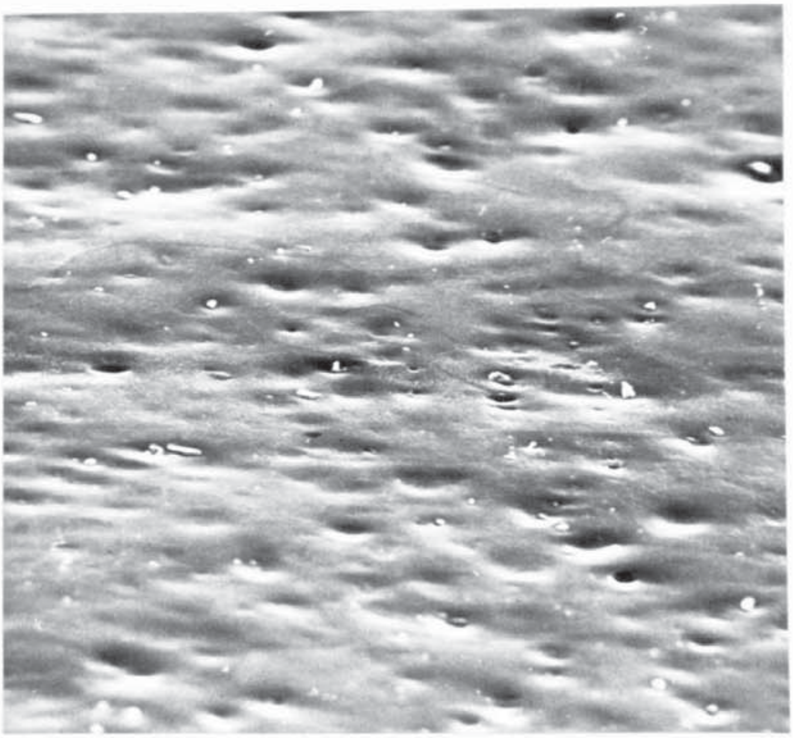


Fig.3.23. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution A (no Nitric acid) for 30 seconds. X 500.

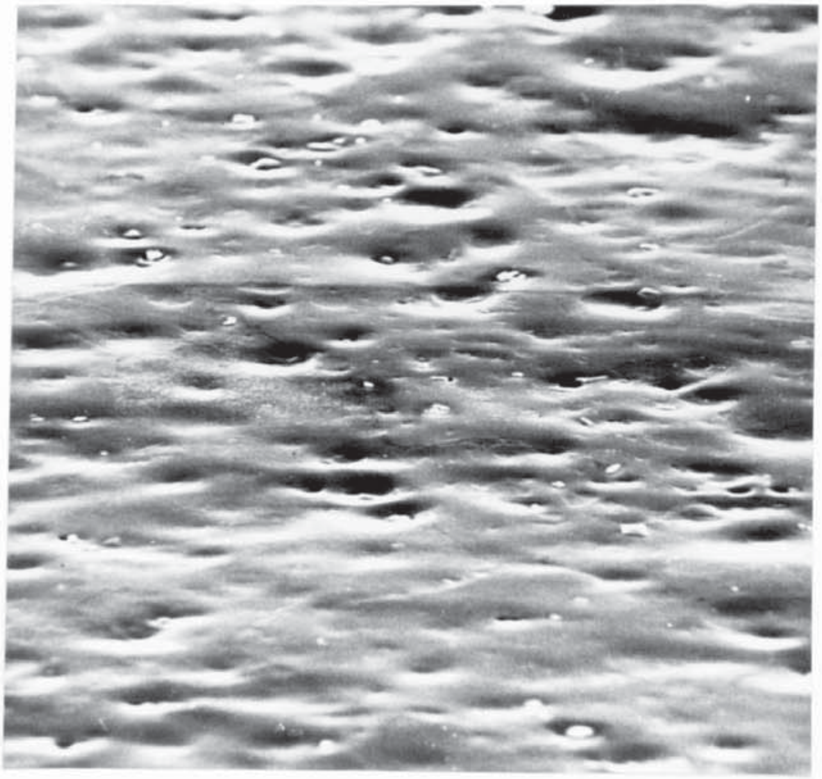


Fig.3.24. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution A (no Nitric acid) for I20 seconds. X 500.

the pattern size, and direction, depending on the grain orientation. In addition on some grains no patterns were visible (fig.3.25). A higher magnification shows in more detail the nature of the change in pattern between two grains at a grain boundary (fig.3.26). A closer examination of one of these patterns (fig.3.27) revealed the pattern to be composed of interconnected ridges over the surface, and not furrows, as has been suggested by some previous authors(49-56).

The pitting caused by inclusion was found to be most extensive around those inclusions that were Iron rich (fig.3.28 & 3.29). (The y-axis in the 'Kevex' x-ray analysis of Fig.3.29 and all subsequent 'Kevex' analysis refer to the total number of x-ray counts x$10^3$, and the x-axis refers to the x-ray energy x$10^3$). Titanium rich inclusions were found, (fig.3.30 & 3.31) but showed little, if any, preferential dissolution in their vicinity.

No evidence of the peaks of aluminium were found on the surface in this solution unlike the 99.99% aluminium.

### 3.3.1.3. Solution B (6% Nitric acid), 99.99% Aluminium

The addition of 6% nitric acid to the solution, in solution B, had a pronounced effect on the specular reflectivity of the 99.99% aluminium, as it showed an improvement after the initial drop in the first 30 secs., unlike solution A containing no nitric acid. The reason for this became clear as the surface was examined after progressively longer polishing times.

The surface of the aluminium after 5 secs. polishing showed no significant difference from solution A. However, after only 10 secs. polishing (fig.3.32) the surface was covered by the etch pits to the same extent found on previous samples after 20 secs. polishing. As the polishing time was increased, the surface morphology changed in the

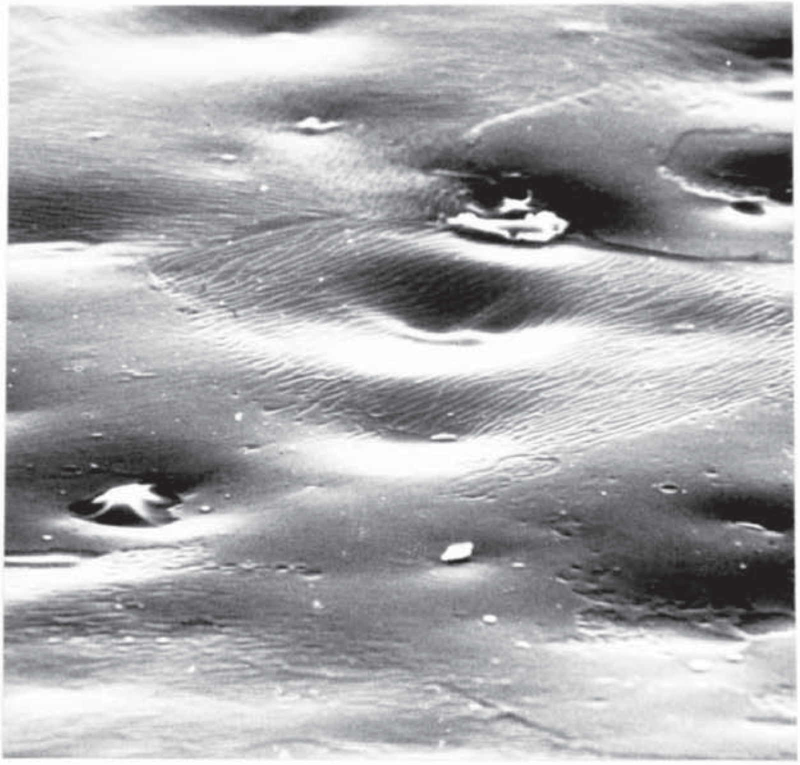


Fig.3.25. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution A (no Nitric acid) for I20 seconds. X 2000.

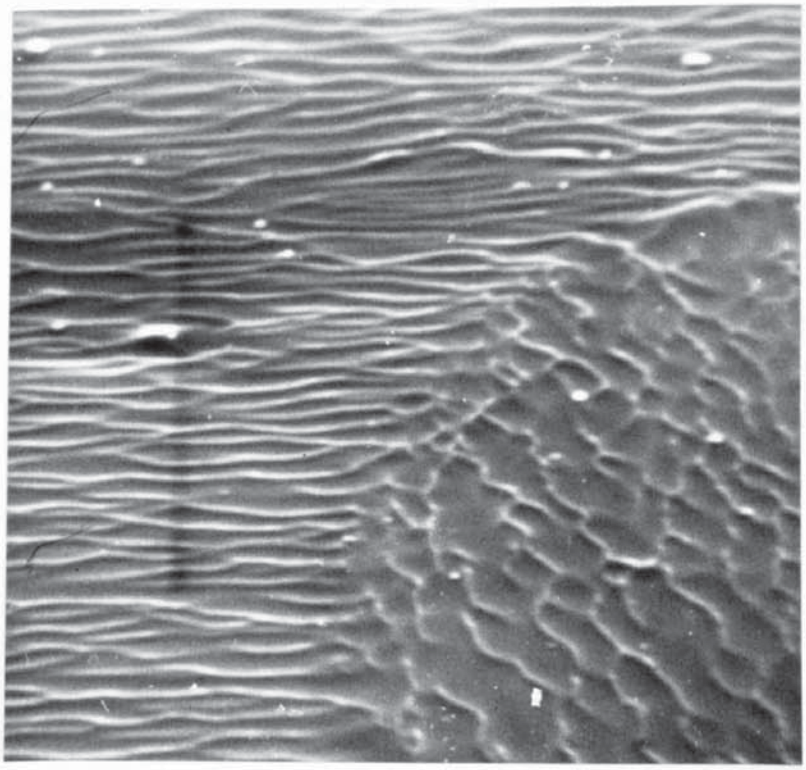


Fig.3.26. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution A (no Nitric acid) for I20 seconds. X 5000.

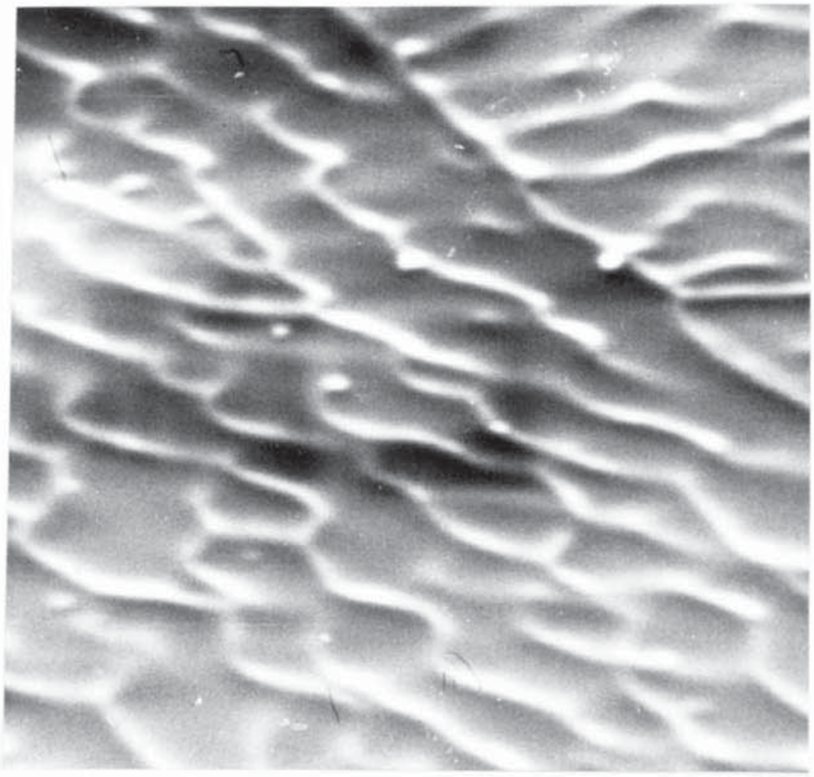


Fig.3.27. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution A (no Nitric acid) for I20 seconds. X 23,000.

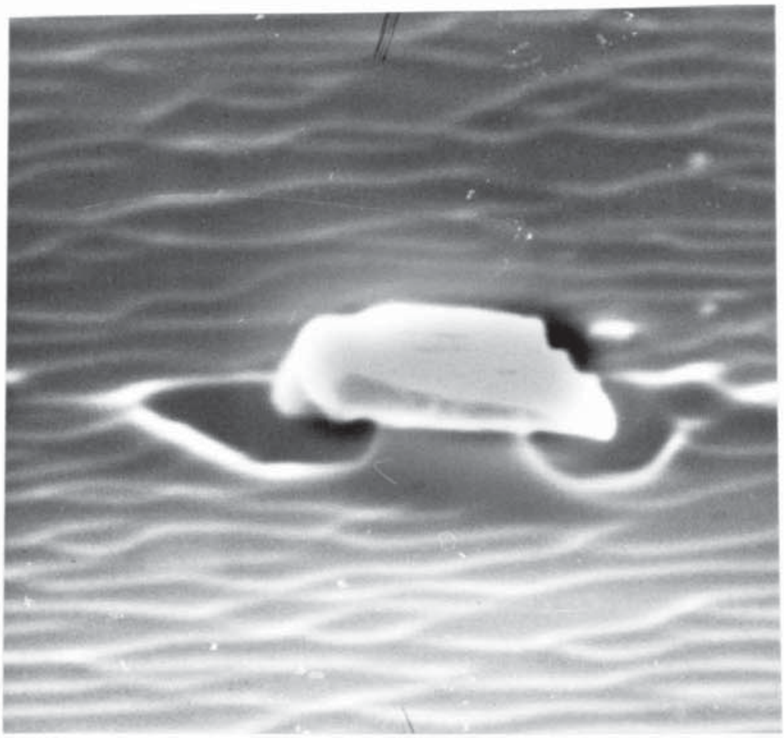


Fig.3.28. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution A (no Nitric acid) for I20 seconds. X 20,000.

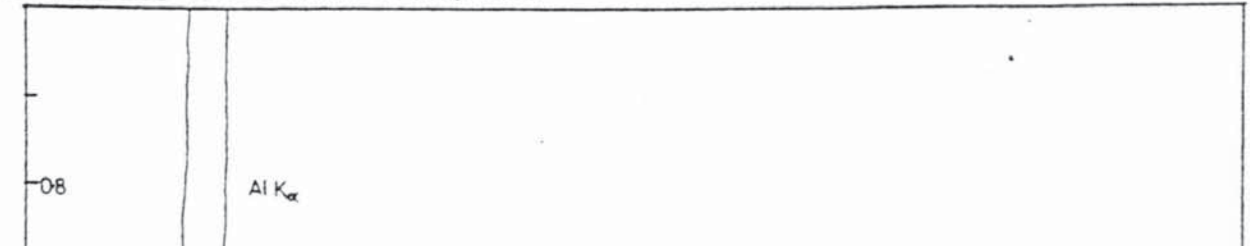


Fig.3.29. 'Kevex' x-ray analysis of the particle in Fig.3.28. above.

Fig.3.30. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution A (no Nitric acid) for I20 seconds. X I3,000.

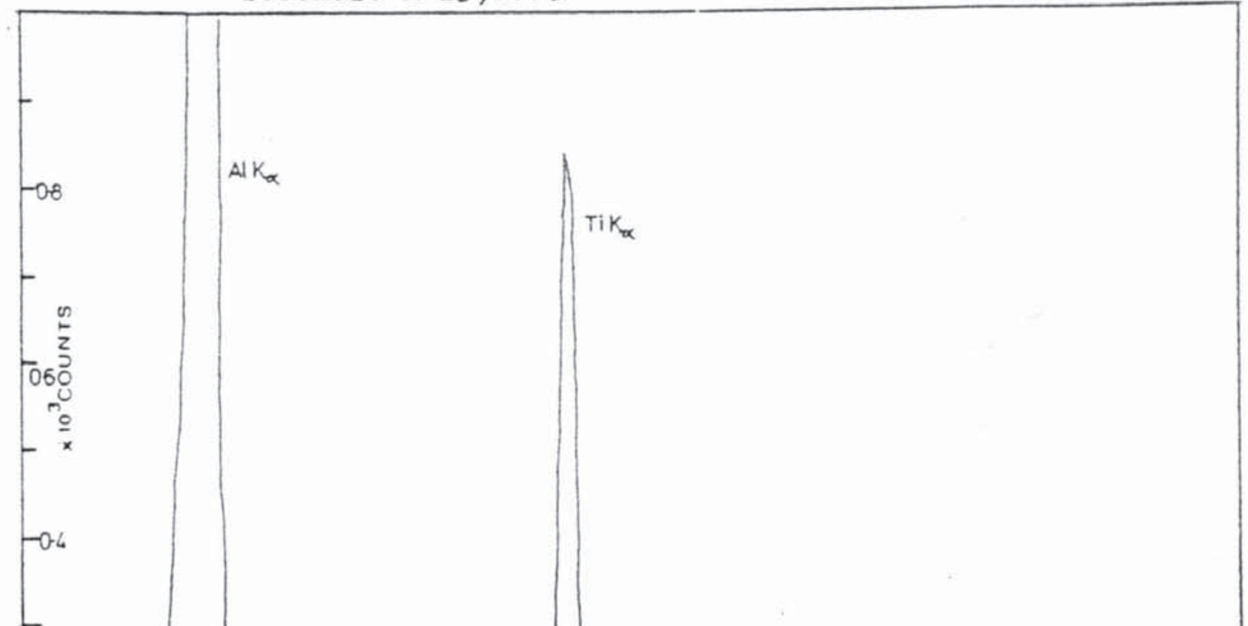


Fig.3.3I. 'Kevex' x-ray analysis of the particle in Fig.3.30. above.

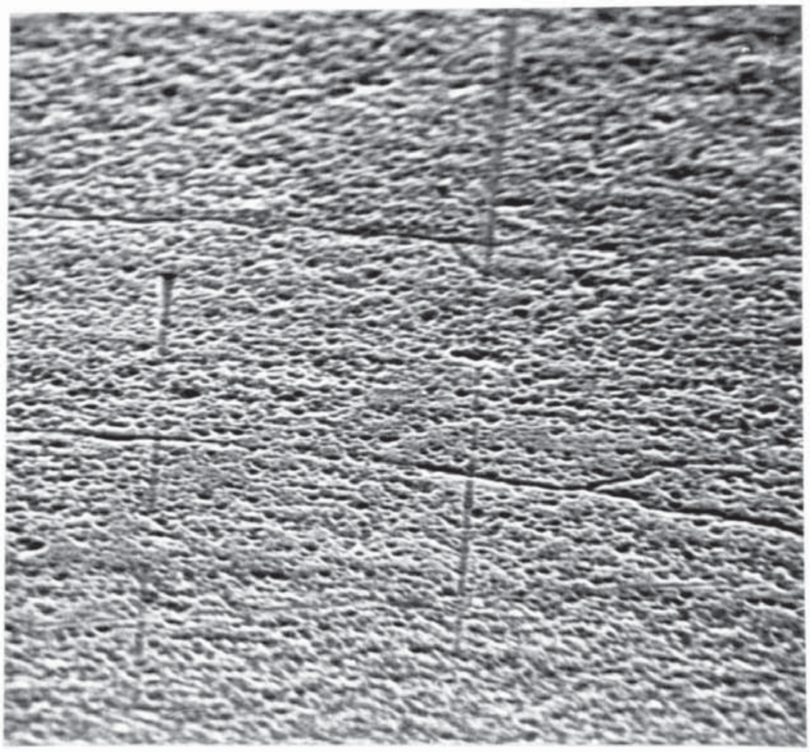


Fig.3.32. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution B (6% Nitric acid) for IO seconds. X 2000.

Fig.3.33. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution B (6% Nitric acid) for I80 seconds. X I,200.

same manner as it had on previous samples in previous solutions, with the exception that by 180 secs. polishing (fig.3.33) there was no preferential dissolution of different grains, as had been found on 99.99% aluminium in solution A. The peaks of aluminium were still present, but a closer examination (fig.3.34) showed the size to be less than that found in solution A, and in addition there was little evidence of any annular groove surrounding the peak. Consequently, the reflectivity of the 99.99% aluminium in this solution was considerably greater than in the previous solution.

### 3.3.1.4 Solution B (6% Nitric acid), 99.5% Aluminium

The surface of the 99.5% aluminium after 2 secs. polishing in this solution had the completely etched surface (fig.3.35) found after 5 secs. polishing in solution A containing no nitric acid. After 10 secs. polishing (fig.3.36) the reflectivity of the surface was further reduced by the pitting action of the predominantly iron rich inclusions. Following 30 secs. of polishing (fig.3.37) fewer inclusions remained on the surface of the aluminium in this solution than in the previous solution. Polishing for 60,120 and 180 secs. (figs. 3.38 - 3.40 respectively) increased the extent of the pitting. As the aluminium front receded more inclusions were exposed on the surface and were responsible for increased dissolution in their vicinity, they were then undercut and/or dissolved into the solution. The extent of the pitting that the inclusion caused, increased with time due to the increase in the number of inclusions exposed as the period of polishing was extended.

Also significant in this solution was the appearance of peaks of aluminium as found on the 99.99% aluminium in the solution not containing nitric acid (fig.3.41).

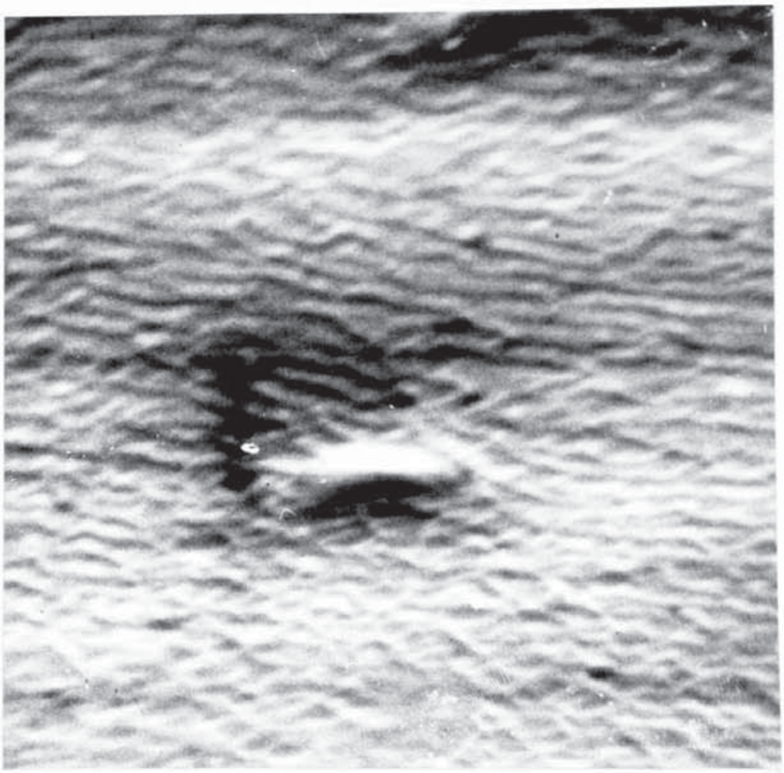


Fig.3.34. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution B (6% Nitric acid) for I80 seconds. X II,000.

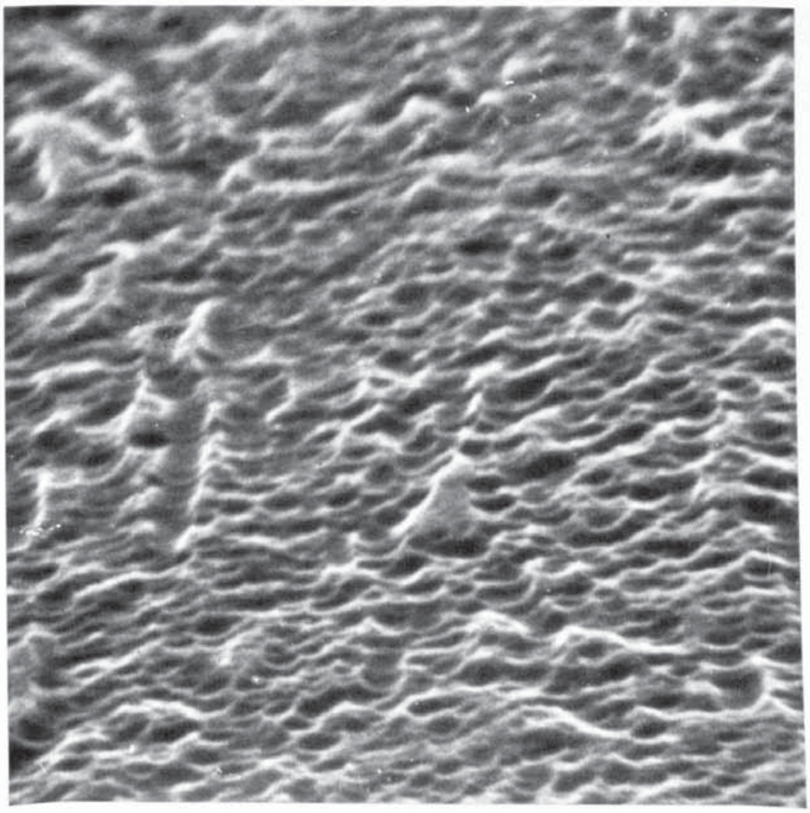


Fig.3.35. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution B (6% Nitric acid) for 2 seconds. X 7000.

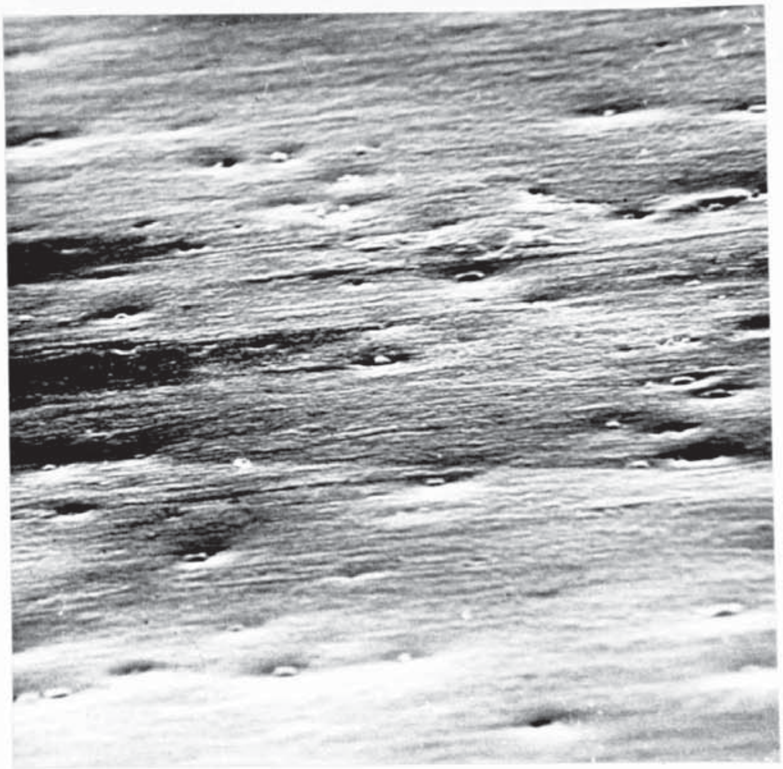


Fig.3.36. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution B (6% Nitric acid) for IO seconds. X 600.

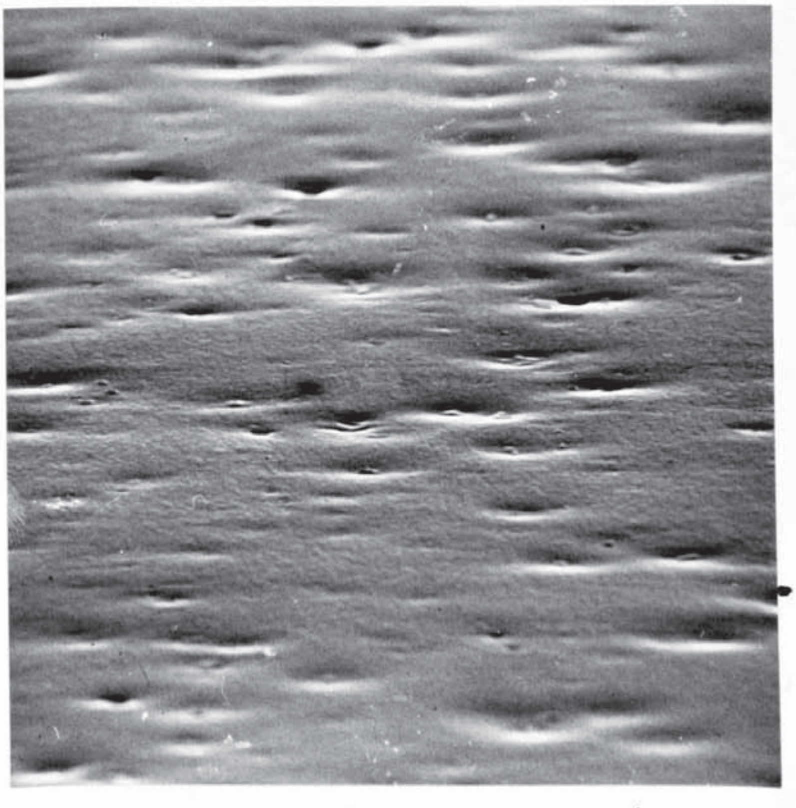


Fig.3.37. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution B (6% Nitric acid ) for 30 seconds. X 600.

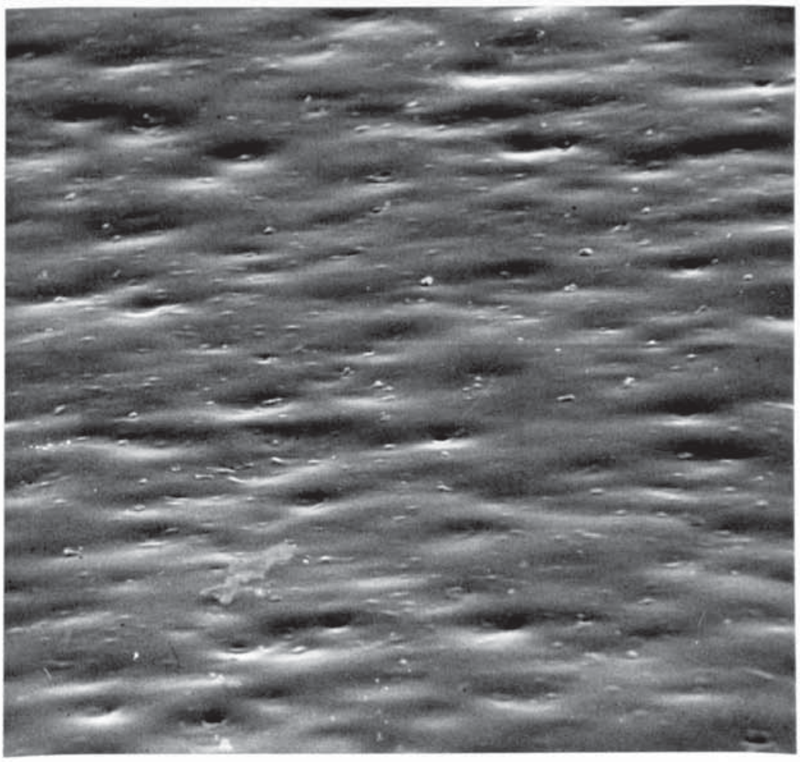


Fig.3.38. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution B (6% Nitric acid) for 60 seconds. X 500.

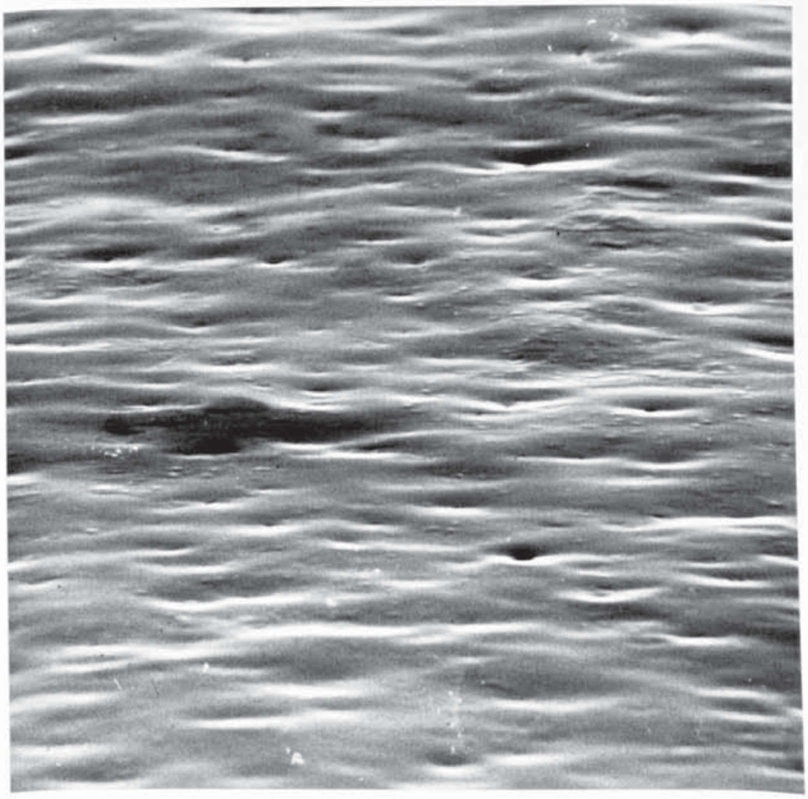


Fig.3.39. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution B (6% Nitric acid) for I20 seconds. X 500.

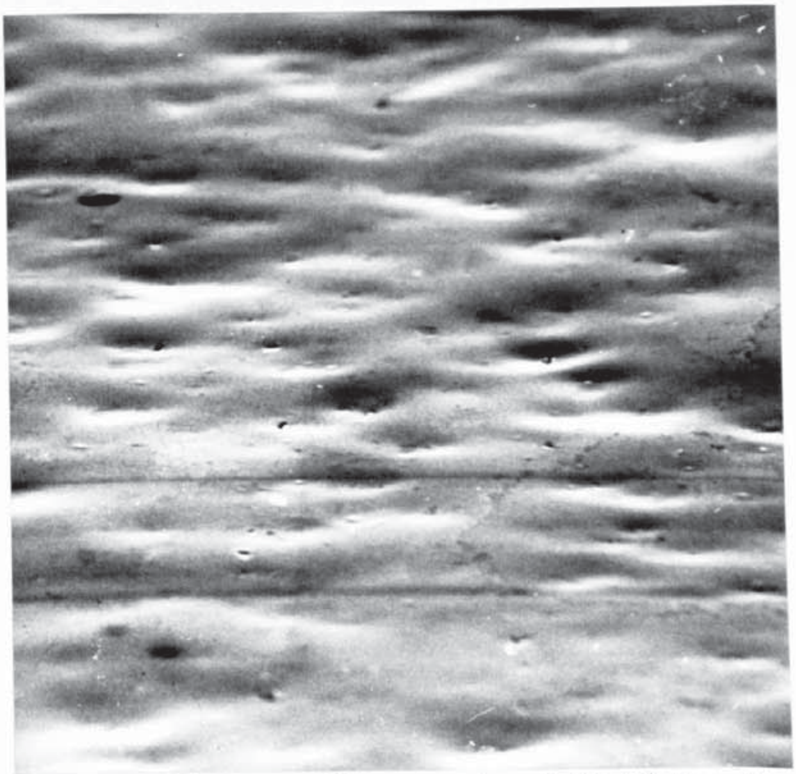


Fig.3.40. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution B (6% Nitric acid) for 180 seconds. X 500.

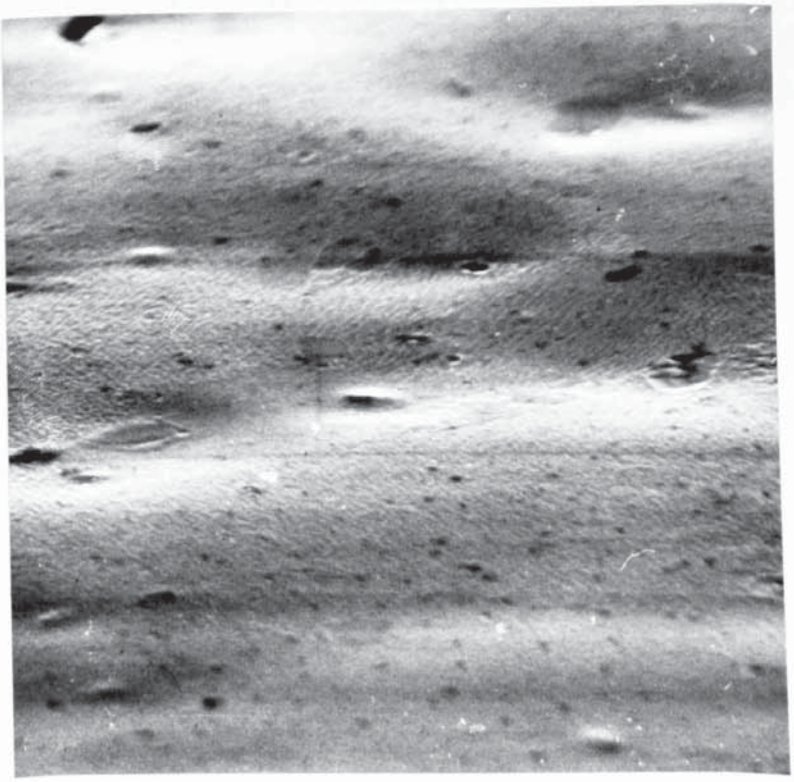


Fig.3.41. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution B (6% Nitric acid) for 180 seconds. X 2,300.

### 3.3.1.5. Solution C (20% Nitric acid), 99.99% Aluminium

After 10 secs. polishing (fig.3.42) the surface had only just begun to be etched. The surface was completely etched after 20 secs. (fig.3.43) but the depth of the etch pits was reduced compared with the 99.99% aluminium in the two previous solutions. After 40 secs. polishing (fig. 3.44) the etched network had been levelled, but the scratches present on the surface at the beginning of the polishing had not been removed. As with the two previous solutions, peaks of aluminium were found on the surface, although the number of these defects was less (after the same polishing time) than in the previous solutions. The peaks also showed pitting on the top of the peaks, not found previously (Fig.3.45). The scratches still present on the surface after 40 secs. polishing were eventually levelled after 300 secs. polishing (fig.3.46). In addition, the number of peaks on the surface had increased by this time. The sub-micro patterns present on the surface after polishing in solutions containing no nitric acid and 6% nitric acid, were not visible on the surface after polishing in this solution.

### 3.3.1.6. Solution C (20% Nitric acid), 99.5% Aluminium

This solution produced even more superficial etching of the surface of the 99.5% aluminium than that found on the 99.99% aluminium (fig. 3.47). The surface also showed pitting due to the presence of Iron rich inclusions. Further polishing for 180 secs. resulted in an increase in the incidence of this pitting (fig.3.48). Few of the inclusions remained on the surface, but their influence was clear. Due to the nature of the pitting on these samples it was difficult to determine if peaks of aluminium were present or not. No evidence of the sub-micro patterns formed in solutions containing no nitric acid and 6% nitric acid was found.

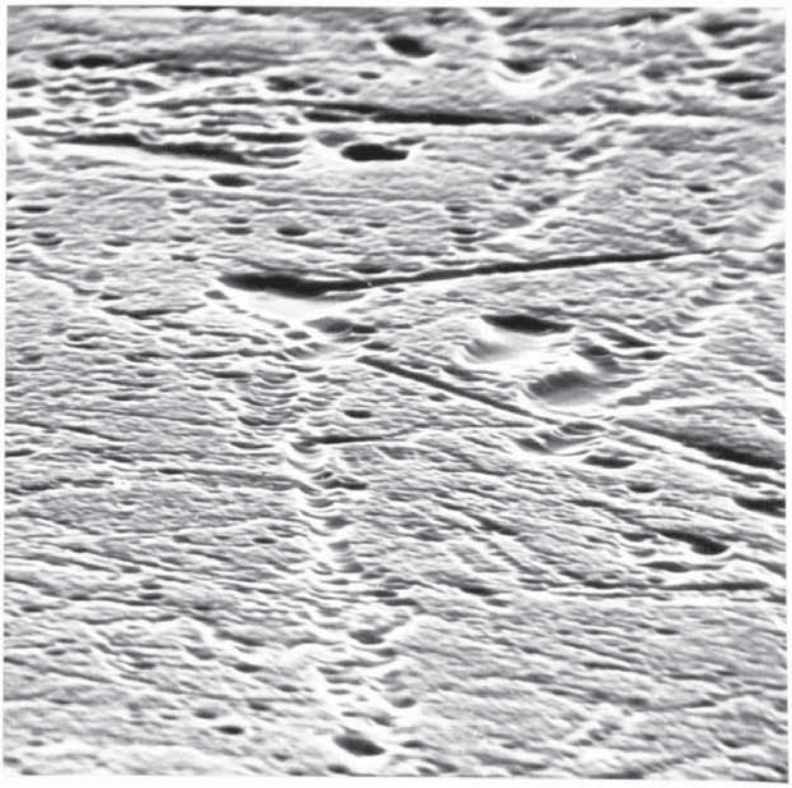


Fig.3.42. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution C (20% Nitric acid) for IO seconds. X 2000.

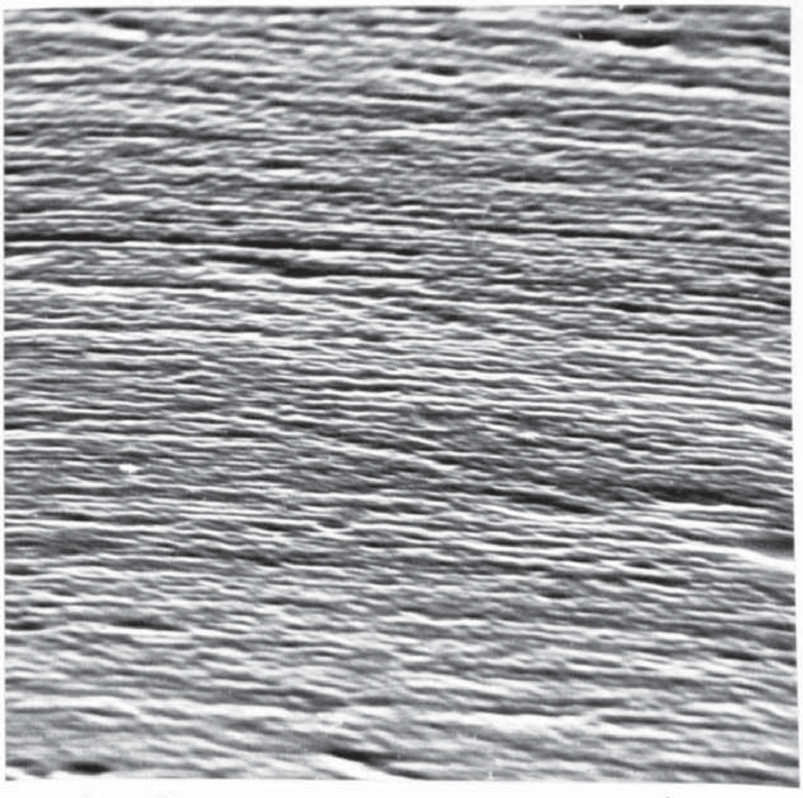


Fig.3.43. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution C (20% Nitric acid) for 20 seconds. X 2000.

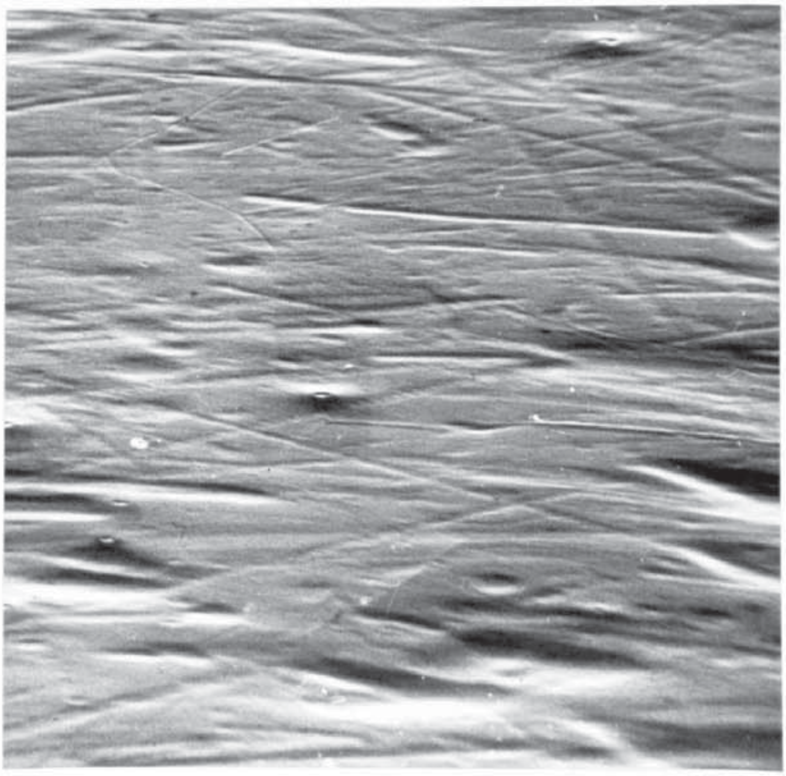


Fig.3.44. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution C (20% Nitric acid) for 40 seconds. X I000.

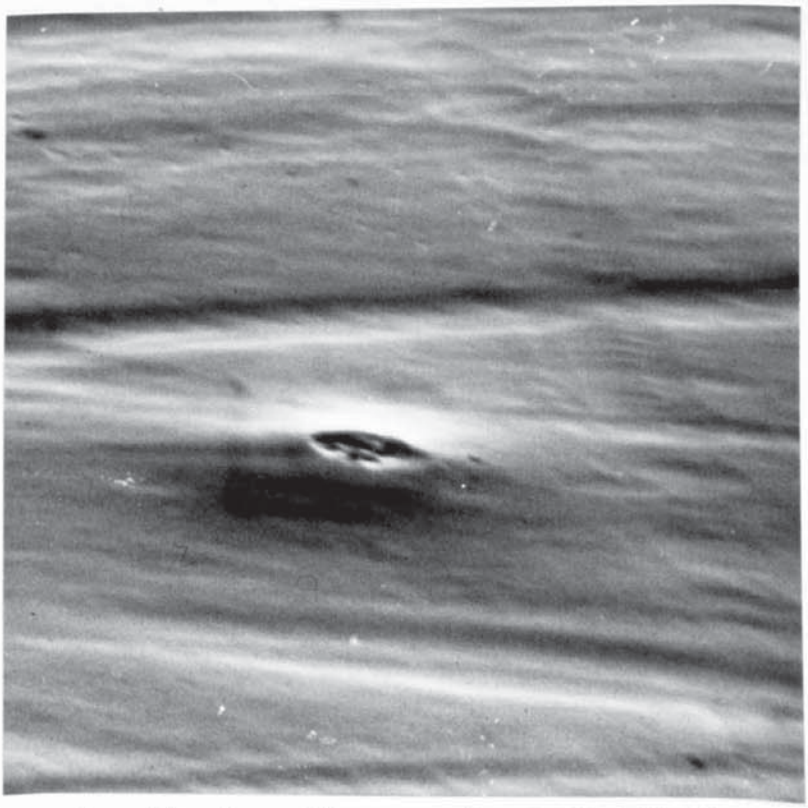


Fig.3.45. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution C (20% Nitric acid) for 40 seconds. X 5000.

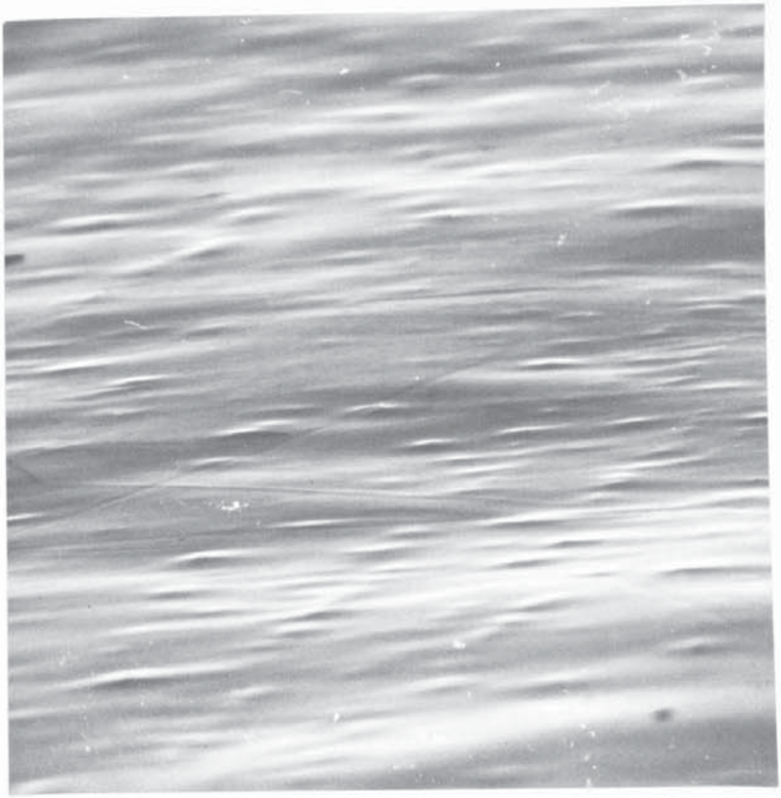


Fig.3.46. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution C (20% Nitric acid) for 300 seconds. X I,200.

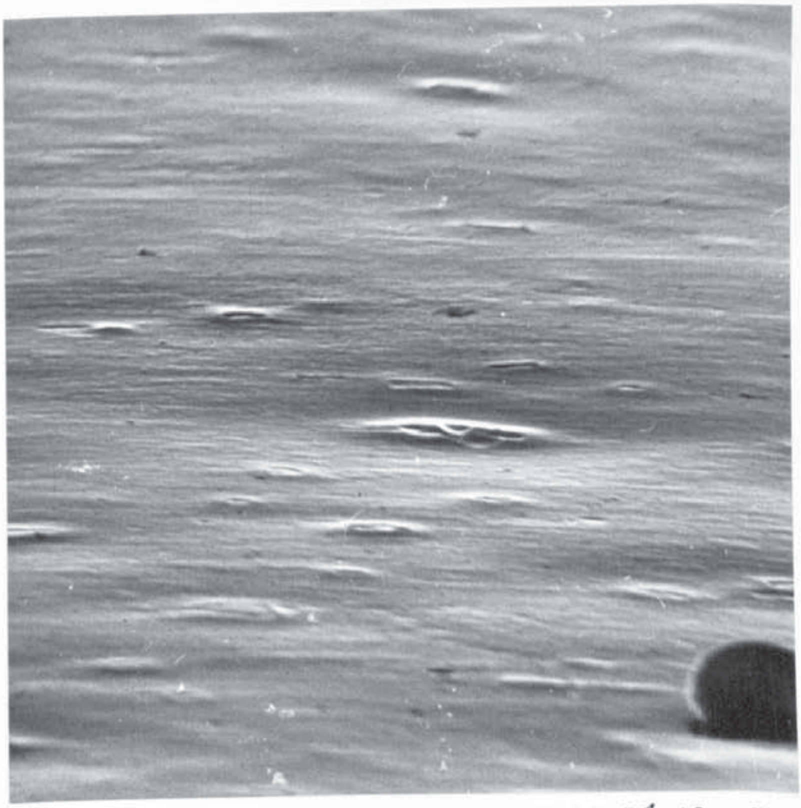


Fig.3.47. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution C (20% Nitric acid) for IO seconds. X 2000.

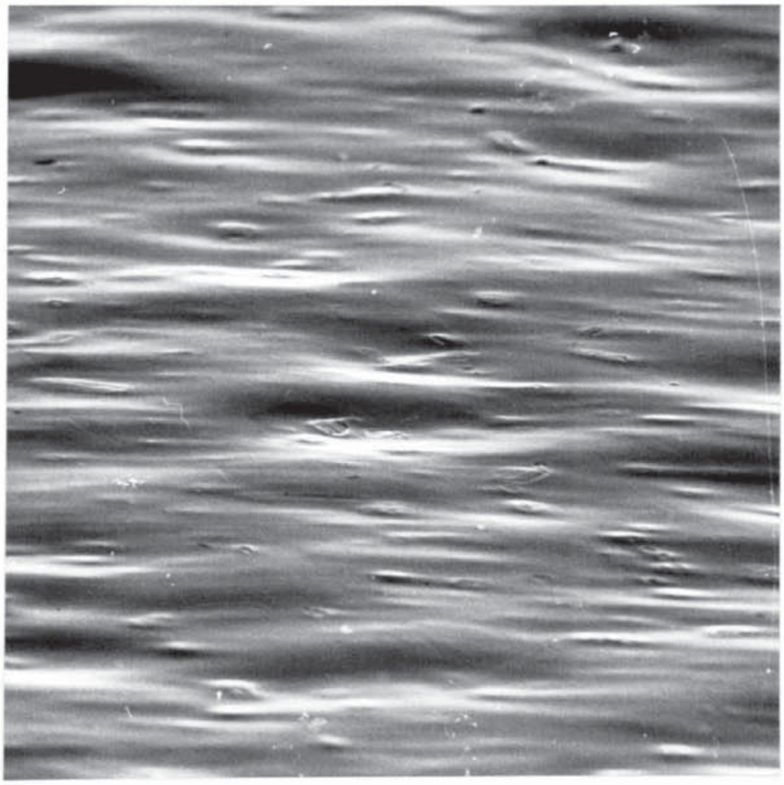


Fig.3.48. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution C (20% Nitric acid) for 180 seconds. X 1000.

### 3.3.2. The influence of Nitric acid in solutions containing Copper

#### 3.3.2.1. Solution D (no Nitric acid), 99.99% Aluminium

The surface after 5 secs. polishing, was heavily etched, in a similar manner to the 99.99% aluminium in solution A (no nitric acid), although to a greater extent (fig.3.49). A higher magnification of the surface revealed the presence of deposited copper (figs.3.50 & 3.51). At this time of polishing the deposits of copper on the surface were of two different sizes, the smaller, approximately 0.25µm, and the larger approximately 1.5µm. in diameter. The copper tended to deposit onto defect sites on the surface e.g. scratches (fig.3.52), which were also preferentially attacked by the solution.

After 10 secs. polishing (fig.3.53) the surface had also begun to be levelled by the polishing action of the solution. Fig.3.54 shows the surface after 30 secs. polishing. The amount of copper deposited on the surface had increased. The size of the smaller deposits was now approximately 1.0µm., and the larger deposits had an average size of 20µm. These larger deposits can be seen to be sited in depressions in the surface. The surface of the same sample, after the copper had been removed in a 50% by volume nitric acid solution, showed the extent of the influence of these larger deposits (fig.3.55), and it also showed that these pits or depressions were smooth, and not rough, internally. Further polishing for 120 secs. increased the surface pitting due to these larger copper deposits (fig.3.56). The sub-micro patterns found previously on both 99.99% and 99.5% in solutions containing no nitric acid and 6% nitric acid (but no copper), were again present on the surface (fig.3.57). However, peaks of aluminium most prevalent on the 99.99% aluminium in solution A (no nitric acid) were not found on the surface.

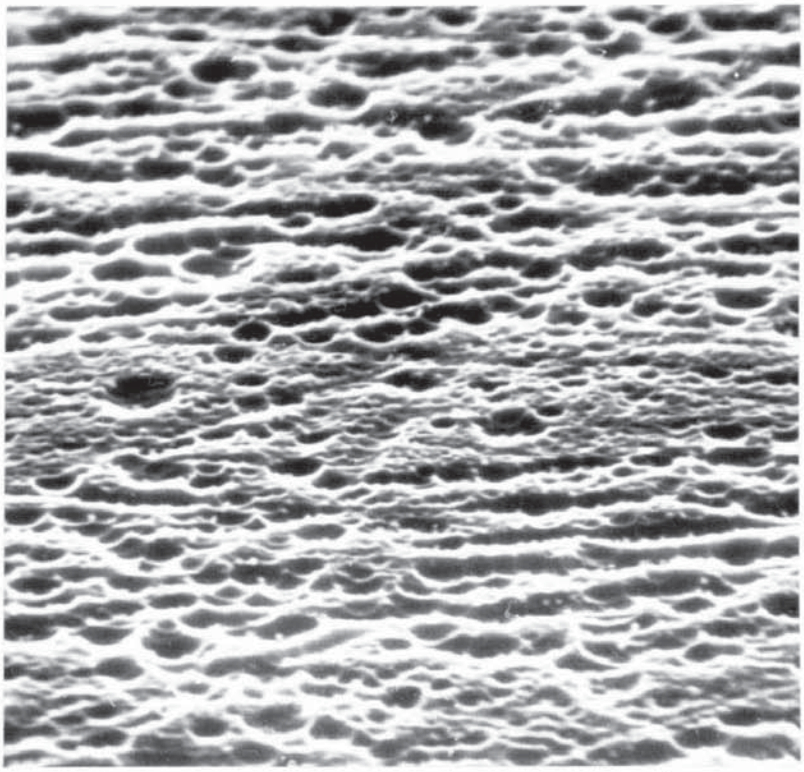


Fig.3.49. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for 5 seconds. X 5000.

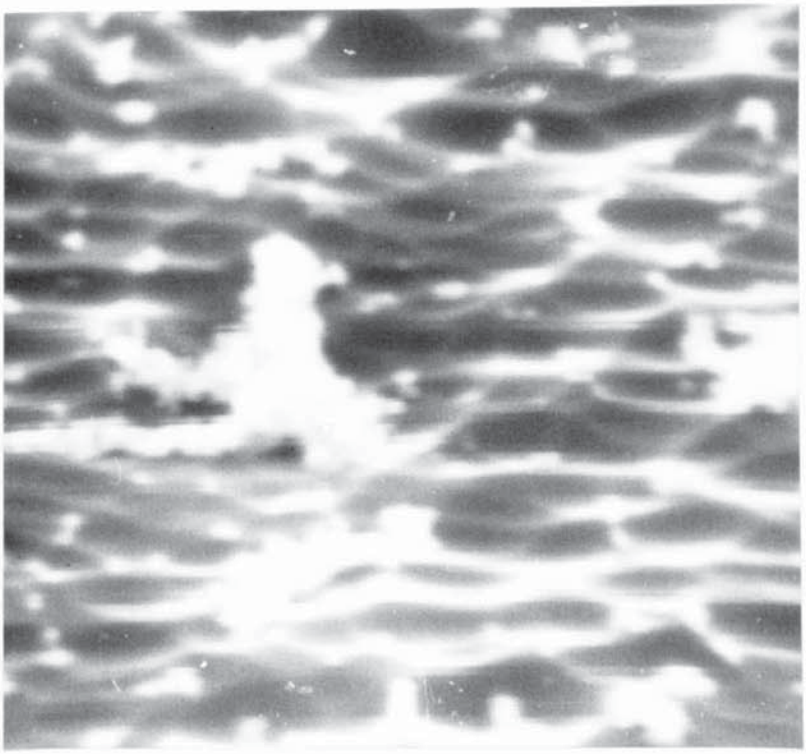


Fig.3.50. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for 5 seconds. X 20,000.

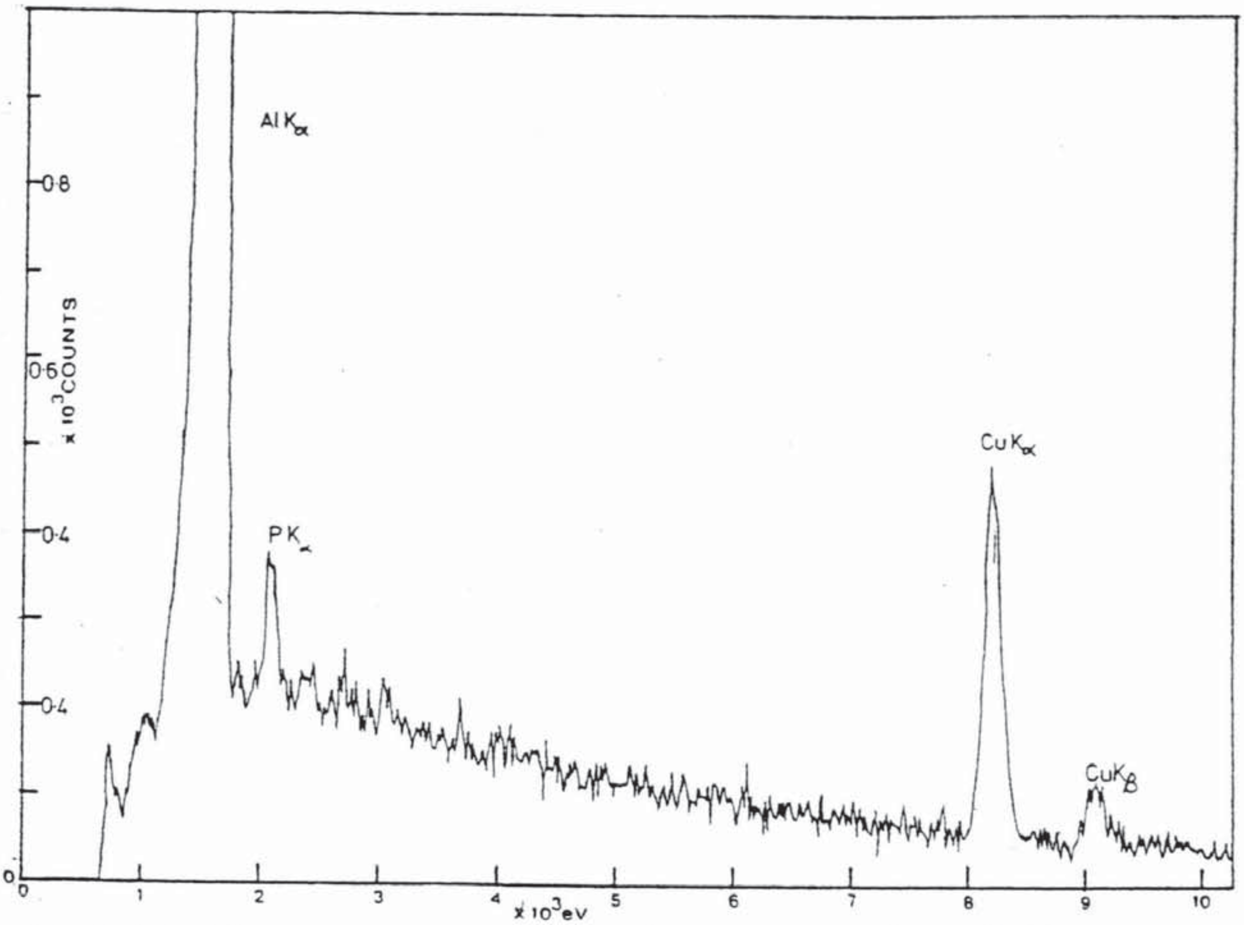


Fig.3.5I. 'Kevex' x-ray analysis of the particle in Fig.3.50. on the preceeding page.

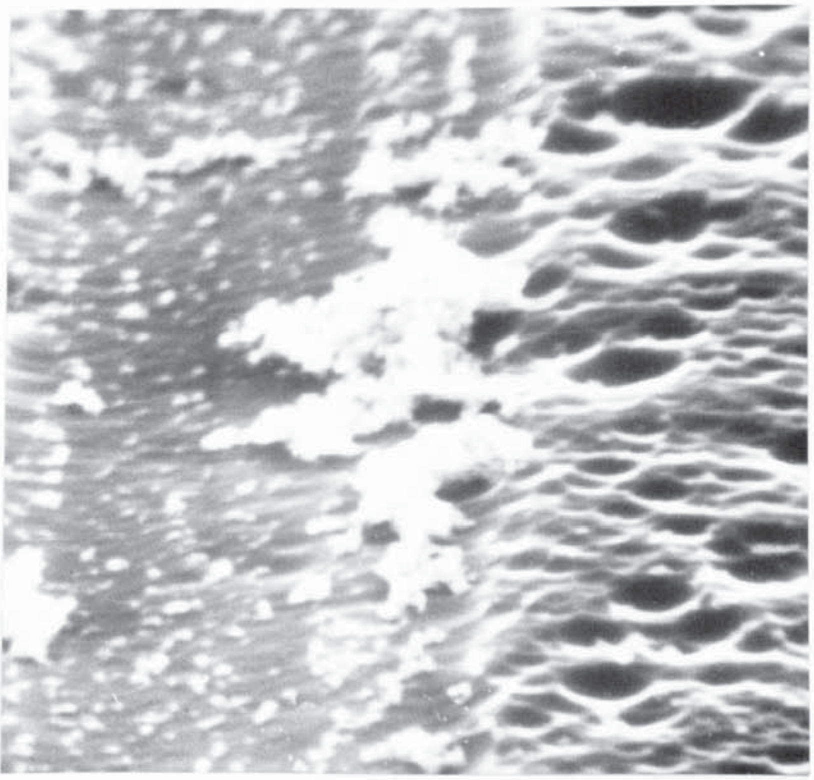


Fig.3.52. Scanning Electron Micrograph of 99.99. Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for 5 seconds. X IO,000.

Fig.3.53. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for IO seconds. X 2,400.

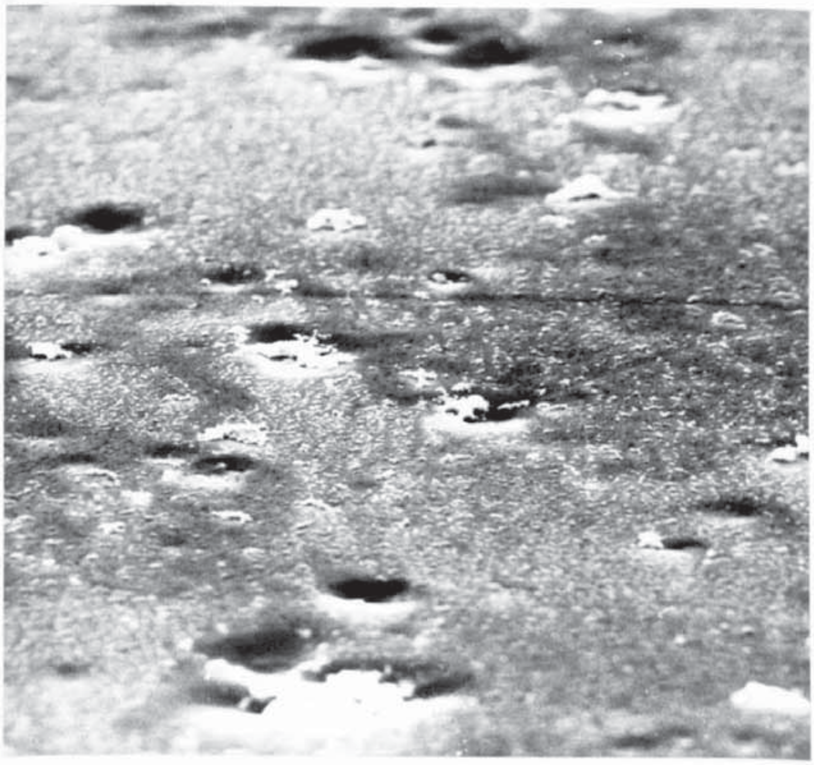


Fig.3.54. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for 30 seconds. X 600.

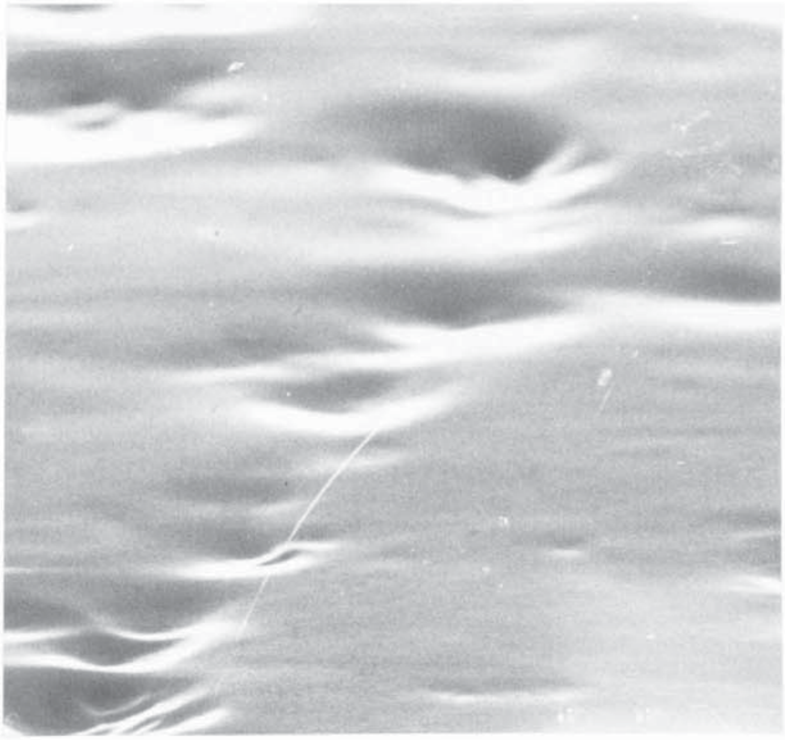


Fig.3.55. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for 30 seconds, with the deposited copper removed. X 6000.

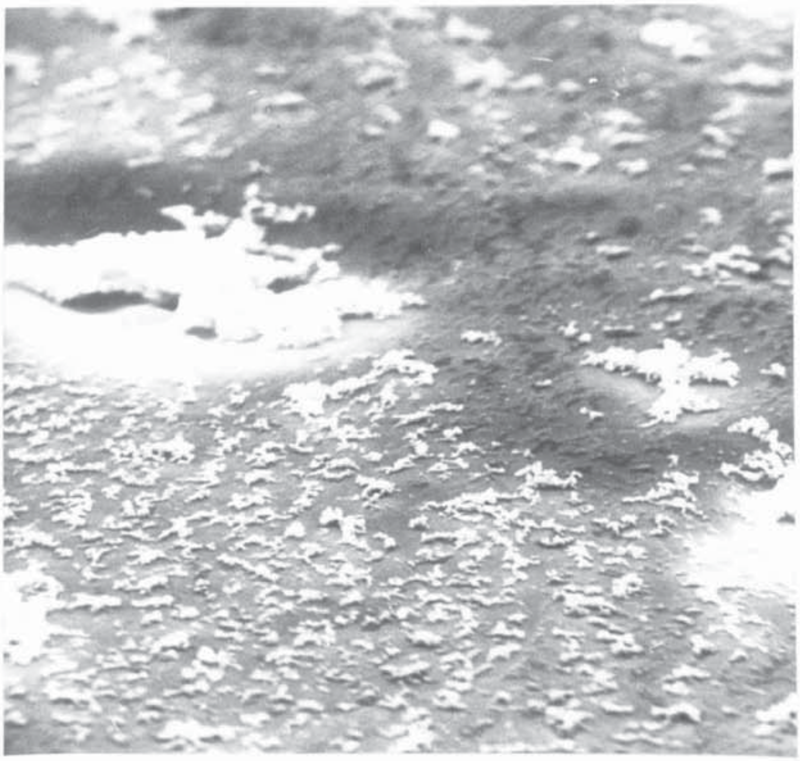


Fig.3.56. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for I20 seconds. X 2,400.

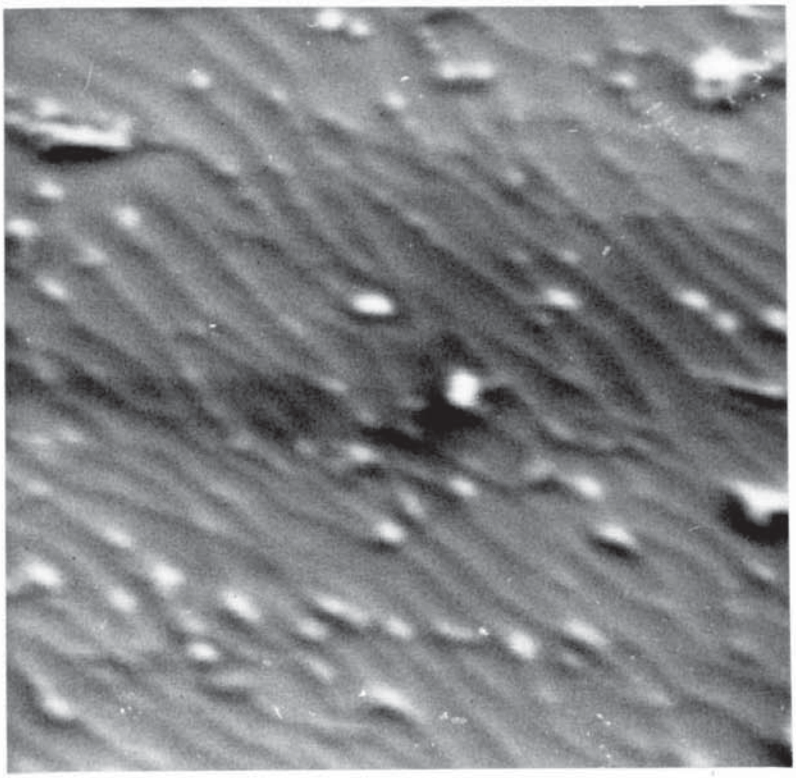


Fig.3.57. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for I20 seconds. X 20,000.

### 3.3.2.2. Solution D (no Nitric acid), 99.5% Aluminium

The etching of the surface after 5 secs. polishing was more superficial in this case than was found on the 99.99% aluminium, in this solution (fig.3.58), again copper deposits were found.

The surface had also been pitted by the Iron rich inclusions in the matrix (3.59). After 10 secs. polishing (fig.3.60), the etching of the surface had been levelled and there was a clear division of the copper deposits into two sizes. The small deposits, slightly smaller than were found on the 99.99% aluminium in this solution at this time were approximately 0.6µm. in diamter, and the larger deposits, approximately 10µm. Fig.3.61 shows the surface after 30 secs. polishing with the surface copper removed (in a 50% by volume solution of nitric acid) and shows that both the iron rich inclusions and the larger copper deposits were causing pitting of the surface. Further polishing of the surface for 180 secs. increased the extent of this pitting (fig.3.62).

Again, the peaks of aluminium as found in the solutions containing no nitric acid and 6% nitric acid with no dissolved copper were not present on the surface. The sub-micro patterns were present (fig.3.63). This micrograph not only shows the pattern ridges, but also that the smaller copper particles tend to deposit along the pattern ridges, and not in between the ridges, indicating the cathodic nature of the ridges. The larger deposits, due to their size, cover a number of the ridges. The copper was also found to deposit preferentially onto the iron rich inclusions, and to a limited extent reduce the pitting caused by the presence of the iron (fig.3.64 and 3.65).

### 3.3.2.3. Solution E (6% Nitric acid), 99.99% Aluminium

This solution represents the optimum operating conditions for the solutions covered in this chapter, and produced the most specular

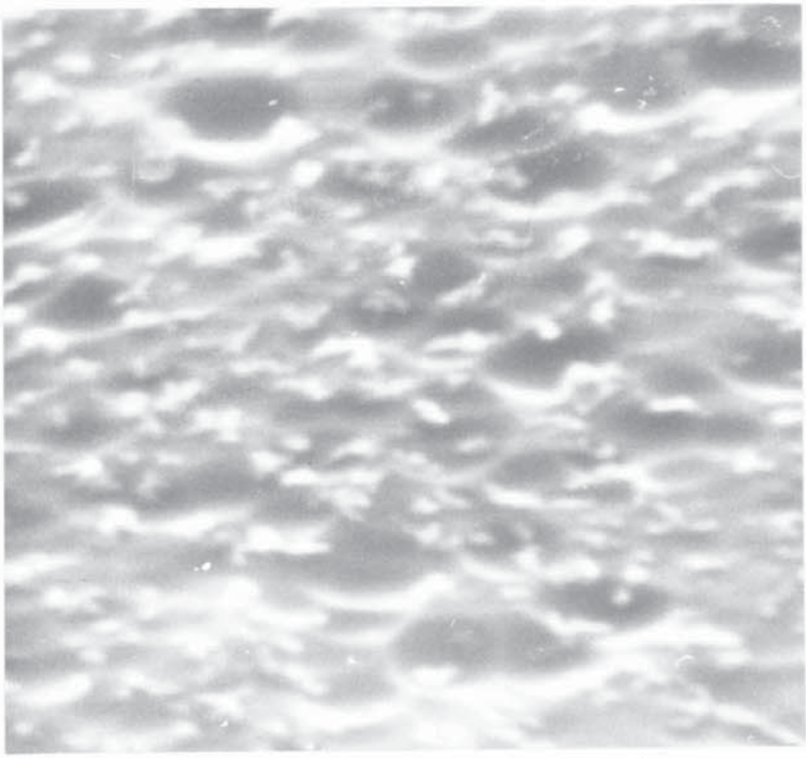


Fig.3.58. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for 5 seconds. X 20,000.

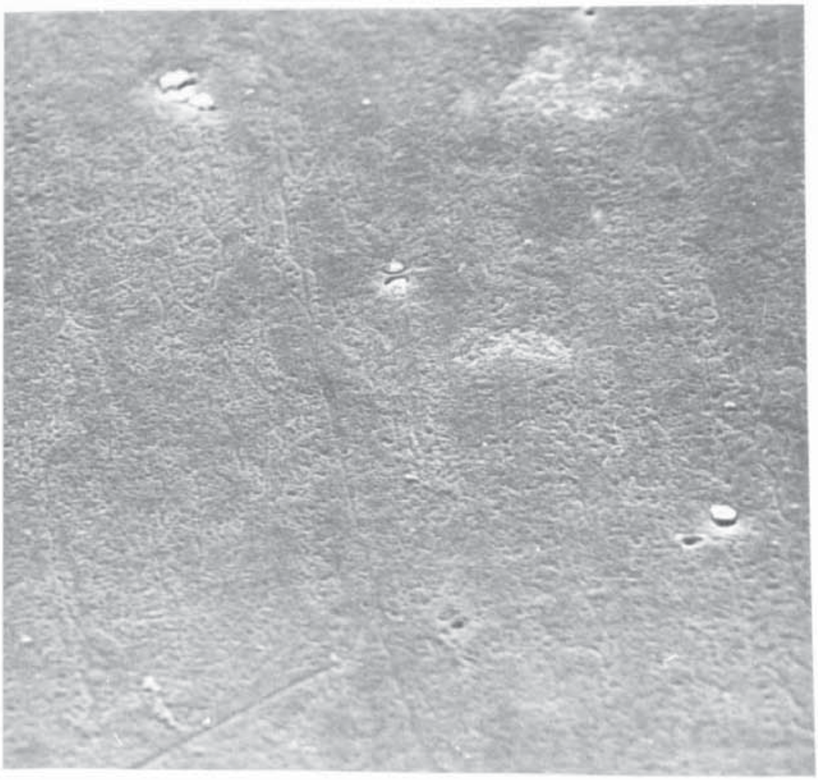


Fig.3.59. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for 5 seconds. X 1000.

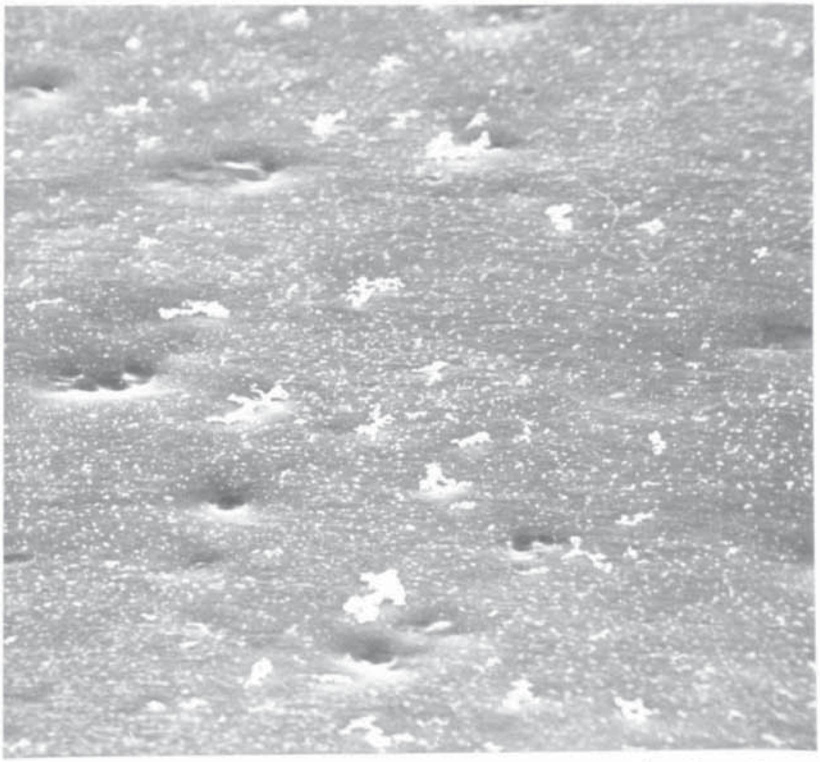


Fig.3.60. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for IO seconds. X IOOO.

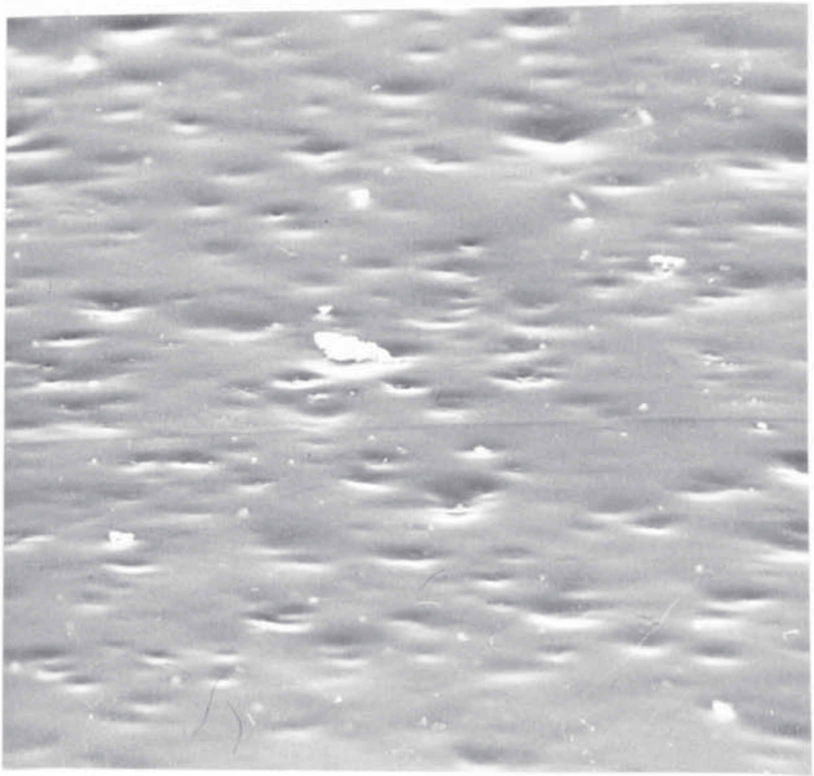


Fig.3.6I. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for 30 seconds. X 500.

Fig.3.62. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for I80 seconds. X 2000.

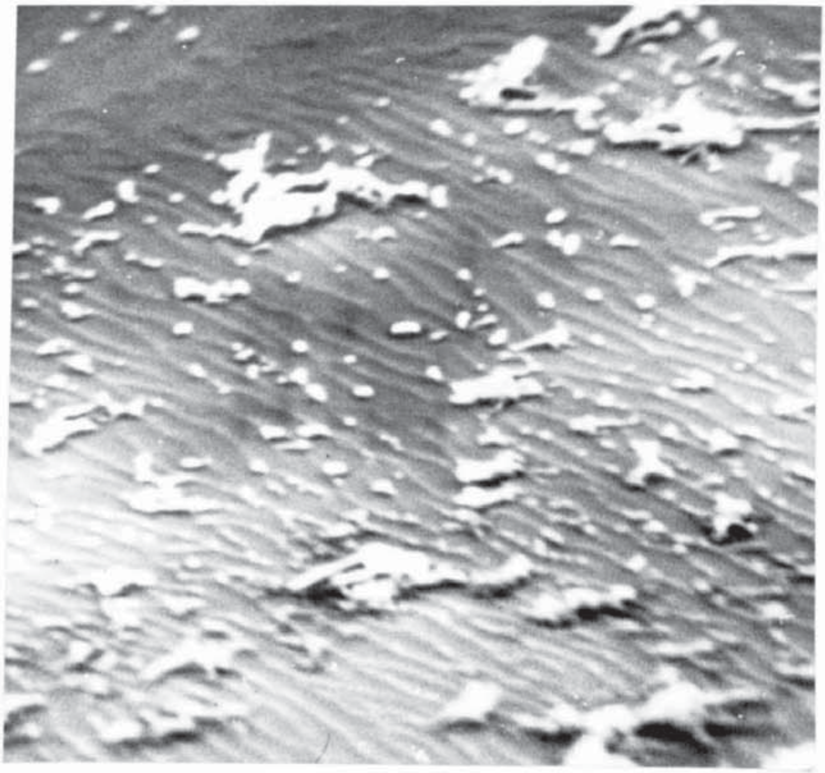


Fig.3.63. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for I80 seconds. X I0,000.

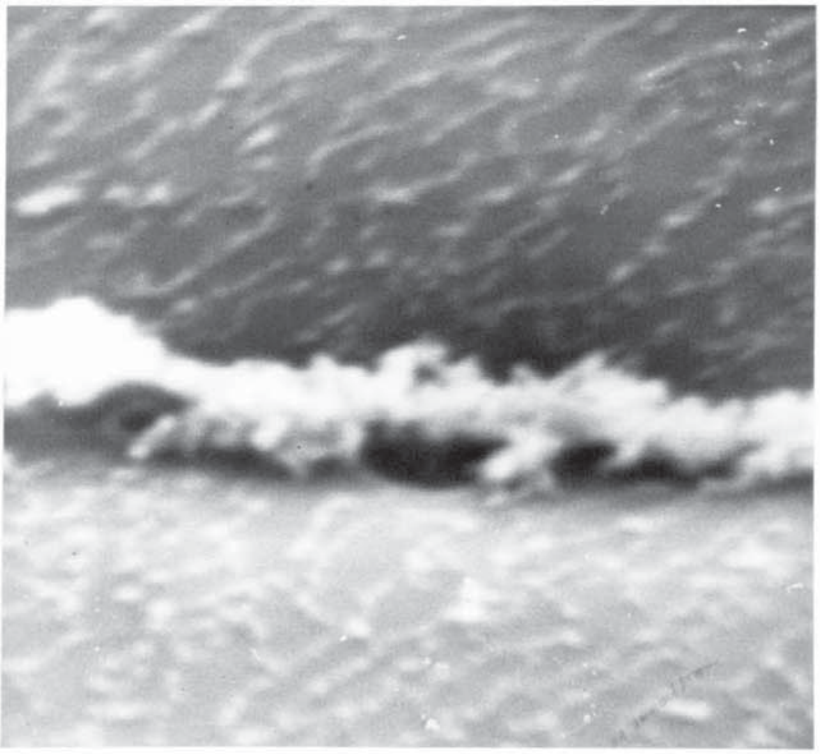


Fig.3.64. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution D (no nitric acid & Ig/l Cu) for I80 seconds. X 20,000.

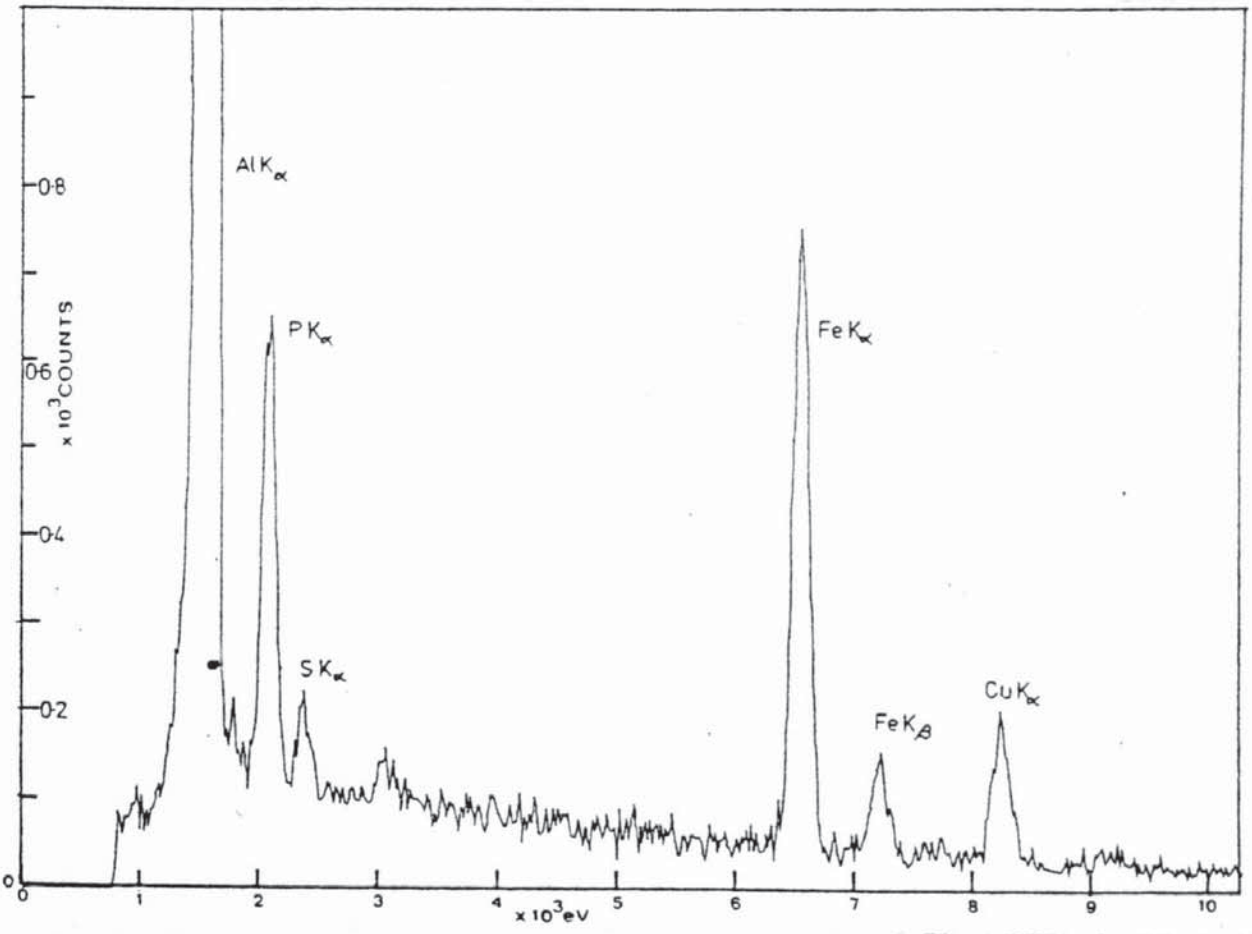


Fig.3.65. 'Kevex' x-ray analysis of the particle in Fig.3.64. above.

finish on aluminium polished in it.

After 5 secs. polishing (fig.3.66), the surface had the characteristic etched surface, however, the distribution of the copper deposits, unlike solution D (no nitric acid), was even, and the size of the deposits was approximately the same (0.4µm.) The distribution of the copper deposits after 40 secs. polishing remained even, although the amount and size of the deposits had increased (fig.3.67). The average size had increased to 1.5µm. After 90 secs. polishing (fig.3.68), there were still no isolated copper deposits larger than the majority. The average size of the deposits had increased again however, to approximately 2.0µm. The size of the copper deposits did not increase with continued polishing, although after 120 secs. polishing (fig.3.69), the amount, had increased. A higher magnification of this surface revealed the presence of sub-micro patterns under the copper deposits (fig.3.70). Removal of this deposited copper in a 50% nitric acid solution (fig.3.71), showed the absence of any surface pitting. The only surface features visible were the sub-micro patterns.

### 3.3.2.4 Solution E (6% Nitric acid), 99.5% Aluminium

The surface of the 99.5% aluminium polished in this solution showed the same changes in surface morphology as the 99.99% aluminium. The copper was evenly distributed over the surface, and after 120 secs. polishing covered the iron rich inclusions and reduced the extent of the pitting they had caused in previous solutions (fig.3.72 and 3.73). Titanium rich inclusions were also found, and showed no pitting in their vicinity (fig.3.74 & 3.75).

Fig.3.76 shows the surface of the aluminium after 180 secs. polishing, with the deposited copper removed in a 50% (by volume) nitric acid solution, and shows the absence of pitting around an iron rich inclusion visible standing proud of the surface. (fig.3.77)

Fig.3.66. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution E (6% Nitric acid & Ig/l Cu) for 5 seconds. X 2,400.

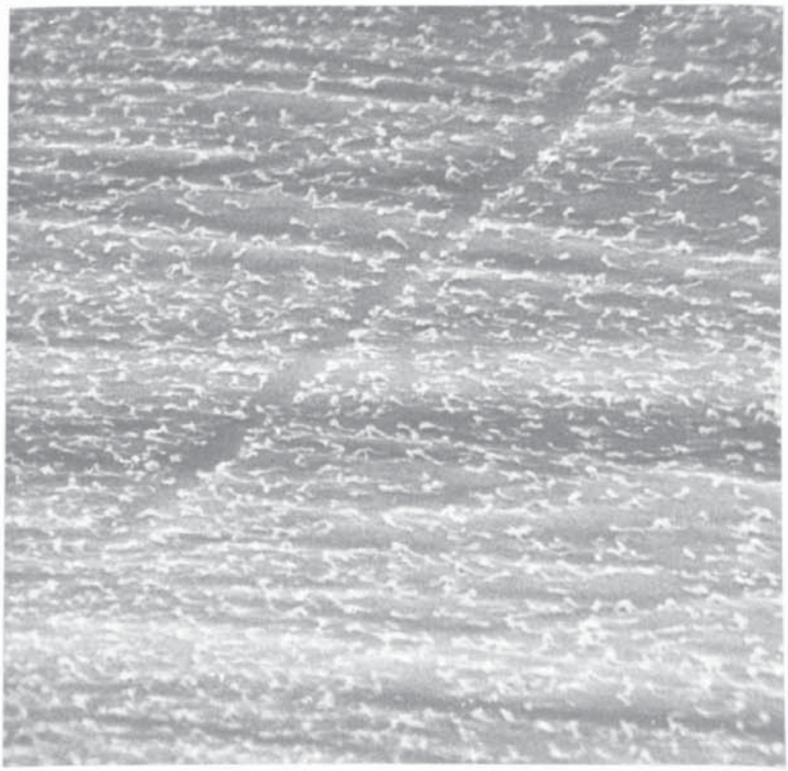


Fig.3.67. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution E (6% Nitric acid & Ig/l Cu) for 40 seconds. X 2000.

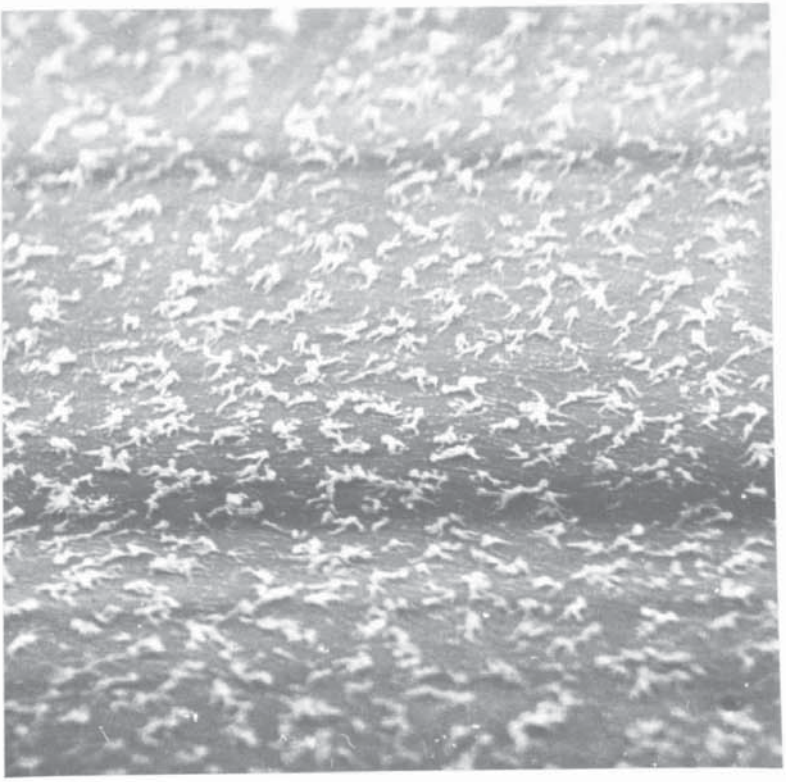


Fig.3.68. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution E (6% Nitric acid & Ig/l Cu) for 90 seconds. X 2,400.

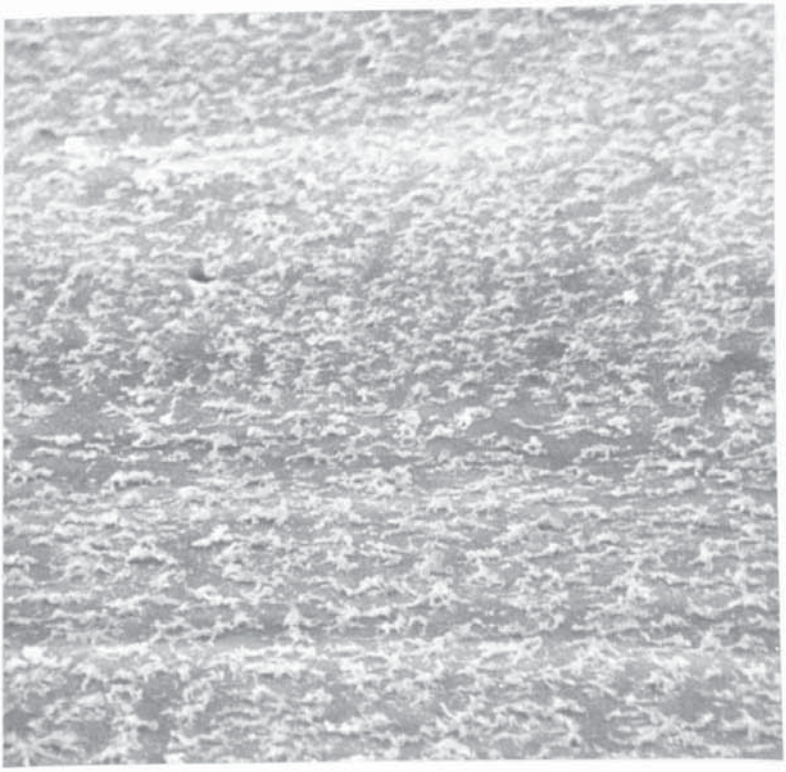


Fig.3.69. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution E (6% Nitric acid & Ig/l Cu) for I20 seconds. X 2000.

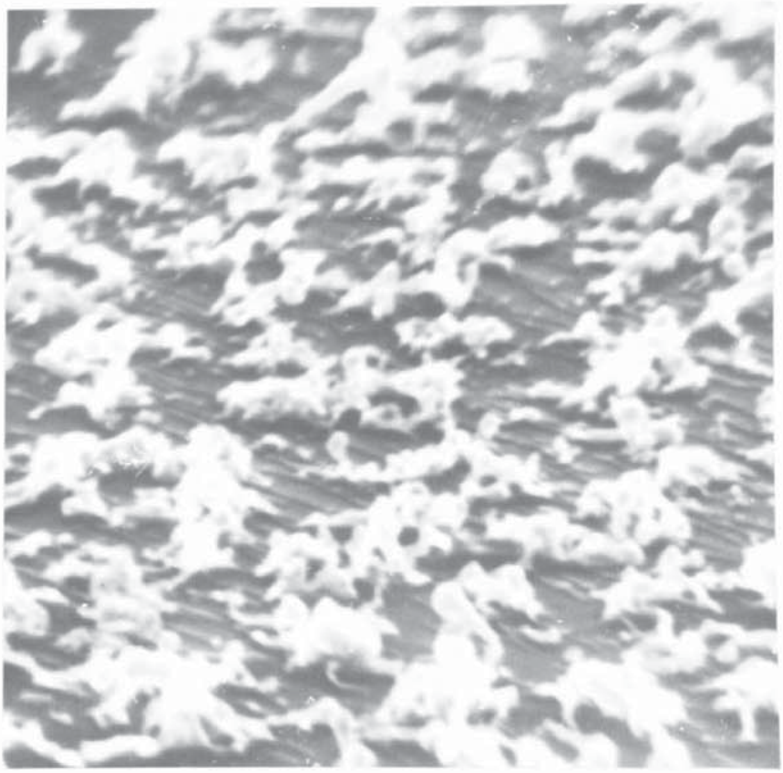


Fig.3.70. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution E (6% nitric acid & Ig/l Cu) for I20 seconds. X II,000.

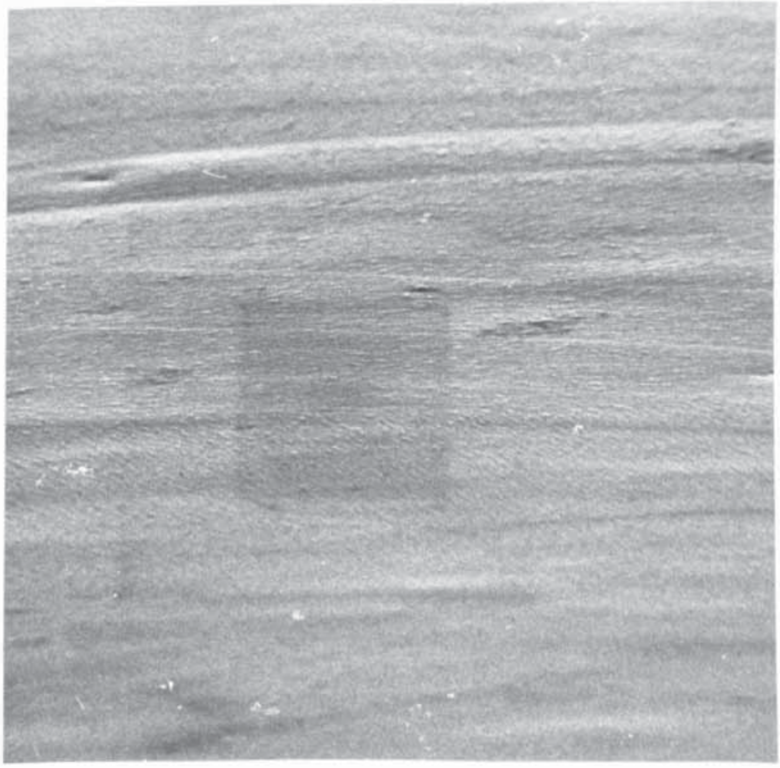


Fig.3.7I. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution E (6% nitric acid & Ig/l Cu) for I20 seconds,with the deposited copper removed. X 2,300.

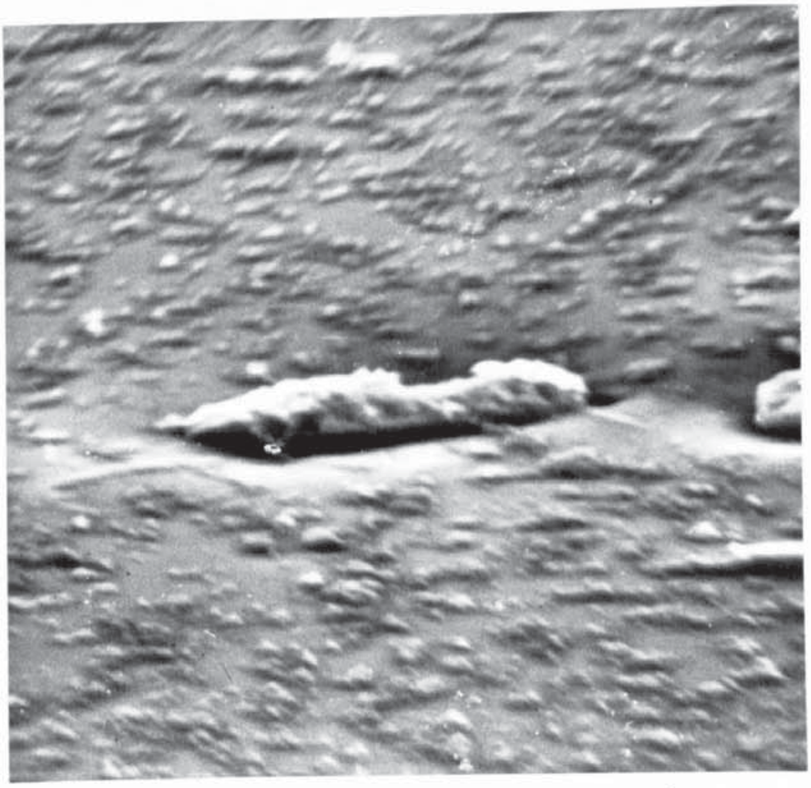


Fig.3.72. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution E (6% Nitric acid & Ig/l Cu) for I20 seconds. X 6000.

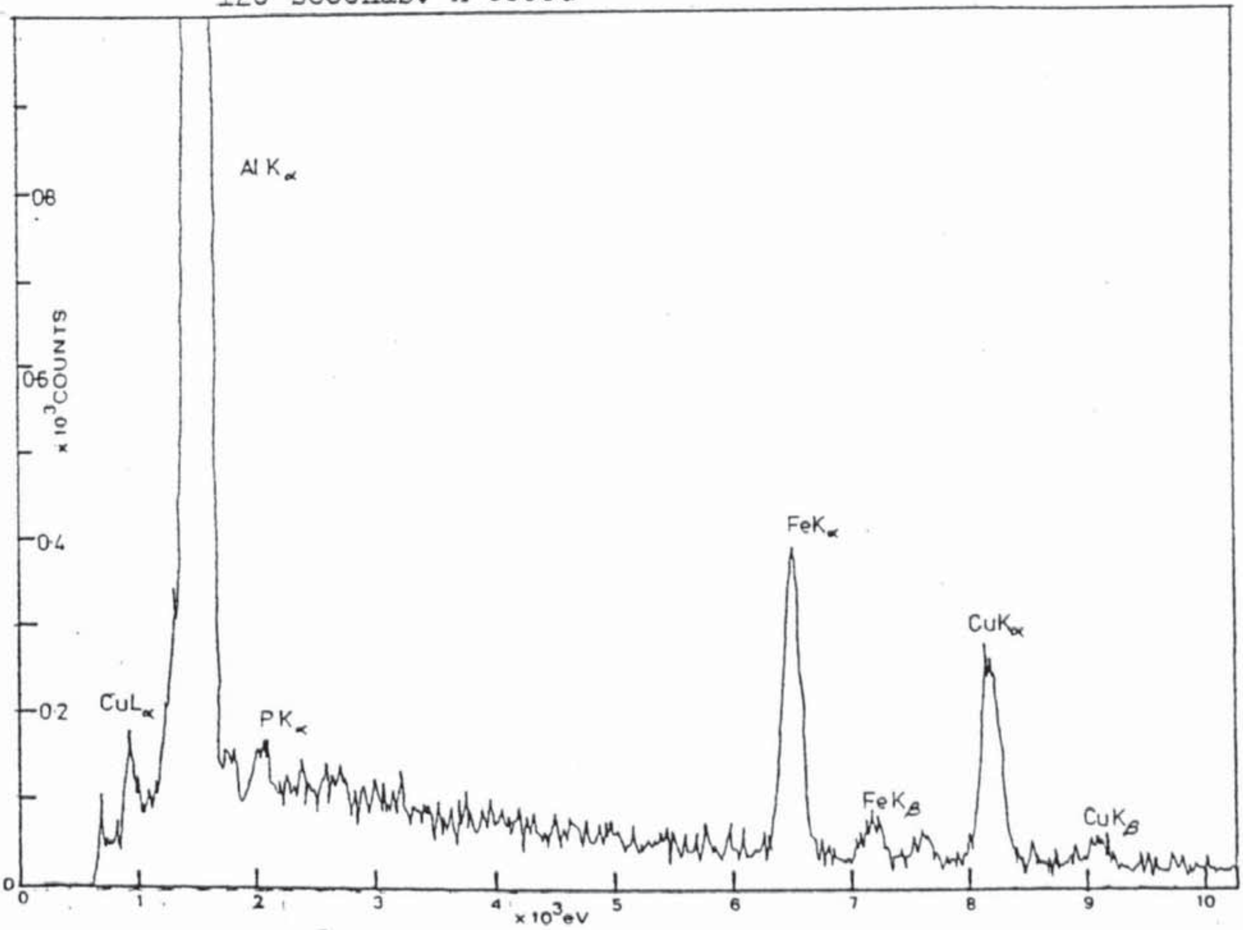


Fig.3.73. 'Kevex' x-ray analysis of the particle in Fig.3.72. above.

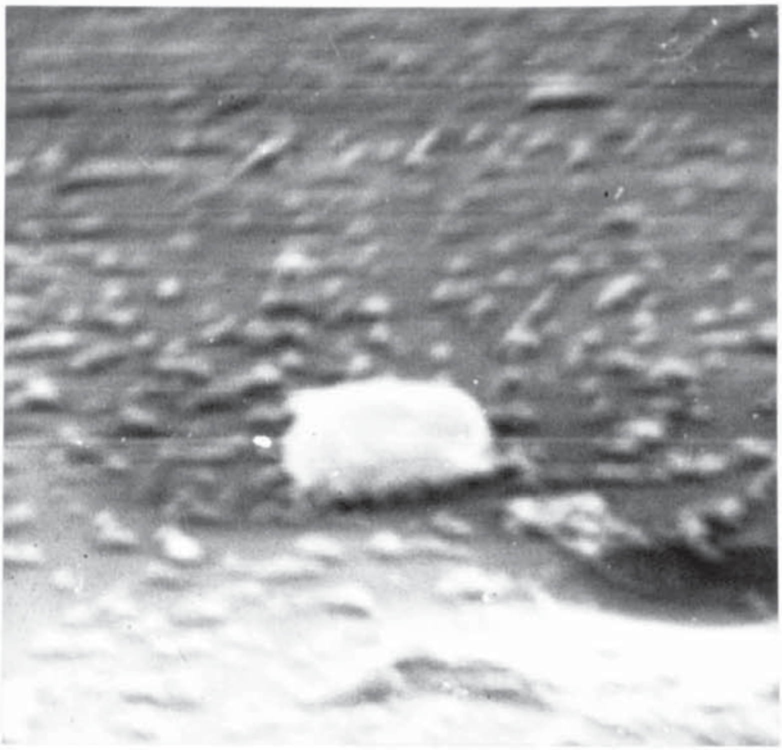


Fig.3.74. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution E (6% Nitric acid & Ig/l Cu) for I20 seconds. X I0,000.

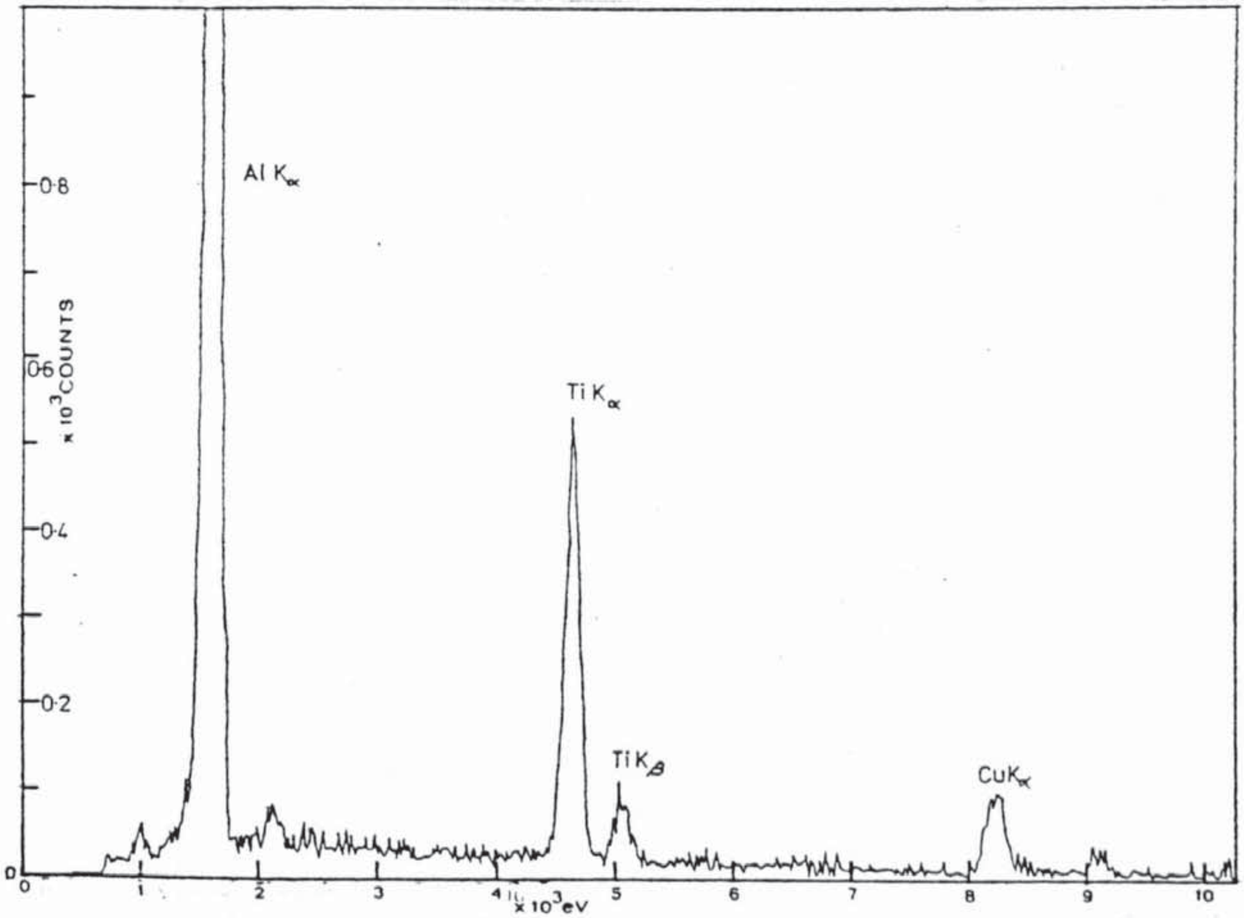


Fig.3.75. 'Kevex' x-ray analysis of the particle in Fig.3.74. above.

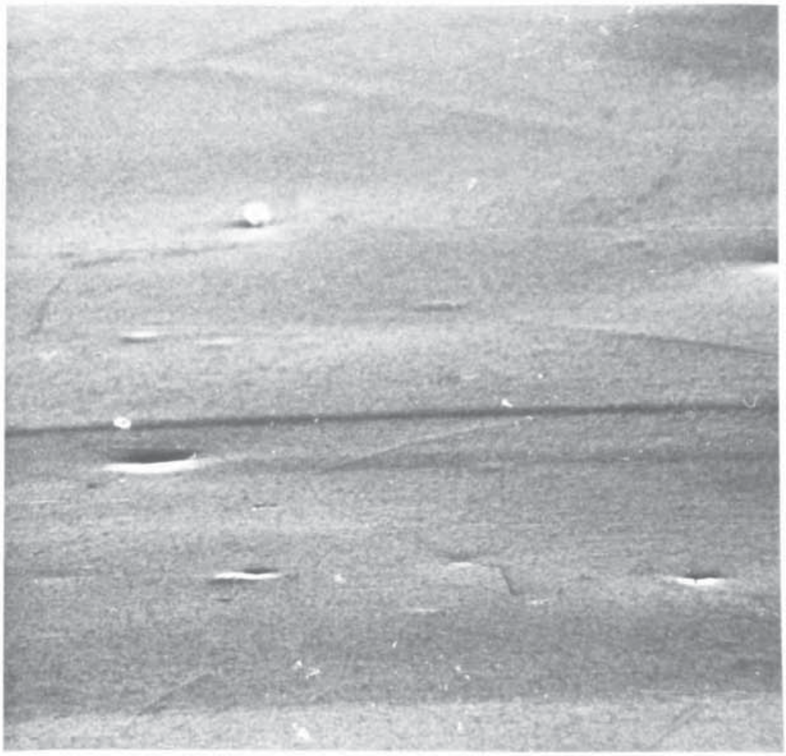


Fig.3.76. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution E (6% Nitric acid & Ig/l Cu) for I80 seconds, with the deposited copper removed. X I,IOO.

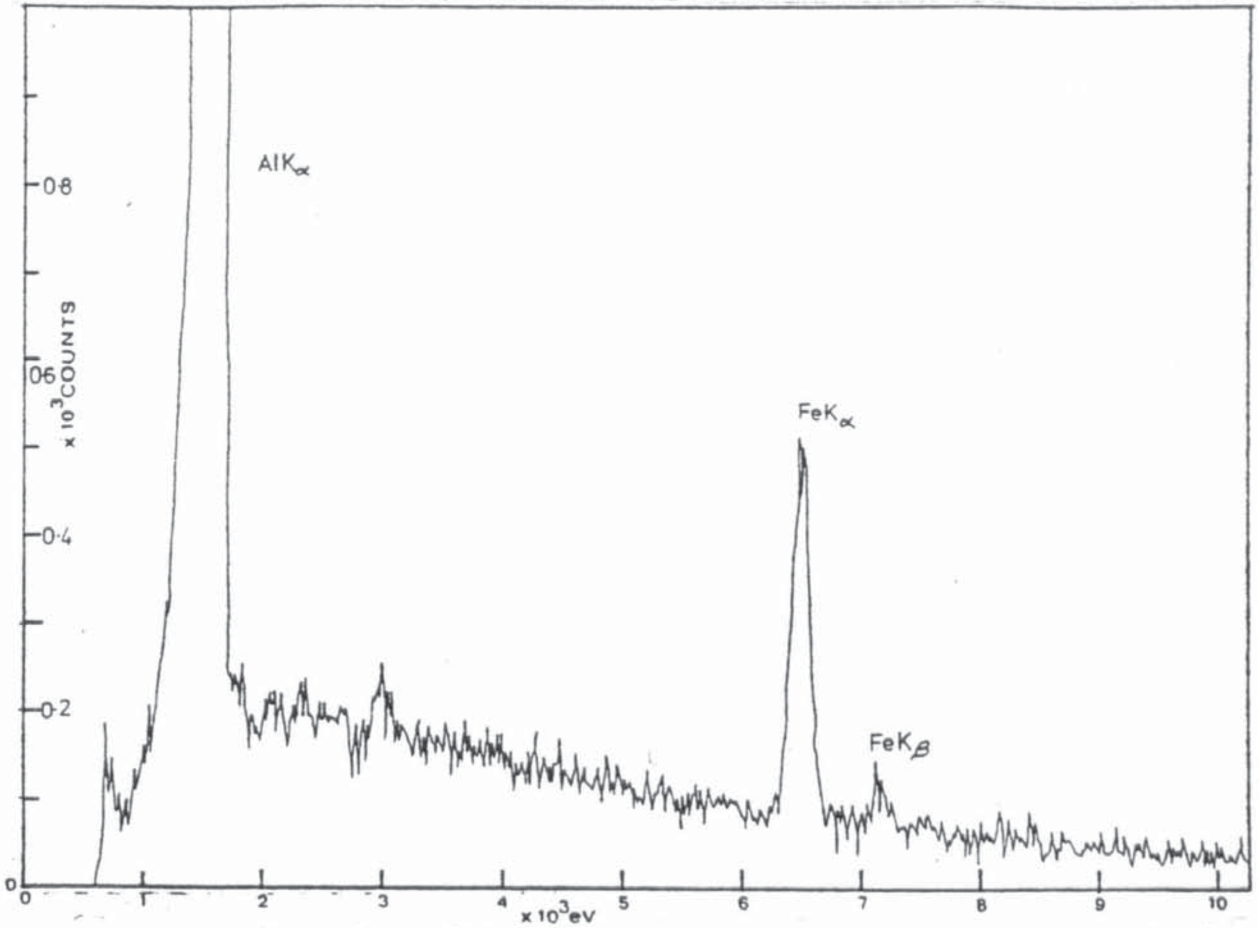


Fig.3.77. 'Kevex' x-ray analysis of the particle in Fig.3.76. above.

### 3.3.2.5 Solution F (20% Nitric acid). 99.99% Aluminium

The specular reflectivity in this solution showed a brief increase after approximately 30 secs. polishing, but the reflectivity was consistently low apart from this short period. The surface after 10 secs. polishing (fig.3.78) showed considerably less deposited copper than was found on the 99.99% aluminium in the solutions containing no nitric acid and 6% nitric acid. In addition the copper that was deposited was relatively small in size (approx. 0.2μm). The degree of etching was similar to that found in previous solutions. After 20 secs. polishing the surface still showed very little deposited copper (fig.3.79). The etched surface had been levelled to a greater extent than had been found in previous solutions at this time. A higher magnification of this surface (fig.3.80) showed small etch pits developing. After 40 secs. polishing the surface could be divided into distinct regions of grains of different orientation, (fig 3.81). The grain on the right-hand side of this micrograph at a higher magnification (fig.3.82) showed the presence of few randomly sited copper deposits, and some pitting of the surface. The grain on the left-hand side of fig.3.81 at higher magnification (fig.3.83) showed an undulating surface with a large number of pits, which at a still higher magnification (fig.3.84) could be seen to contain very small copper deposits (fig.3.85). With 120 secs. polishing the division of the surface into grains of different orientation had become more extensive, and at least three different regions could be distinguished, as indicated in (fig.3.86). The surface of region I. (fig. 3.87) showed a ribbed structure, with copper deposits on the top of the ribs. Region 3 showed that the pits found in fig. 3.83 had grown laterally and merged to cover a large percentage of the surface (fig.3.89), and that the amount of copper deposited had increased. Region 2, however, (fig 3.88) showed a relatively smooth surface with few randomly sited copper deposits.

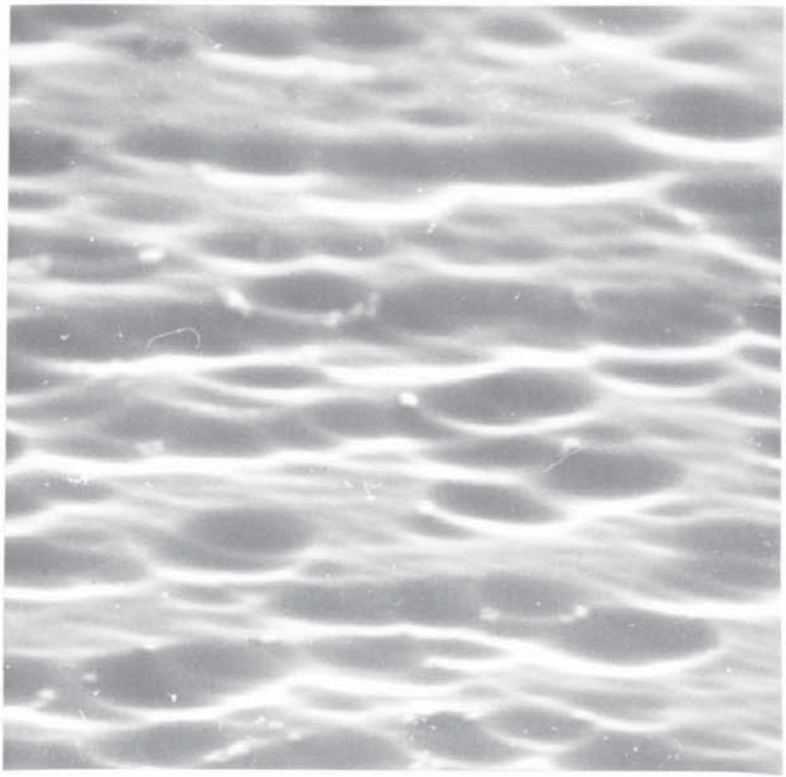


Fig.3.78. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution F (20% Nitric acid & Ig/l Cu) for IO seconds. X IO,000.

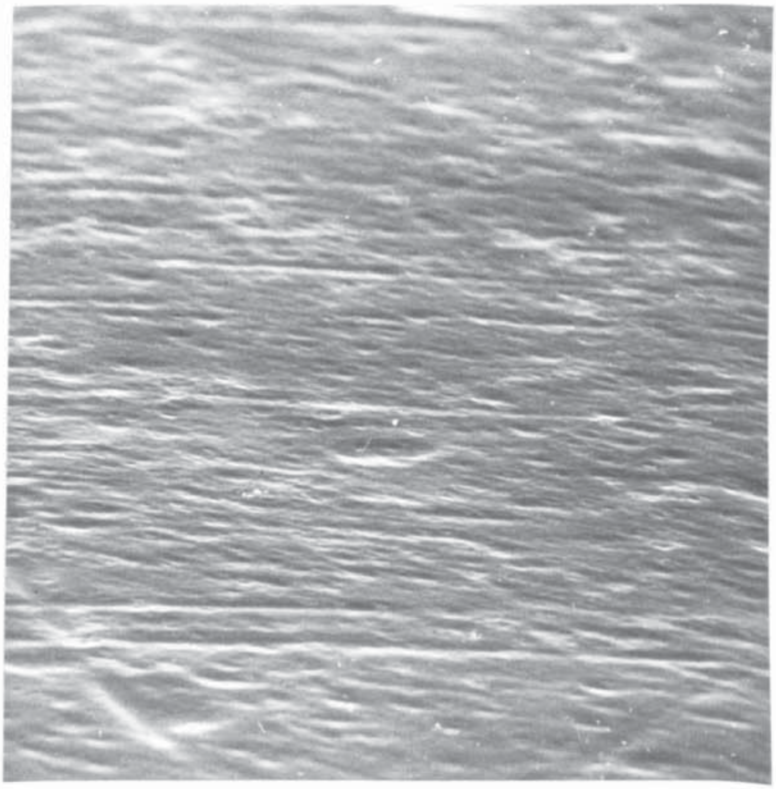


Fig.3.79. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution F (20% Nitric acid & Ig/l Cu) for 20 seconds. X 2000.

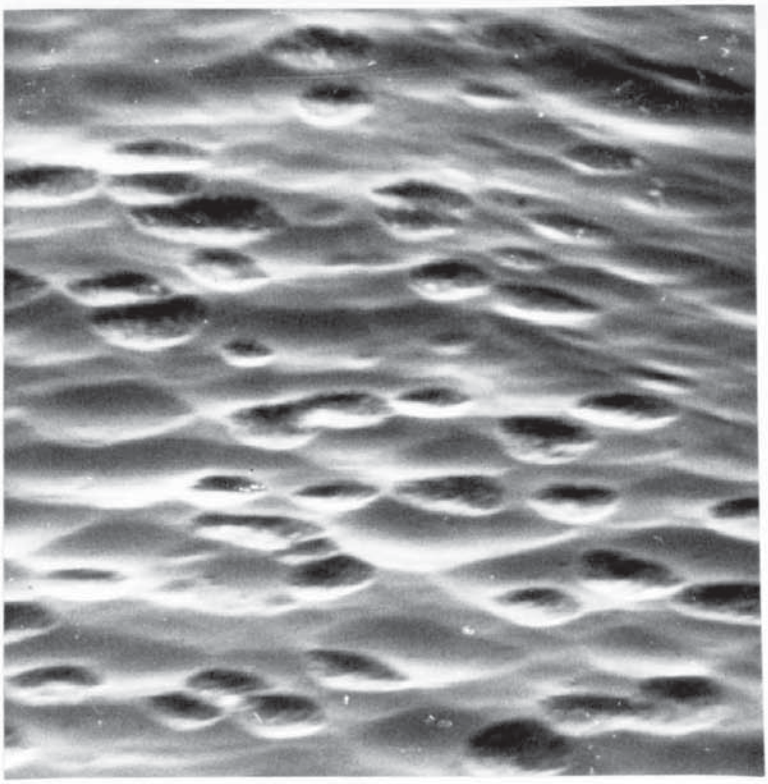


Fig.3.80. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution F (20% Nitric acid & Ig/l Cu) for 20 seconds. X I0,000.

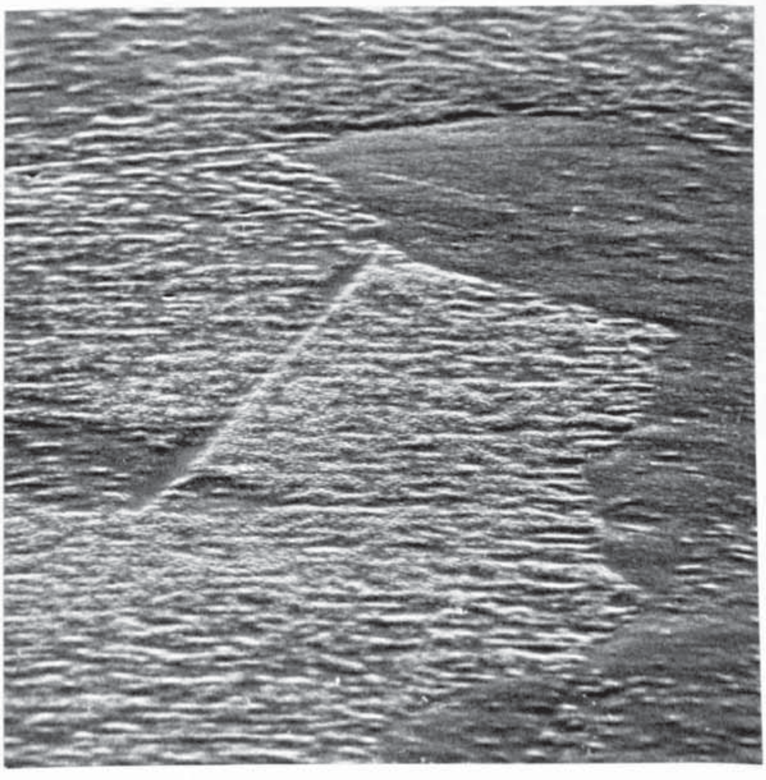


Fig.3.8I. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution F (20% Nitric acid & Ig/l Cu) for 40 seconds. X 500.

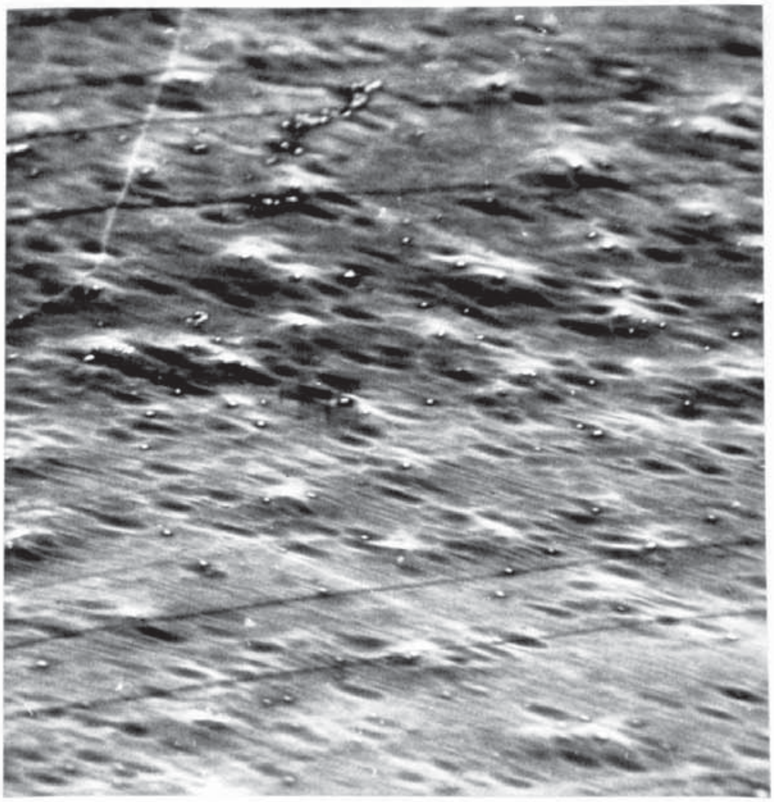


Fig.3.82 Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution F (20% Nitric acid & Ig/l Cu) for 40 seconds. X 2000.

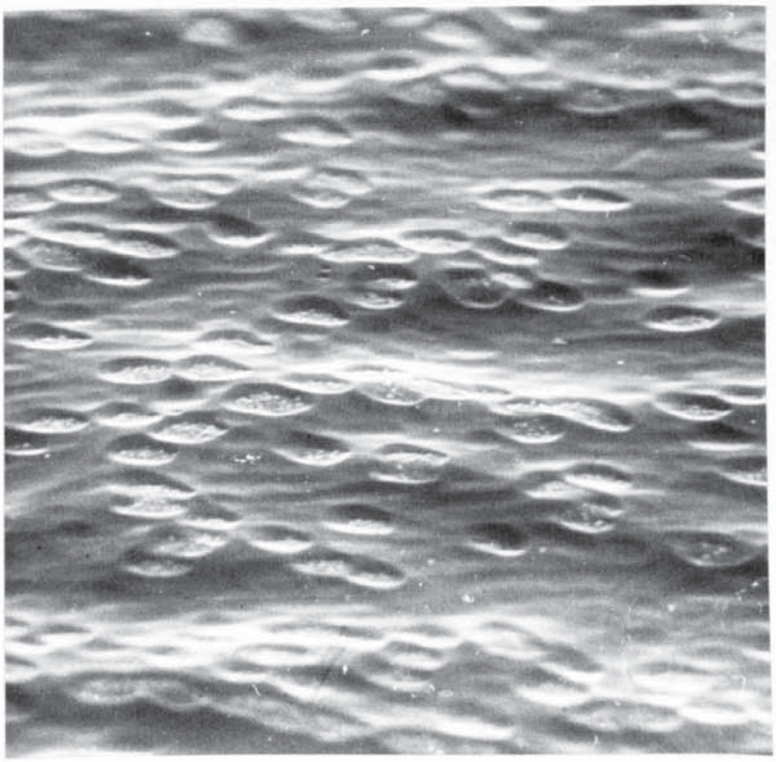


Fig.3.83. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution F (20% Nitric acid & Ig/l Cu) for 40 seconds. X 5000.

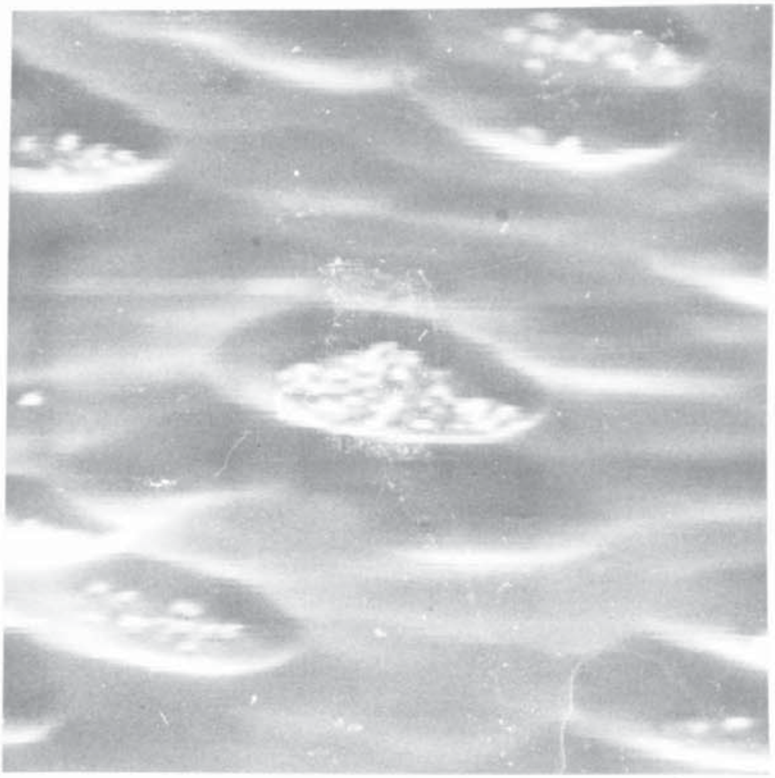


Fig.3.84. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution F (20% Nitric acid & Ig/l Cu) for 40 seconds. X 20,000.

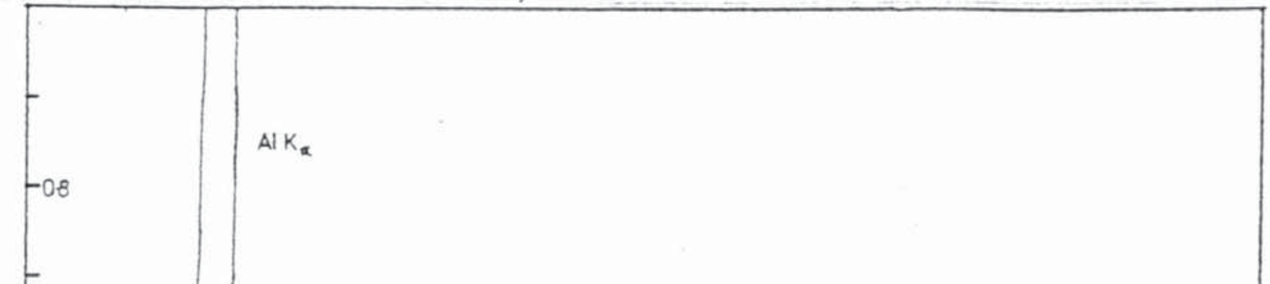


Fig.3.85. 'Kevex' x-ray analysis of the pit in the centre of Fig.3.84.

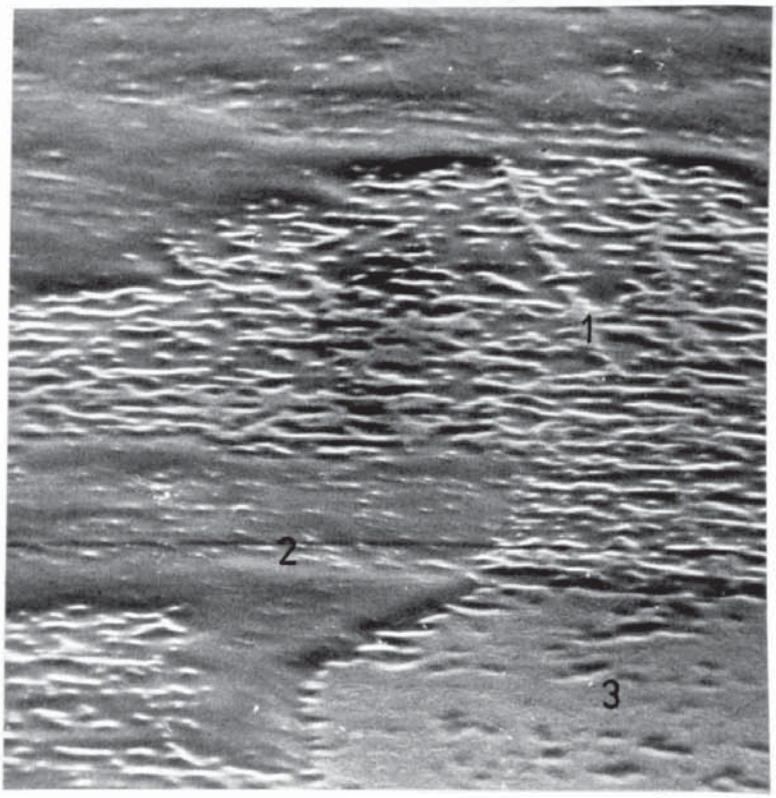


Fig.3.86. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution F (20% Nitric acid & Ig/l Cu) for I20 seconds. X 500.

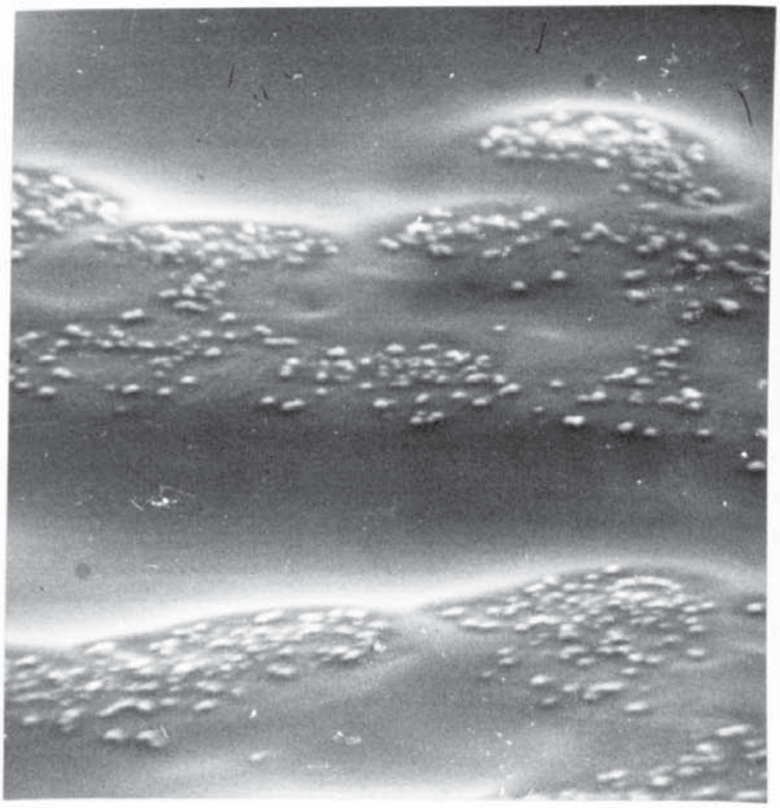


Figure 3.87 Scanning Electron Micrograph of region 1 of Figure 3.86. X 10,000

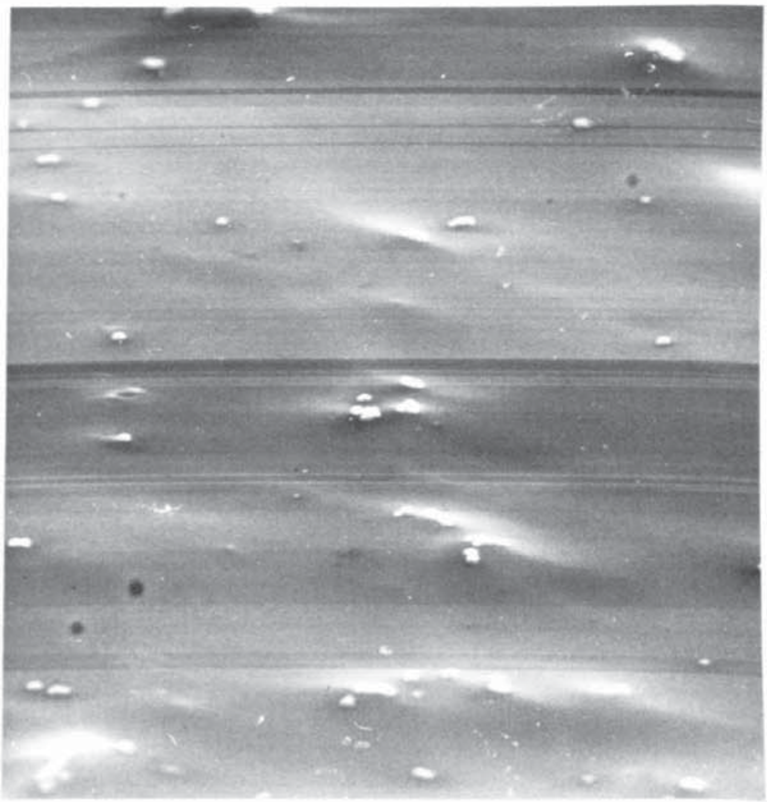


Figure 3.88 Scanning Electron Micrograph of region 2 of Figure 3.86. X 5,000

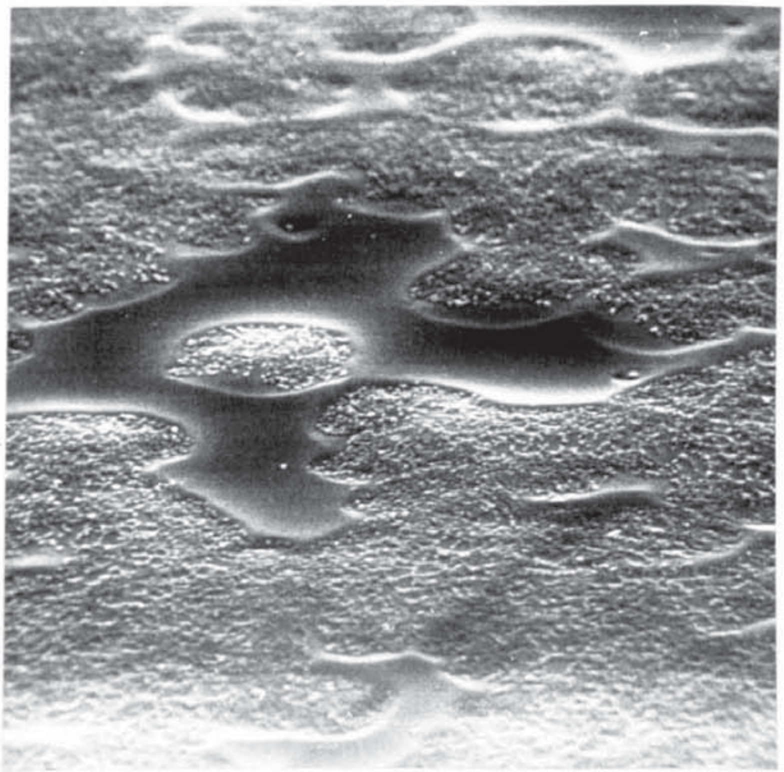


Figure 3.89 Scanning Electron Micrograph of region 3 of Figure 3.86. X 5,000

### 3.3.2.6 Solution F (20% Nitric acid), 99.5% Aluminium

As had been found with previous solutions containing nitric acid, the etched network found in the first few seconds of polishing, on the 99.5% aluminium was less extensive than on the 99.99% aluminium. The surface after 10 secs. polishing (fig.3.90) also showed this reduction in etching. Little deposited copper is present, and pitting due to the presence of iron rich inclusions is extensive. A higher magnification of this surface (fig. 3.91) showed that the iron rich inclusions were causing pitting due to the absence of deposited copper (fig. 3.92) and that the inclusion itself had been attacked by the solution. The titanium rich inclusions did not show the same tendency to cause pitting (fig. 3.93 & 3.94), even in the absence of deposited copper. Further polishing for 120 secs. (fig. 3.95), showed a surface morphology very similar to that of the 99.9% aluminium. Two regions were distinguishable as indicated in fig.3.95 as opposed to the three regions found on the 99.99% aluminium in the same solution. Region I. showed a similarly smooth surface to the 99.99% aluminium, with few randomly sited copper deposits (fig. 3.96). Region 2 showed a resemblence to region 3 of the 99.99% aluminium, after 120 secs. polishing. However, the extent of the pitting can be seen to be less (fig.3.97), and the pits did not show the same amount of deposited copper as had been the case of the 99.99% aluminium. A lower magnification of region 1. fig.3.98 showed that pitting from iron rich inclusions was again present although the inclusions themselves had been dissolved out of the pits. In addition titanium rich inclusions were visible with no associated pitting.

### 3.4 Potential Time Determinations

The changes in potential of the 99.99% aluminium electrodes (with respect to a saturated calomel electrode) with time, in solutions 1-9 listed in Table 3.1., are displayed in fig.3.99. There was a rapid

Fig.3.90. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution F (20% Nitric acid & Ig/l Cu) for IO seconds. X 600.

Fig.3.9I. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution F (20% Nitric acid & Ig/l Cu) for IO seconds. X II,000.

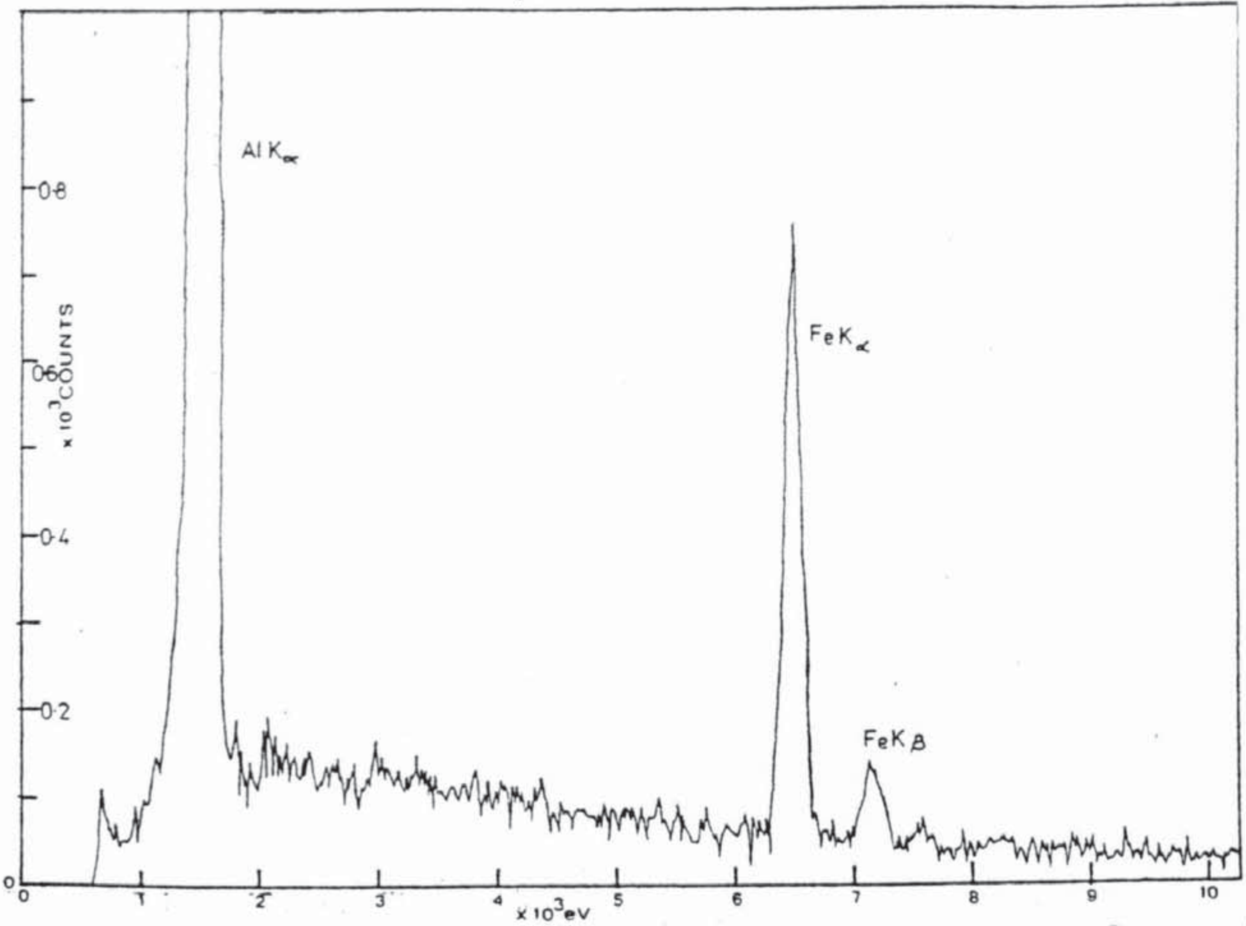


Fig.3.92. 'Kevex' x-ray analysis of the particle in Fig.3.9I. above.

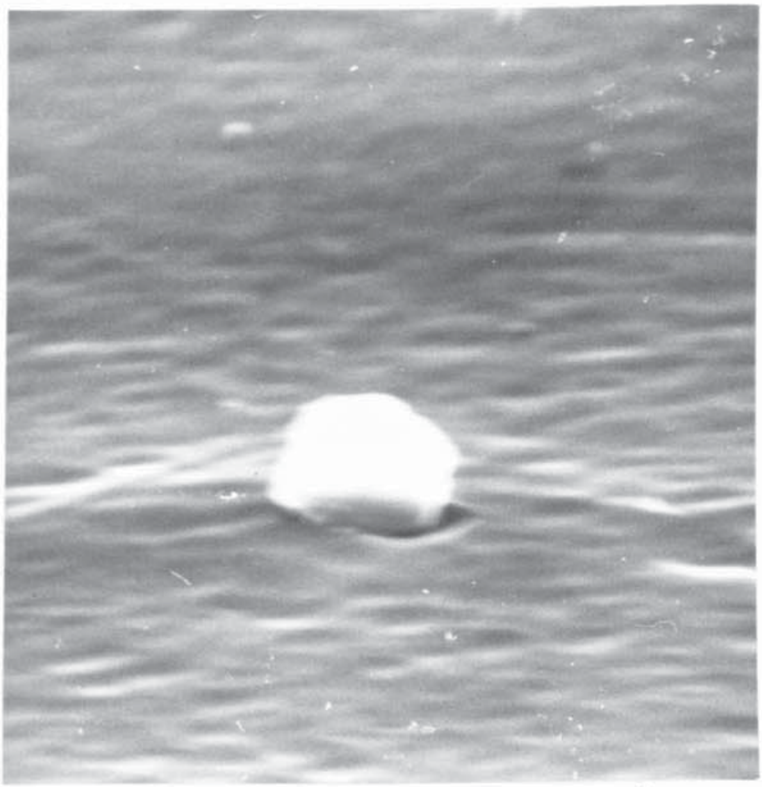


Fig.3.93. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution F (20% Nitric acid & Ig/l Cu) for IO seconds. X II,000.

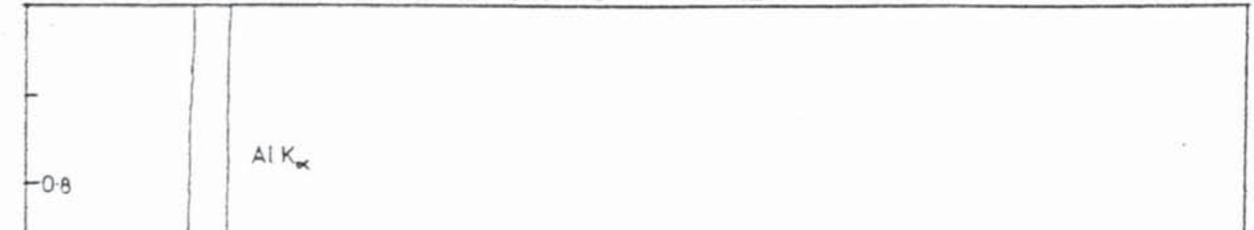


Fig.3.94. 'Kevex' x-ray analysis of the particle in Fig.3.93. above.

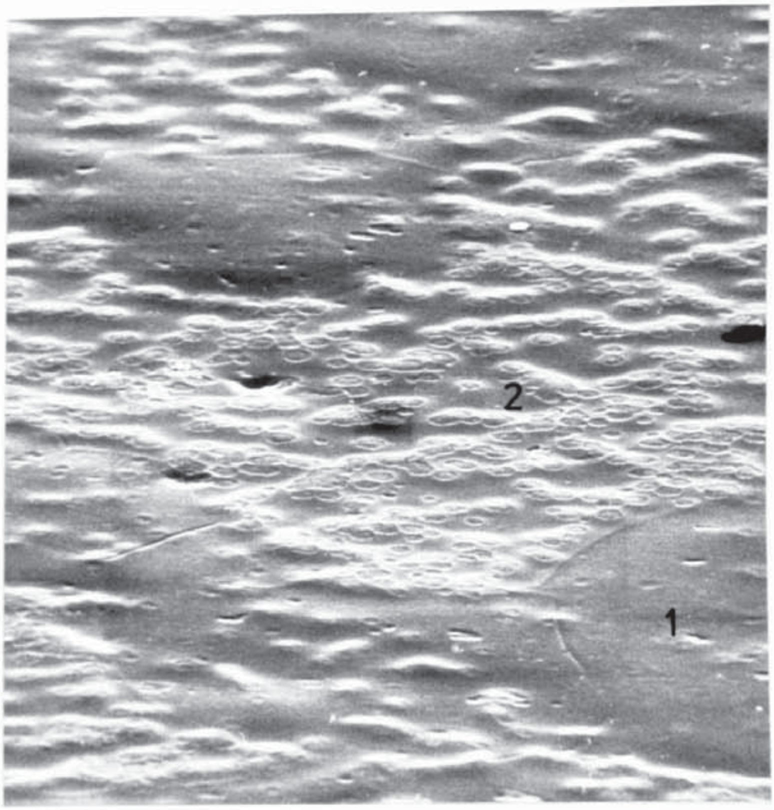


Fig.3.95. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution F (20% Nitric acid & Ig/l Cu) for I20 seconds. X I000.

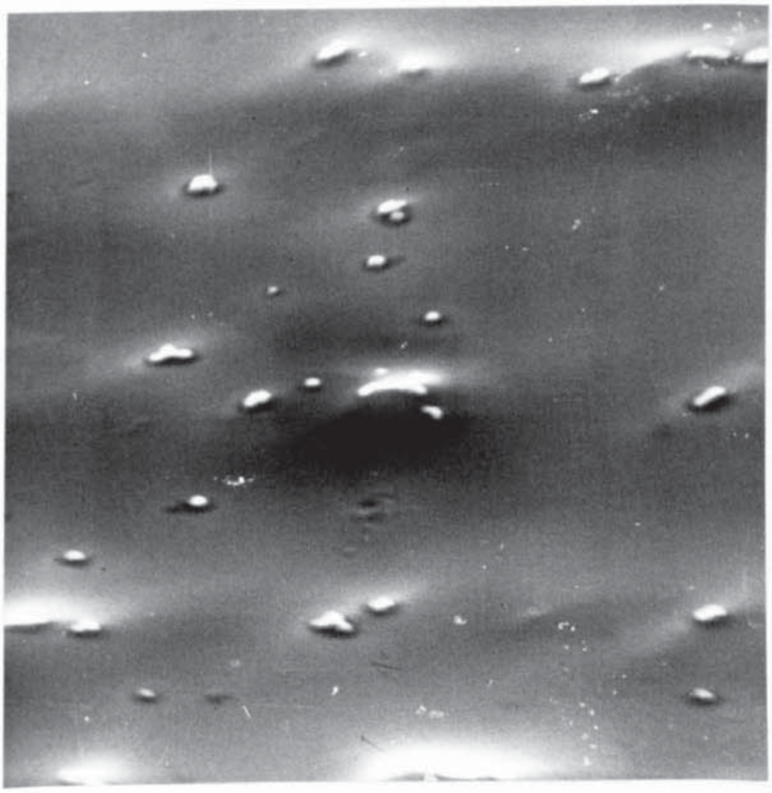


Figure 3.96 Scanning Electron Micrograph of region 1 of Figure 3.95. X 5,500

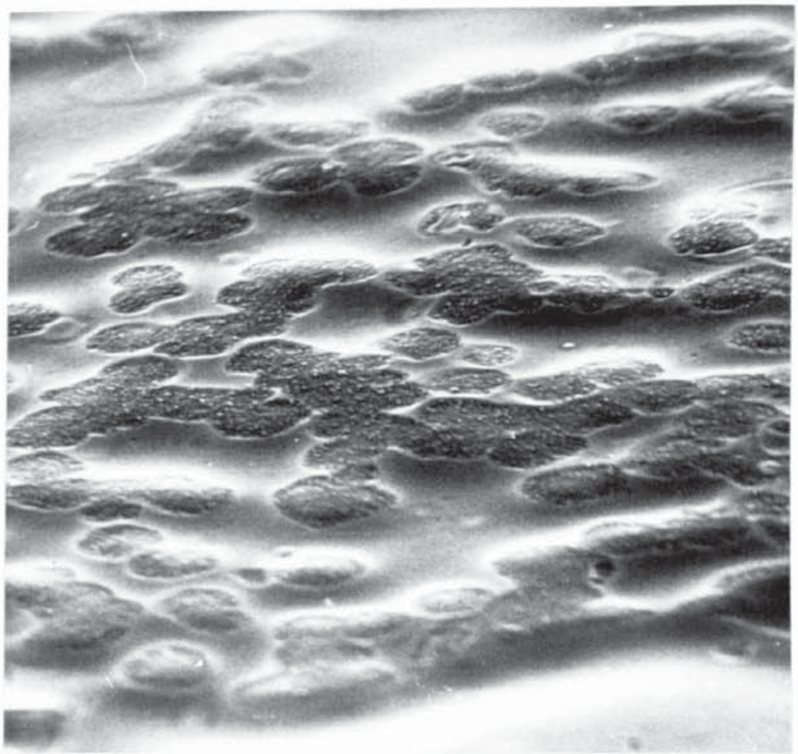


Figure 3.97 Scanning Electron Micrograph of region 2 of Figure 3.95. X 2,400

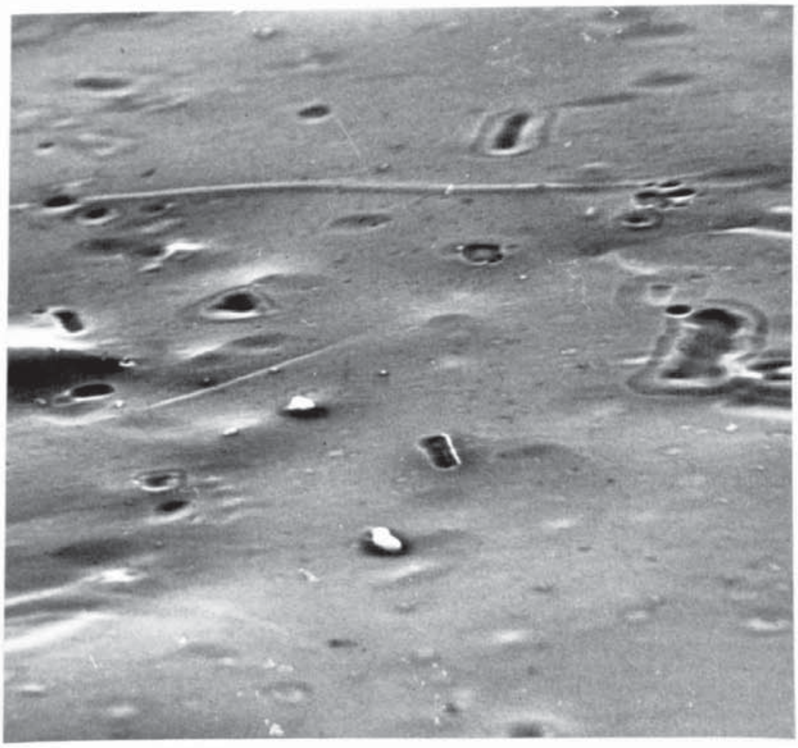


Figure 3.98 Scanning Electron Micrograph of region 1 of Figure 3.95 showing the influence of the iron rich intermetallics. X 2,400

initial surge in negativity, followed by a gradual reduction in this negativity, until a steady state potential was reached. As the nitric acid content was increased the potentials recorded, both the intial surge and the steady state, became more noble. Details of the relevant potentials are given in Table 3.1 below:

TABLE 3.1

| Solution | Phosphoric acid | Sulphuric acid | Nitric acid | Potentials(volts) | |
|---|---|---|---|---|---|
| | (S.G.1.75) | (S.G.1.84) | (S.G.1.5) | (w.r.t. S.C.E.) | |
| | | | | Surge | Steady State |
| 1 | 82.5% | 17.5% | 0 | -1.05v | -0.85v |
| 2 | 80.8% | 17.2% | 2% | -1.05v | -0.75v |
| 3 | 79.2% | 16.8% | 4% | -1.05v | -0.70v |
| 4 | 77.5% | 16.5% | 6% | -1.025v | -0.64v |
| 5 | 75.8% | 16.2% | 8% | -0.90v | -0.61v |
| 6 | 74.2% | 15.8% | 10% | -0.88v | -0.60v |
| 7 | 72.5% | 15.5% | 12% | -0.725v | -0.55v |
| 8 | 70.1% | 14.9% | 15% | -0.50v | -0.38v |
| 9 | 65.9% | 14.1% | 20% | -0.475v | -0.31v |

Percentages quoted in Tables 3.1, 3.2, 3.3, & 3.4 are in volume percent.

The solutions listed above did not contain any dissolved copper. The potentials recorded for the 99.5% aluminium were found to be significantly less noble than the 99.99% aluminium (significant at the 0.2% level), and are listed in table 3.2 below. The change in potential with time of the 99.5% Aluminium (with respect to a saturated calomel electrode) for the solutions listed in Table 3.2, are displayed in Fig.3.100.

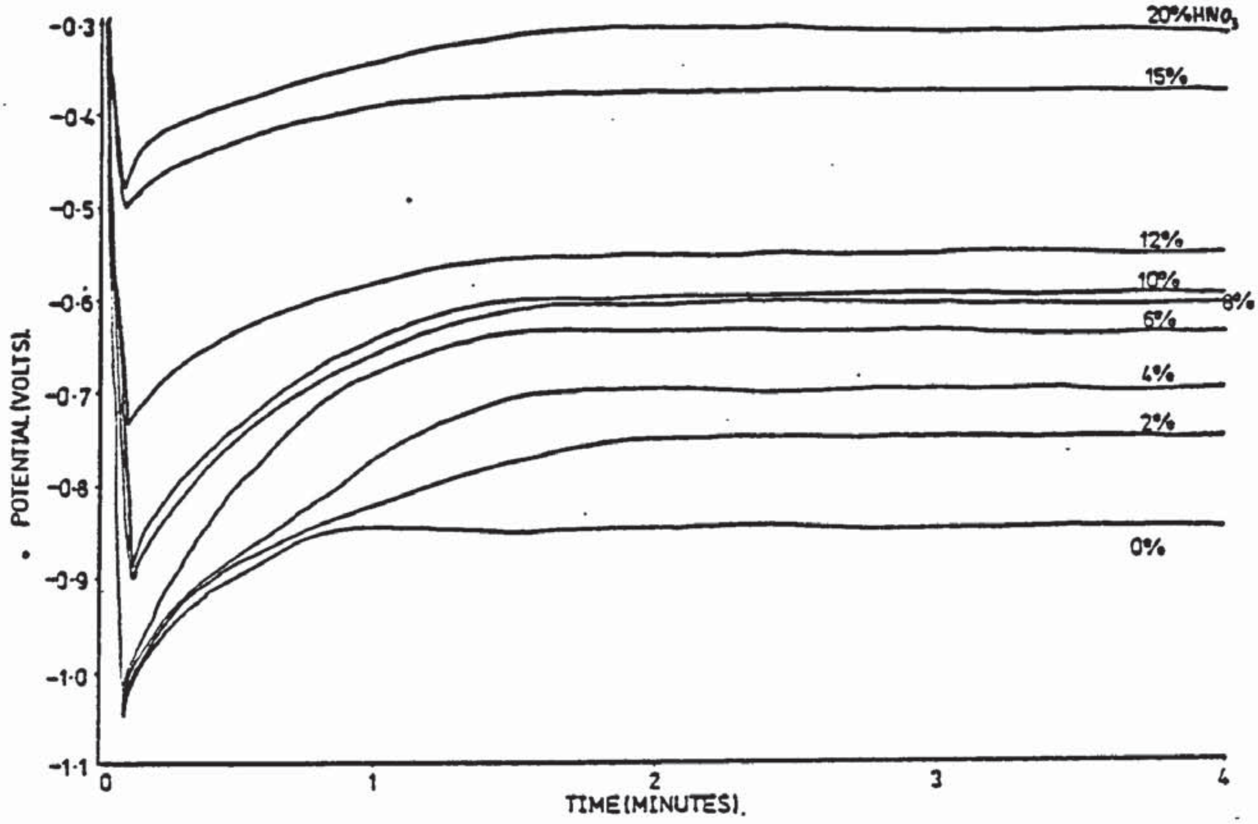


Fig.3.99. Potential vs. Time, of 99.99% Al. in solutions I-9, (Table 3.I.).

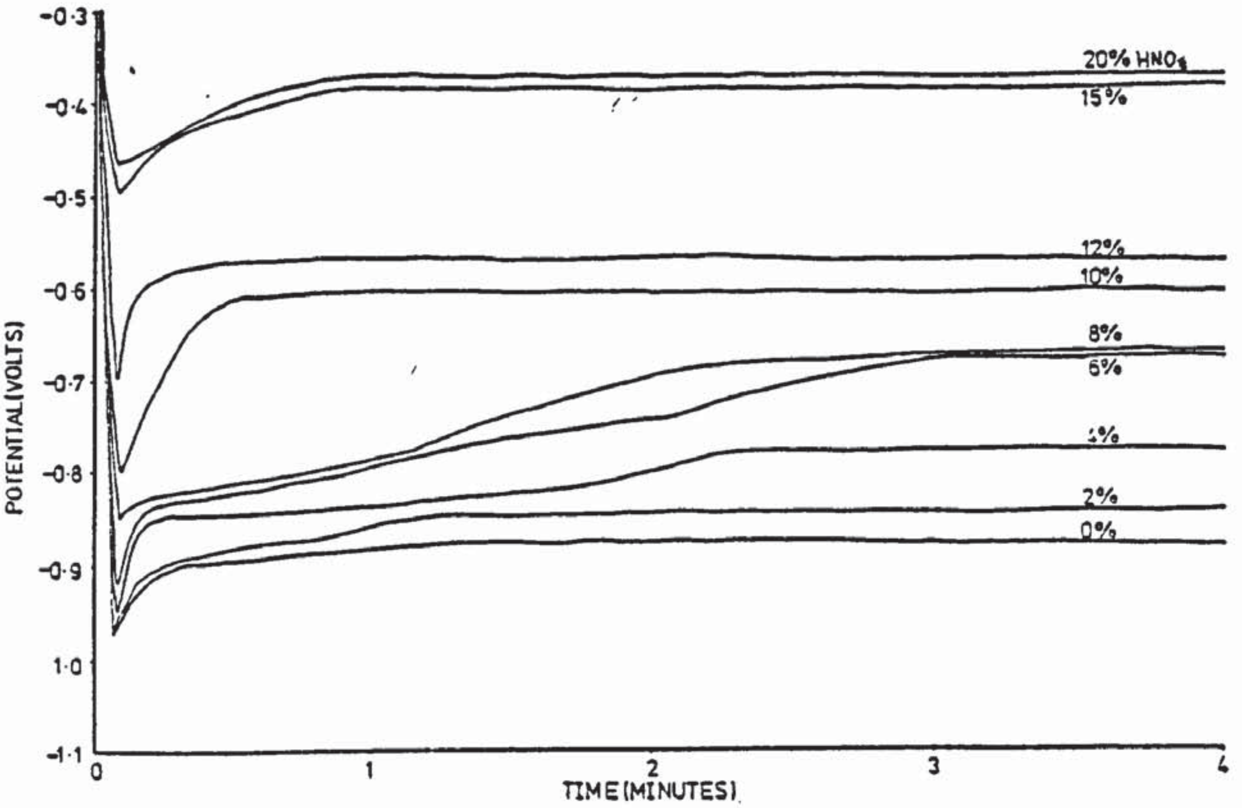


Fig.3.IOO. Potential vs. Time,of 99.5% Al. in solutions I-9, (Table 3.2.).

## TABLE 3.2

| Solution | Phosphoric acid (S.G.1.75) | Sulphuric acid (S.G.1.84) | Nitric acid (S.G.1.5) | Potentials(volts) (w.r.t. S.C.E.) | |
|---|---|---|---|---|---|
| | | | | Surge | Steady State |
| 1 | 82.5% | 17.5% | 0 | -0.975v | -0.88v |
| 2 | 80.8% | 17.2% | 2% | -0.975v | -0.85v |
| 3 | 79.2% | 16.8% | 4% | -0.95v | -0.78v |
| 4 | 77.5% | 16.5% | 6% | -0.925v | -0.68v |
| 5 | 75.8% | 16.2% | 8% | -0.85v | -0.675v |
| 6 | 74.2% | 15.8% | 10% | -0.80v | -0.61v |
| 7 | 72.5% | 15.5% | 12% | -0.70v | -0.575v |
| 8 | 70.1% | 14.9% | 15% | -0.50v | -0.39v |
| 9 | 65.9% | 14.1% | 20% | -0.46v | -0.375v |

None of the solutions listed in Table 3.2 contain any dissolved copper.

The steady state potentials of both 99.99% aluminium and 99.5% aluminium in solutions 1-9 are plotted against Nitric acid content in fig. 3.101, and show that the aluminium electrodes become more noble as the nitric acid content is increased.

The surge, and steady state potentials of the solutions containing Ig/l of dissolved copper for 99.99% aluminium and 99.5% aluminium are given in Tables 3.3 and 3.4 respectively. The aluminium electrodes showed the same type of initial surge in negativity followed by a reduction in the negativity until a steady state was reached. In addition to this, at 2% and 4% nitric acid the aluminium electrodes showed a potential cycle effect. The surge potentials and steady state potentials of the aluminium electrodes in these two soltuions due to their fluctuating values, are not included in the Tables.

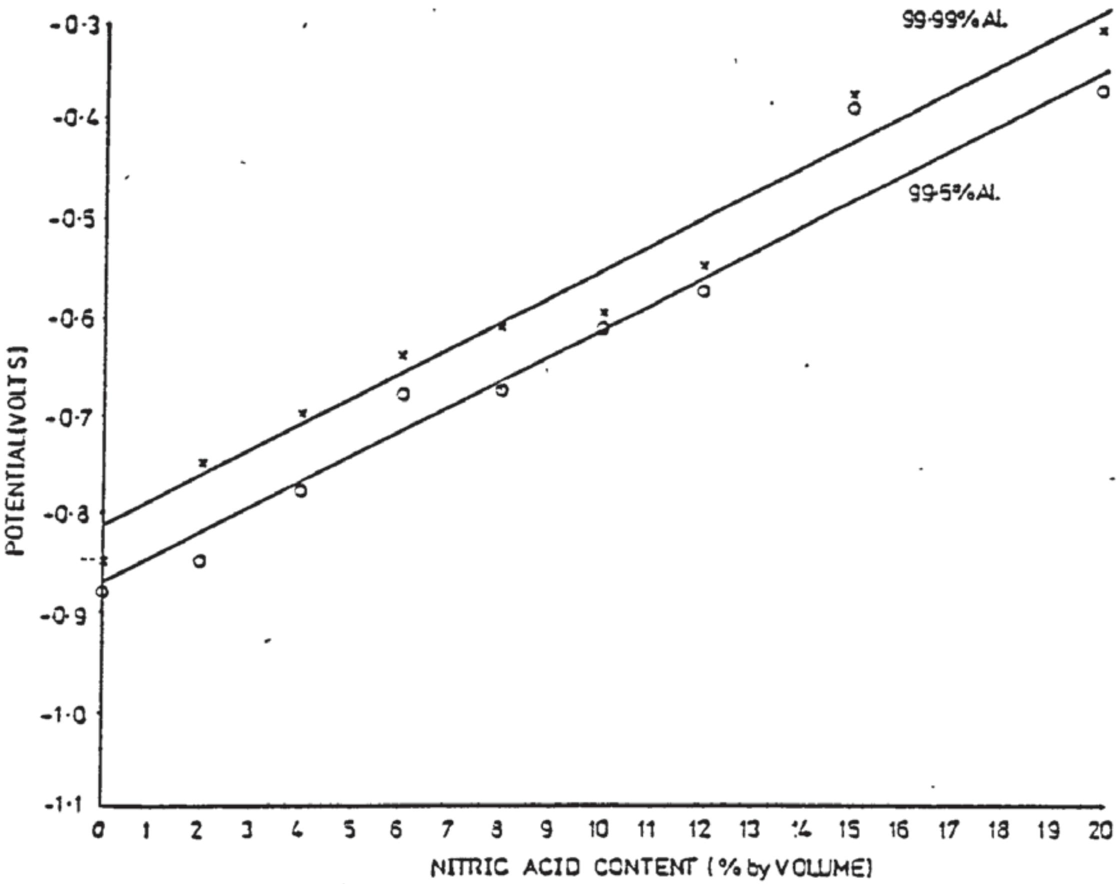


Fig.3.IOI. Steady State Potentials vs. Nitric acid content, of 99.99% and 99.5% Al. in solutions I-9, (containing no dissolved copper).

## TABLE 3.3

| Solution | Phosphoric acid | Sulphuric acid | Nitric acid | Potentials (volts) | |
|---|---|---|---|---|---|
| | (S.G.1.75) | (S.G.1.84) | (S.G.1.5) | (w.r.t. S.C.E.) | |
| | | | | Surge | Steady state |
| 10 | 82.5% | 17.5% | 0 | -0.90v | -0.65v |
| 11 | 80.8% | 17.2% | 2% | - | - |
| 12 | 79.2% | 16.8% | 4% | - | - |
| 13 | 77.5% | 16.5% | 6% | -0.775v | -0.51v |
| 14 | 75.8% | 162% | 8% | -0.75v | -0.45v |
| 15 | 74.2% | 15.8% | 10% | -0.70v | -0.44v |
| 16 | 72.5% | 15.5% | 12% | -0.62v | -0.42v |
| 17 | 70.1% | 14.9% | 15% | -0.60v | -0.37v |
| 18 | 65.9% | 14.1% | 20% | -0.59v | -0.34v |

All the solutions listed above in Table 3.3 contain 1g/1 of dissolved copper, as do the solutions listed in Table 3.4.

## TABLE 3.4

| Solution | Phosphoric acid | Sulphuric acid | Nitric acid | Potentials(volts) | |
|---|---|---|---|---|---|
| | | | | (w.r.t. S.C.E.) | |
| | | | | Surge | Steady state |
| 10 | 82.5% | 17.5% | 0 | -0.82v | -0.75v |
| 11 | 80.8% | 17.2% | 2% | - | - |
| 12 | 79.2% | 16.8% | 4% | - | - |
| 13 | 77.5% | 16.5% | 6% | -0.70v | -0.54v |
| 14 | 75.8% | 16.2% | 8% | -0.67v | -0.50v |
| 15 | 74.2% | 15.8% | 10% | -0.69v | -0.47v |
| 16 | 72.5% | 15.5% | 12% | -0.66v | -0.45v |
| 17 | 70.1% | 14.9% | 15% | -0.475v | -0.39v |
| 18 | 65.9% | 14.1% | 20% | -0.45v | -0.36v |

The changes of potential with time (with respect to a saturated calomel electrode) of both the 99.99% and 99.5% aluminium, in the solutions listed in Tables 3.3. and 3.4 are displayed in figs. 3.102 and 3.103 respectively.

The potential cycling occurred in solutions 11 and 12 (2% and 4% nitric acid). On 99.99% aluminium after the initial surge in negativity the potential gradually became more noble for approximately 60 seconds. At this time there was a short period of small amplitude fluctuations in the potential. The potential then suddenly became significantly more noble for a short period of time before returning to an approximately steady state condition (fig.3.104, 105). This cycle would then repeat itself.

The 99.5% aluminium showed the same type of cycle, although the precise values of the cycling are different (fig.3.106 and fig.3.107). The steady state potentials of both the 99.99% and 99.5% aluminium, are plotted against the nitric acid content in fig. 3.108.

An attempt was made to examine the surface of the aluminium at different stages of the potential cycle, by monitoring the potential and removing the aluminium at relevant points in the cycle. However, the adhesion of the deposited copper was not good, and the copper tended to lift off the surface of the aluminium due to the surface tension of the water in the rinse. However, the surfaces examined did show some important features, although the amounts of copper remaining on the surface in these micrographs may not be the same as on the surface whilst polishing in the solution.

The surface of the aluminium at a point close to that corresponding to the most noble potential (fig.3.109) showed a considerable coverage of copper. This was consistent with the observation that the noble

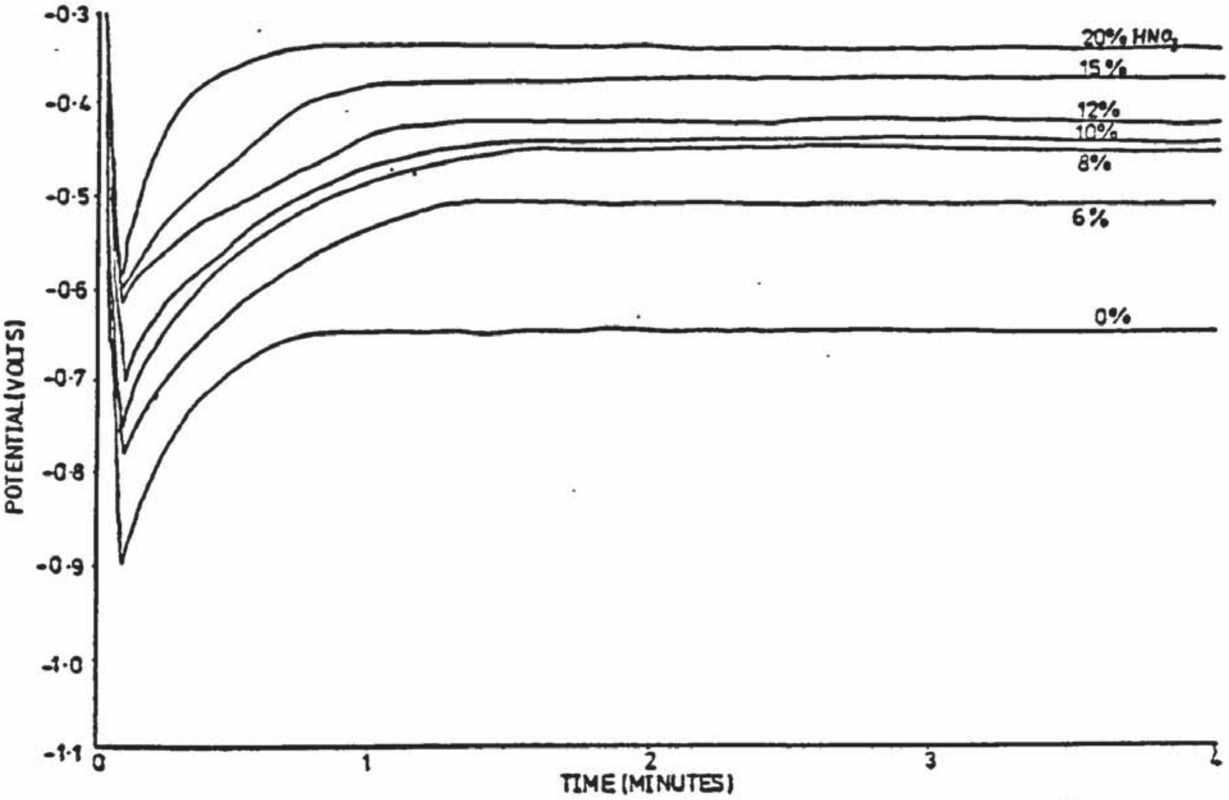


Fig.3.I02. Potential vs. Time of 99.99% Al. in solutions I0-I8, (Table 3.3.).

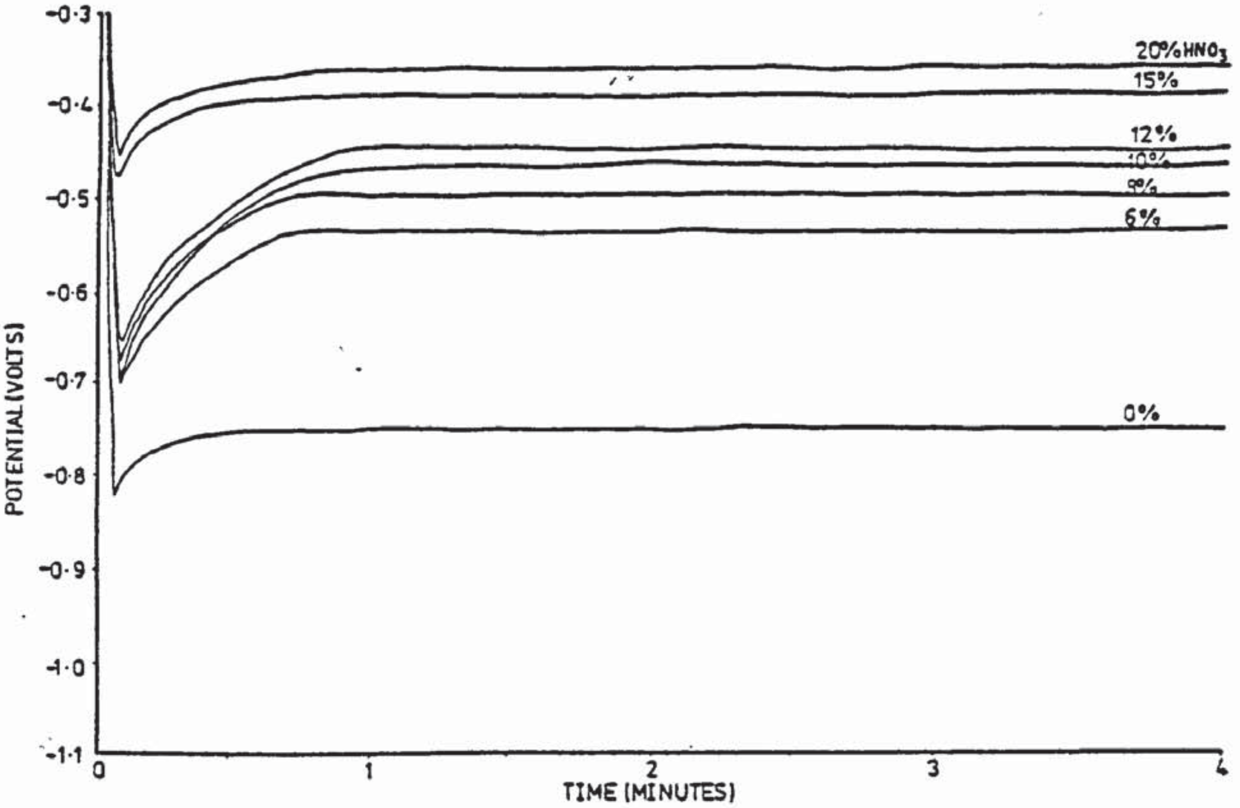


Fig.3.I03. Potential vs. Time of 99.5% Al. in solutions I0-I8, (Table 3.4.).

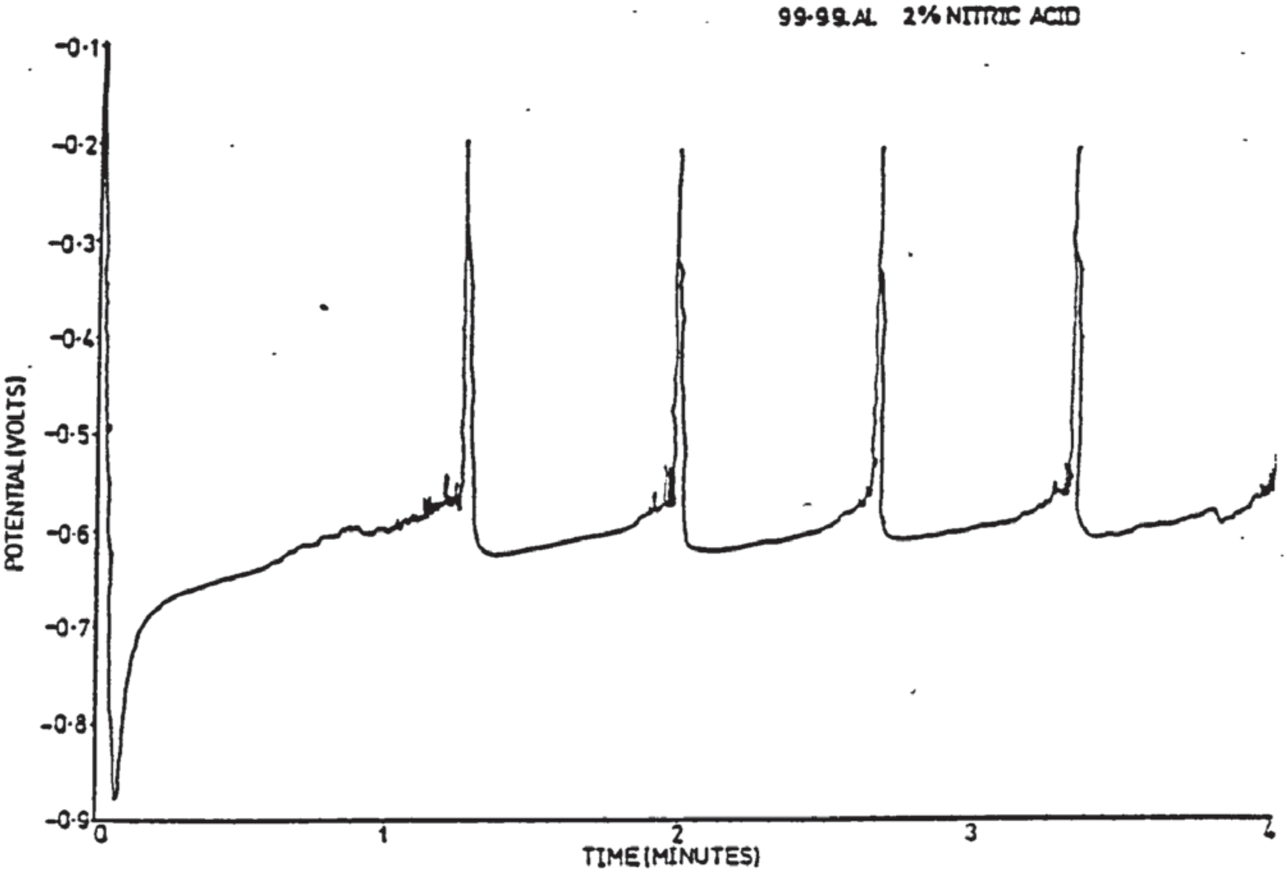


Fig.3.I04. Potential vs. Time of 99.99% Al. in solution I1, (Table 3.3.).

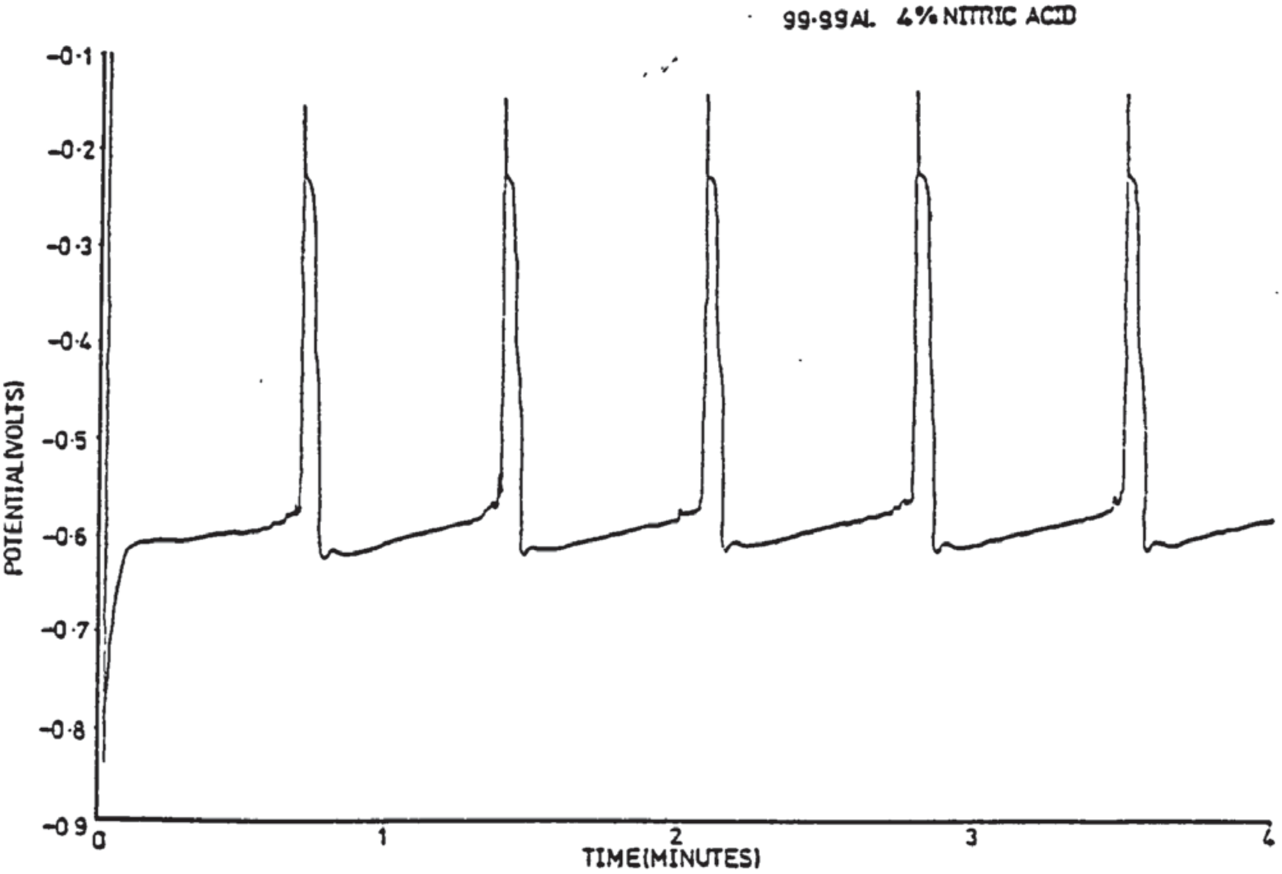


Fig.3.I05. Potential vs. Time of 99.99% Al. in solution I2, (Table 3.3.).

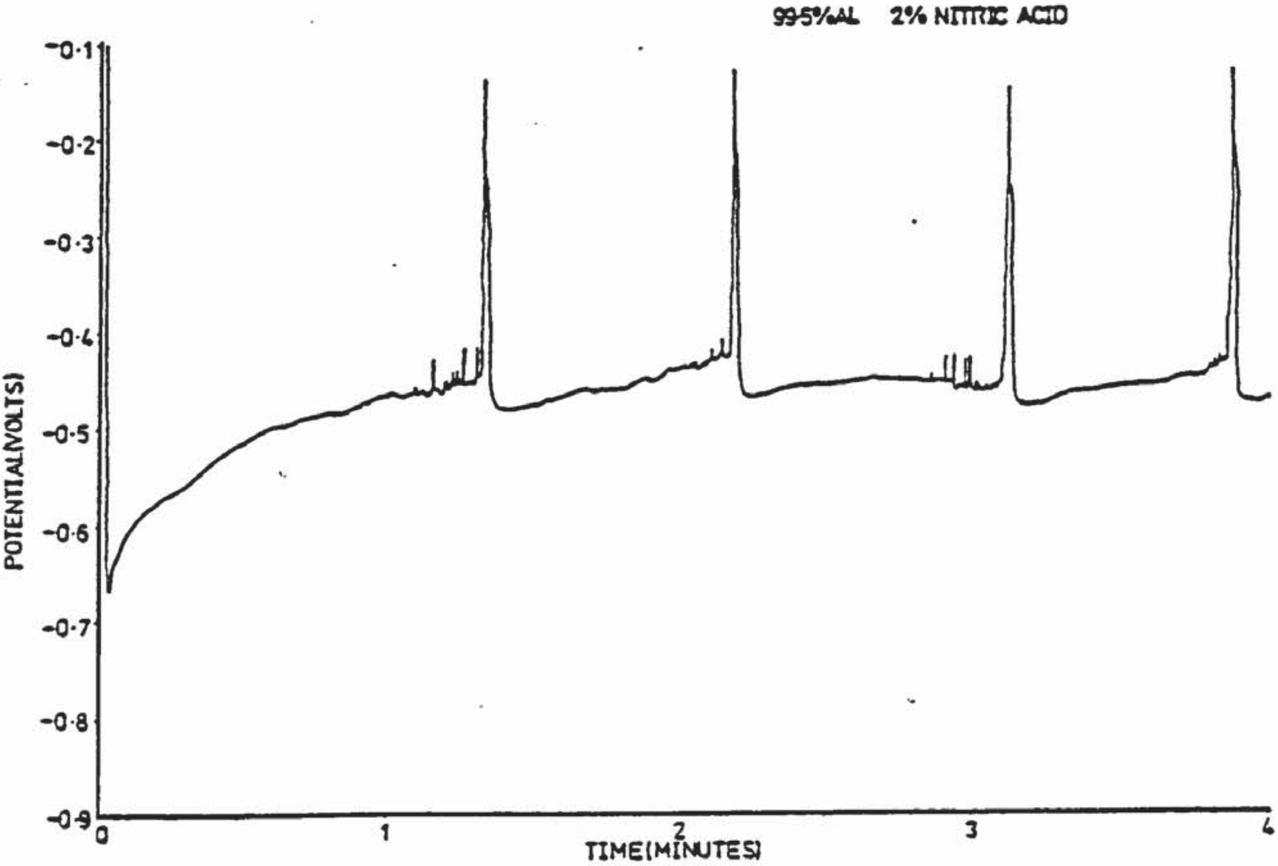


Fig.3.I06. Potential vs. Time of 99.5% Al. in solution II, (Table 3.4.).

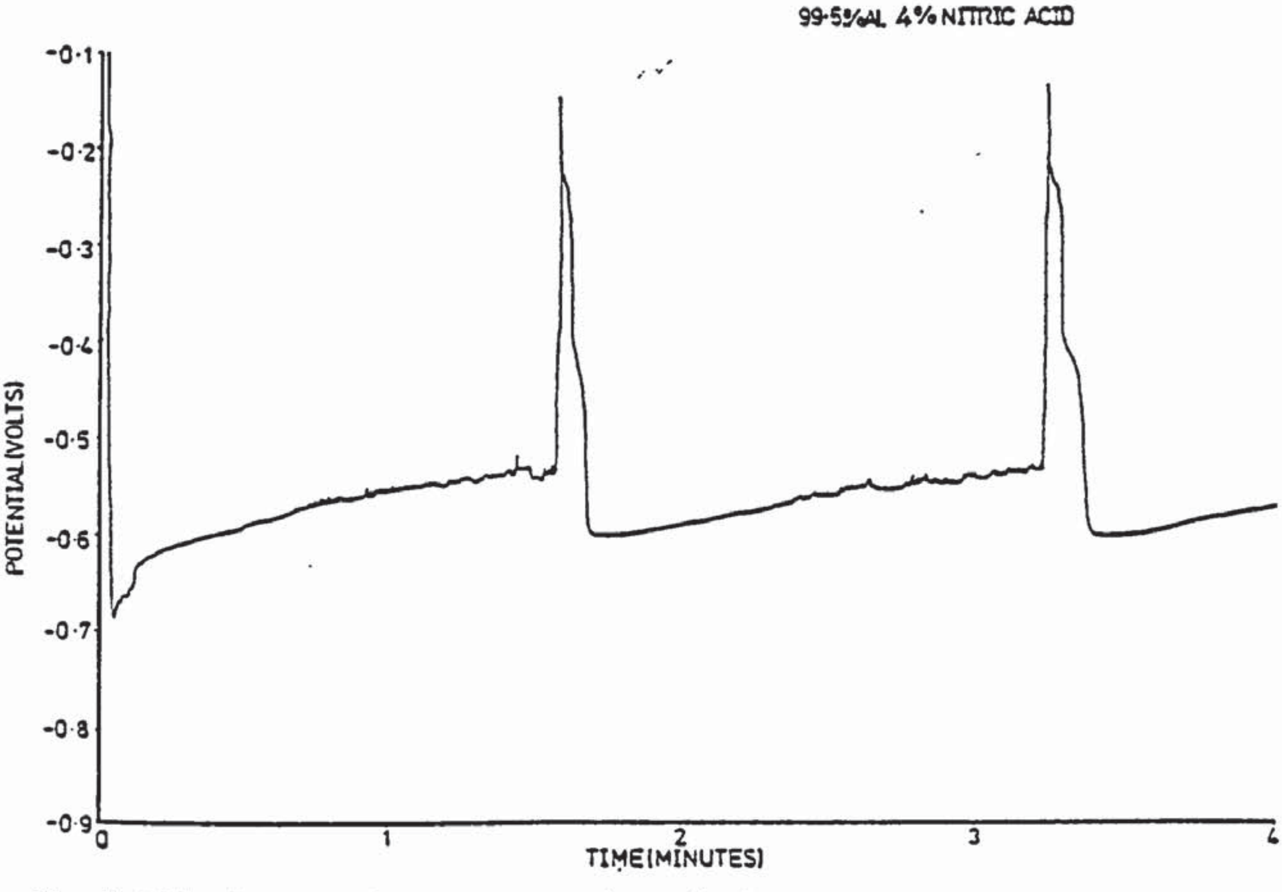


Fig.3.I07. Potential vs. Time of 99.5% Al. in solution I2, (Table 3.4.).

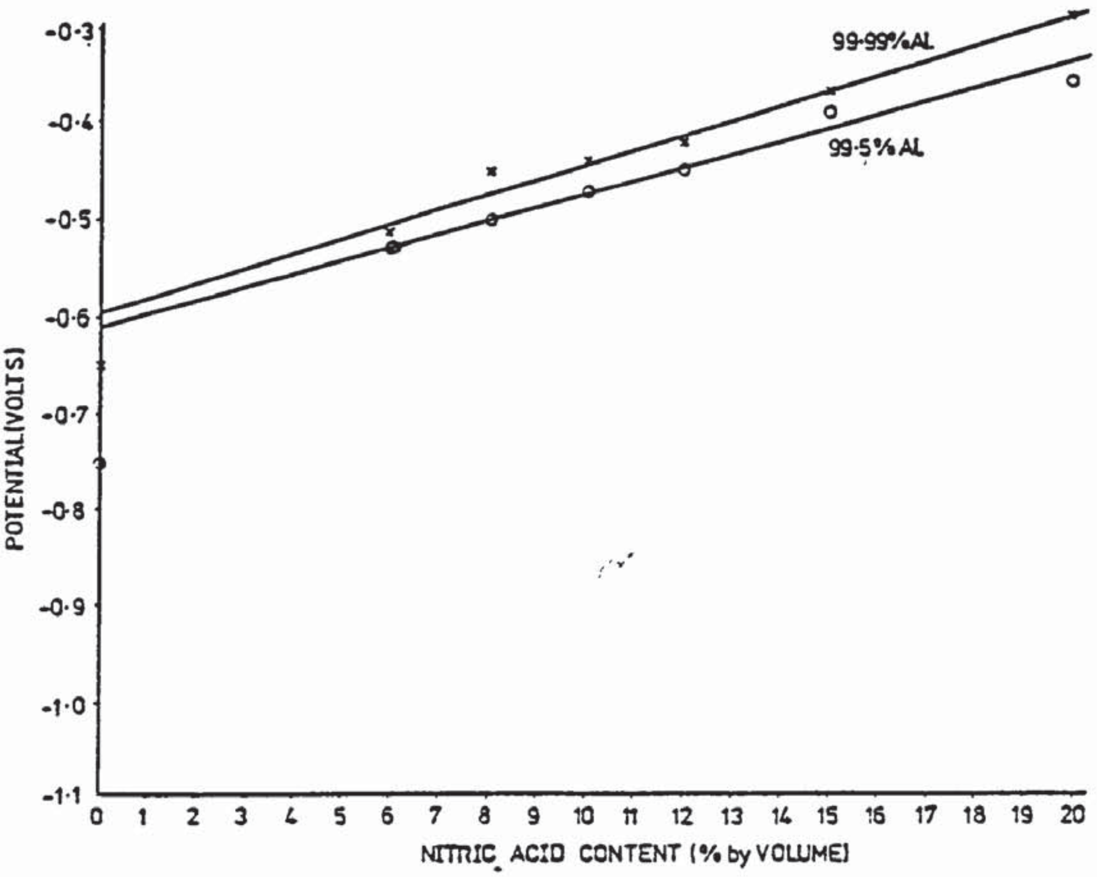


Fig.3.108. Steady State Potentials vs. Nitric acid content, of 99.99% and 99.5% Al. in solutions 10–18, (containing 1g/l of dissolved copper).

potential of the cycle (between-0.1v and-0,2v) corresponded closely to the potential of a pure copper electrode immersed in these solutions (approx-0.08v). 'Kevex' x-ray analysis of this surface (fig.3.110) indicated that a layer of copper of substantial thickness was present. A sample taken just prior to the sudden increase in nobility of the aluminium (fig.3.111) showed distinct alignment of the copper deposits, with some large isolated deposits. Some areas of the sample showed at higher magnification that these deposits were aligned along the ridges of the sub-micro patterns found on previous samples (fig.3110). Another region of the same sample (fig.3.113) showed the copper deposits in the form of isolated islands, with no sub-micro patterns visible.

## 3.5 Examination (by Electron Spectroscopy) of the surface film produced by chemical polishing

### 3.5.1. Introduction

The existence of a surface film during the chemical polishing of aluminium has been shown by a number of previous authors(27-32,60). However, the precise composition and thickness of this film has not been established. The work in this section was intended to obtain this information. The technique used was that of Electron Spectroscopy for Chemical Analysis, combined with Argon ion milling of the surface.

Electron spectroscopy for Chemical Analysis (ESCA)

When a surface is irradiated with either electrons or X-rays, electrons are emitted from the surface layers. The electrons emitted from the surface have energies that are characteristic of the atoms from which they have been emitted.

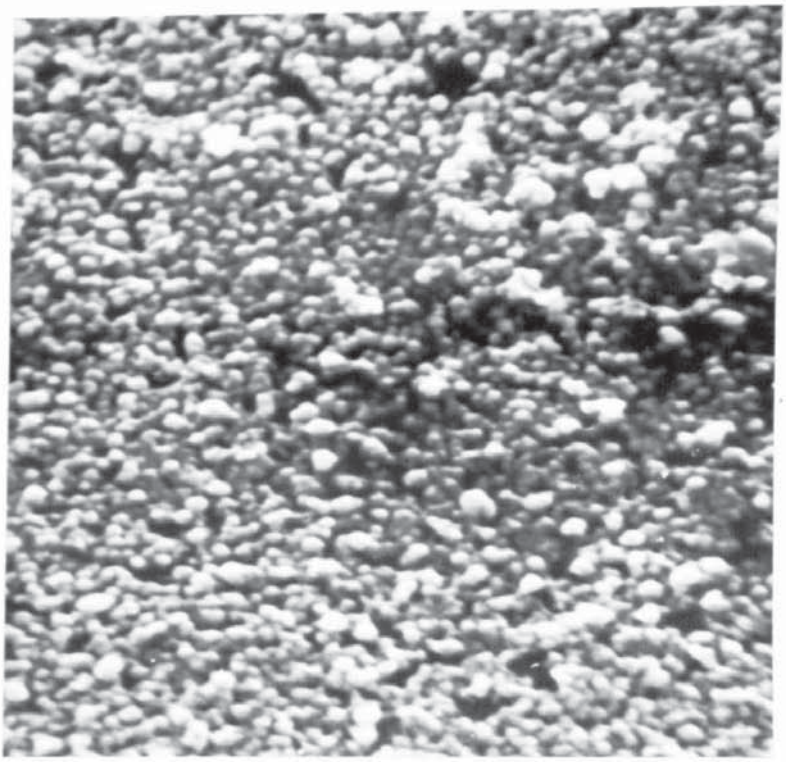


Fig.3.I09. Scanning Electron Micrograph of 99.99% Al. at the most noble potential of the potential cycle. X 5000.

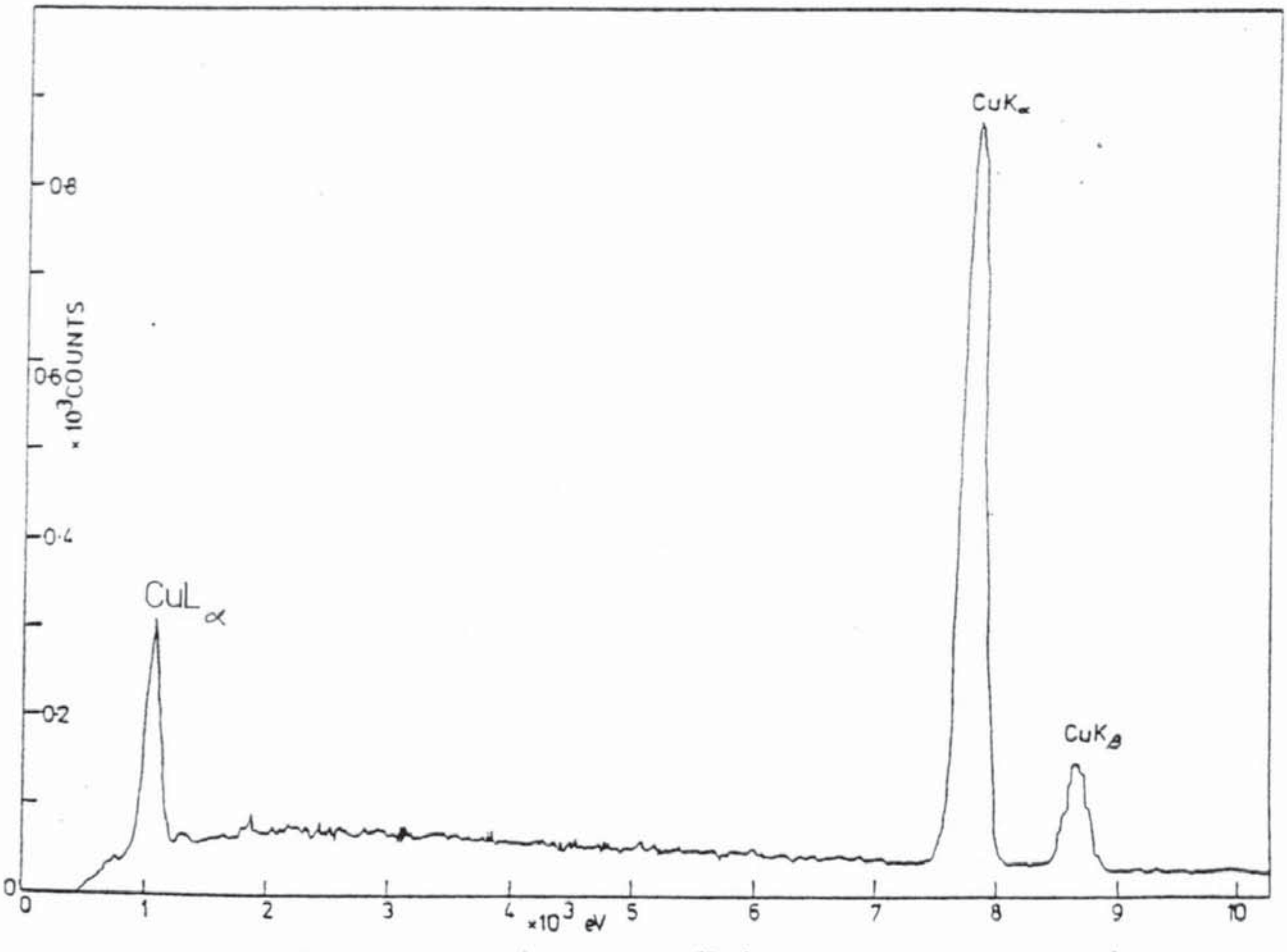


Fig.3.II0. 'Kevex' x-ray analysis of the surface of the Aluminium electrode in Fig.3.I09. above.

Fig.3.III. Scanning Electron Micrograph of 99.99% Al. electrode in the region of potential fluctuations. X 2000.

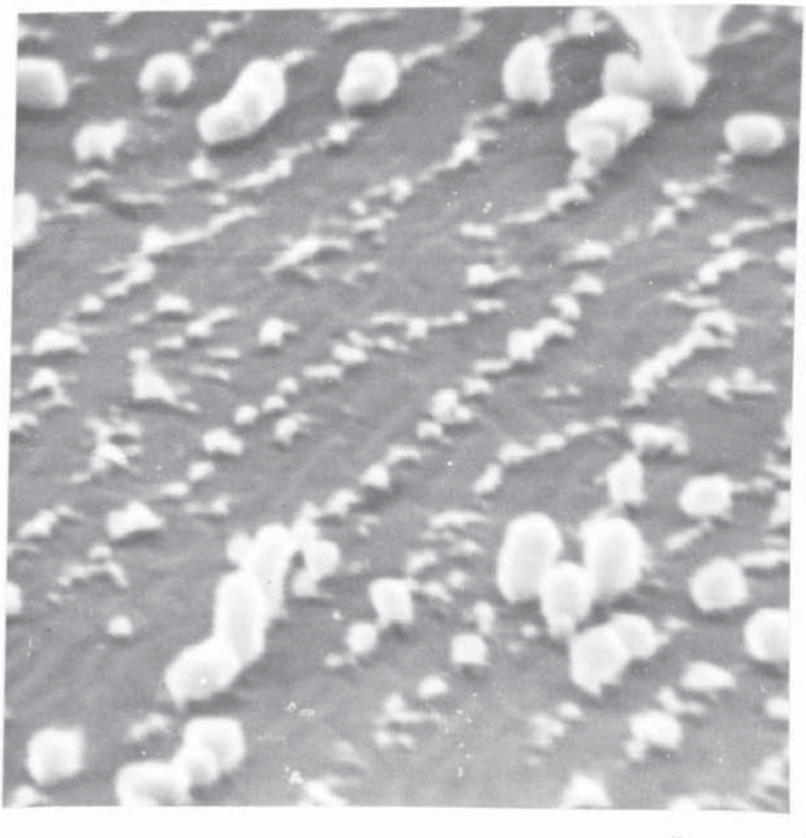


Fig.3.II2. Scanning Electron Micrograph of 99.99% Al. electrode in the region of potential fluctuations. X 20,000.

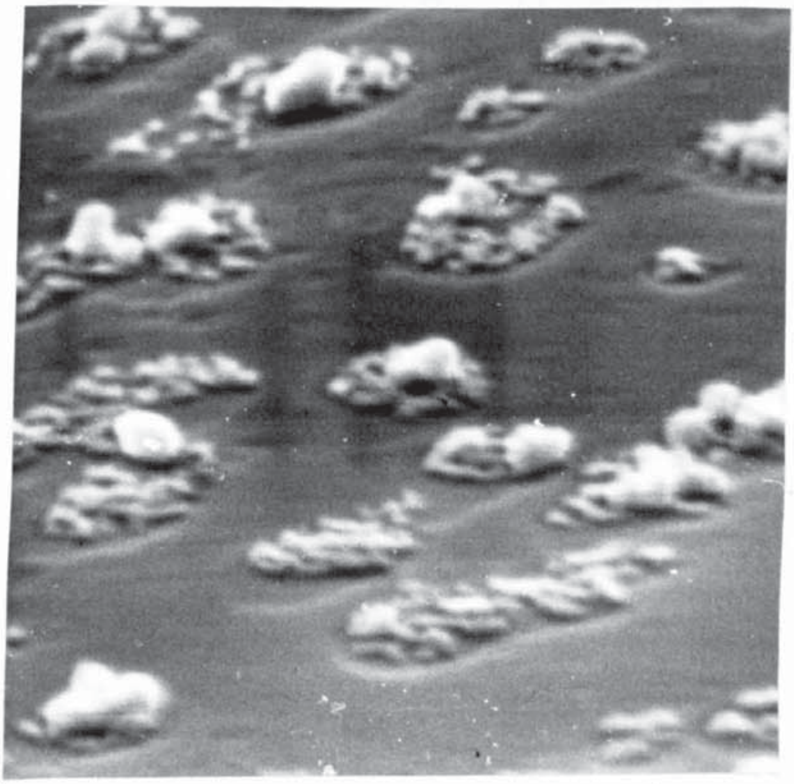


Fig.3.II3. Scanning Electron Micrograph of 99.99% Al. electrode in the region of potential fluctuations. X 20,000.

## Chemical Shift

The binding energy of an electron to an atom or ion, is influenced by the chemical environment of the atom or ion. In oxides the metal ion is positive and the oxygen is negative. The positive ion has a deficit of electrons in the outer shell, and the negative ion has a surplus. When the two are brought together to form a solid, the negative ion repels the core electrons of the positive ion, so that they are nearer the nucleus. So the electron binding energy, which is inversly proportional to its' distance from the nucleus, is increased, relative to it's value in the neutral atom. This energy difference forms the basis for determining the chemical state of the atoms in the surface of a material.

### 3.5.2 Experimental Method

Two samples of 99.99% aluminium were polished in solution B (6% nitric acid: no copper), one for 30 secs (coded sample 5) and another for 60 secs (coded sample 6). The samples were then examined by x-ray photon spectroscopy combined with argon ion milling at A.E.R.E.Harwell.

Three samples of each specimen were inserted into the spectrometer for simultaneous argon ion bombardment, (to reduce end effects). The as received stated was analysed first. Then the surface layer was progressively removed by ion milling, and the surface analysed at the following approximate depths: 20, 60, 150 Angstoms (based on data for aluminium metal(80)). Spectra were then recorded from all the samples consecutively. Concentrations were derived from the peak heights using the data from Jorgensen and Berthou(81) and are given in Tables 3.5, and 3.6, for samples 5 and 6 respectively.

### 3.5.3. Results

For aluminium separate peaks from oxide and metal were visible, and the relative amounts could be estimated; for example in the Table (30M) below the aluminium concentration means that 30% of the figure given is attributable to the metal, and therefore, 70% to the oxide. The sulphur was present as sulphate before the bombardment and as approximately uncombined sulphur afterwards.

Significant amounts of P,S and N were present on the surface of both specimens prior to bombardment. The amounts of P and S were similar on the two specimens, but were relatively less on the sample polished for only 30 secs. On bombardment P,S and N content rapidly decreased.

The Fe, Cr, and Ni observed following the bombardment occur because the body of the ion gun being used was made of stainless steel, and some ions of the material were deposited during bombardment, and should, therefore, be ignored. The source of the Ne is unknown, but may be present as an impurity in the argon used for the bombardment.

## TABLE 3.5.

## ESCA analyses of Sample 5 (atomic %)

| Element | Piece B As received | Piece A ~ 20 Å removed | Piece B 60 Å removed | Piece C 150 Å removed | Piece C Σ600 Å removed | Piece B Σ1200 Å removed | Piece A Σ600 Å removed |
|---|---|---|---|---|---|---|---|
| Al | 17.8<br>(38 M) | 34.7<br>(30 M) | 42.0<br>(48 M) | 47.2<br>(65 M) | 38.4<br>(45 M) | 71.2<br>(90 M) | 92.6<br>(~100 M) |
| O | 39.3 | 55.8 | 49.5 | 40.2 | 51.8 | 25.5 | 5.2 |
| C | 33.7 | 5.6 | 6.3 | 12.5 | 9.3 | 3.2 | ~ 2.2 |
| Sulphate | 2.0 | - | - | - | - | - | |
| Sulphur | - | 1.4 | ~0.4 | trace | - | - | |
| P | 3.0 | ~ 0.5 | - | - | - | - | |
| N | 1.8 | ~ $0.3_5$ | ~ $0.4_5$ | - | - | trace | |
| Si | 0.9 | ~ 0.5 | ~ 0.2 | - | - | - | |
| Cu | $0.0_7$ | $0.1_4$ | 0.2 | 0.2 | | ~ $0.0_6$ | |
| Na | 1.4 | 0.9 | - | - | - | - | |
| (Fe) | - | (0.3) | (0.5) | (1.2) | (3.8) | (2.8) | (4.3) |
| (Ni) | - | - | (0.1) | (0.2) | (0.7) | (0.5) | |
| (Cr) | - | - | - | (0.3) | (1.7) | (0.8) | |
| (Ne) | - | (0.5) | (0.3) | - | - | - | |
| Cl | - | - | - | - | 0.5 | - | |

## TABLE 3.6.

## ESCA analyses of Sample 6 (atomic %)

| Element | Piece B<br>As received | Piece 6A<br>~ 20 Å removed | Piece 6B<br>60 Å removed | Piece 6C<br>150 Å removed |
|---|---|---|---|---|
| Al | 19.6<br>(40 M) | 33.8<br>(30 M) | 44.2<br>(53 M) | 53.8<br>(85 M) |
| O | 46.5 | 54.4 | 44.6 | 29.6 |
| C | 25.1 | 11.3 | 10.2 | 16.3 |
| Sulphate | 2.6 | - | - | - |
| Sulphur | - | 1.4 | ~0.3 | - |
| P | 3.7 | - | - | - |
| N | 1.1 | - | - | trace |
| Si | ~0.3 | ~0.4 | - | - |
| Cu | 0.1 | 0.2 | 0.4 | 0.4 |
| Na | 1.4 | 0.5 | 0.3 | - |
| (Fe) | - | (0.2) | (0.4) | (1.9) |
| (Ni) | - | - | (trace) | (~0.3) |
| (Cr) | - | - | - | (~0.3) |
| (Ne) | - | - | (0.2) | (~0.3) |

The amount of copper detected increased as the surface layers were removed.

### 3.5.4. Examination (by Energy Dispersive x-ray Analysis) of the surface film produced by chemical polishing.

#### 3.5.4.1. Introduction

Preliminary experiments, using the x-ray analysis facilities on the scanning electron microscope, indicated that by reducing the accelerating voltage (and hence the depth of penetration of the electron beam into the metal), and inclining the specimen to an angle of 5° to the electron beam, a larger percentage of the surface film could be analysed.

#### 3.5.4.2 Experimental Method

A series of samples were polished in solution B (Phosphoric acid: 77.5%; Sulphuric acid: 16.5%; Nitric acid: 6%; no dissolved copper) for 5,10,30,60,90,120,150 and 180 seconds.

The accelerating voltage used was 4KV and the specimen was inclined at an angle of 5° to the electron beam. Focussing of the different samples was achieved by adjusting the specimen height, so that the electron beam characteristics were not altered. A count time of $3X\ 10^2$ seconds was used on all of the specimens.

#### 3.5.4.3. Results

The background Bremsstrahlung radiation was subtracted from the aluminium and phosphorous peaks. The resulting figures were then expressed as the ratio of phosphorus to aluminium for each sample and plotted against the polishing time (Fig.3.114). There was considerable spread in the figures for a given polishing time. There is however, a slight increase in the percentage of phosphorous to aluminium counts with an increase in the polishing time.

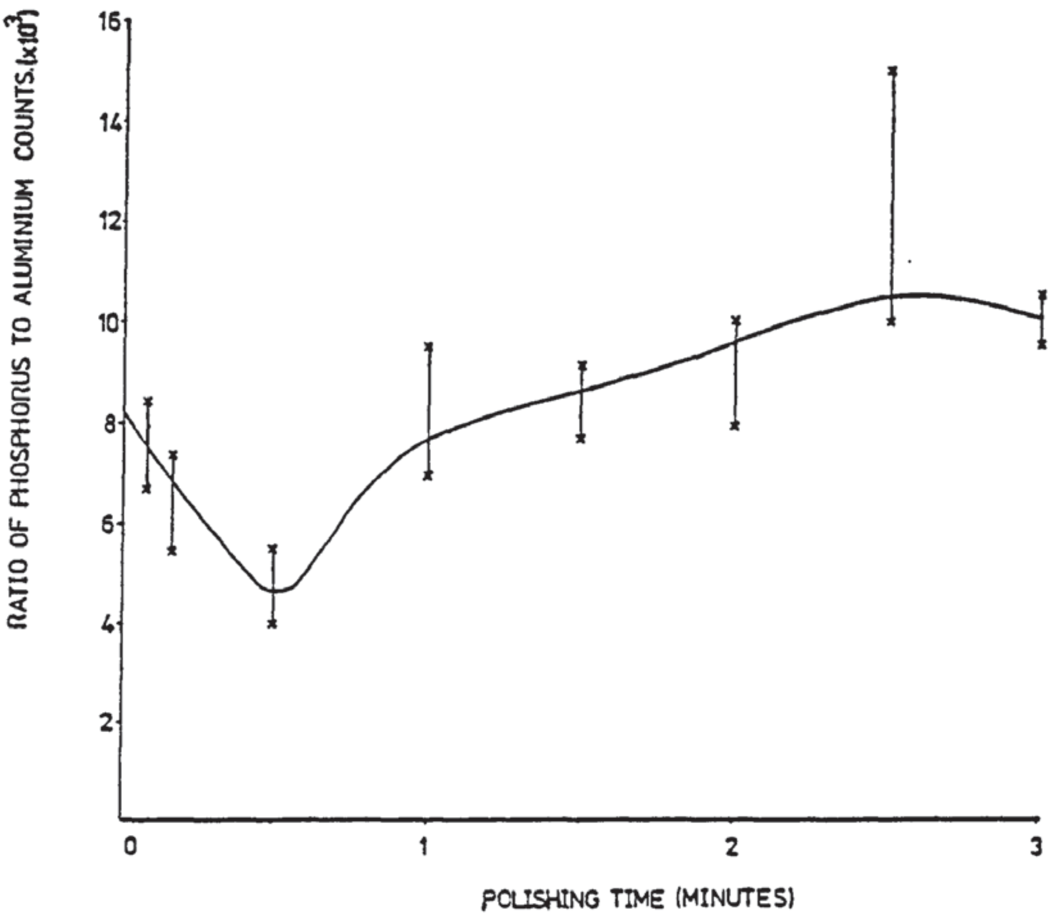


Fig.3.II4. Ratio of Phosphorus to Aluminium counts vs. polishing time of 99.99% aluminium polished in solution B.

The sulphur counts were not included as these were found to be very low and gave inconsistent figures.

## 3.6 Discussion

### 3.6.1. Specular Reflectivity

A number of authors(62,63 & 82) have studied the effect of alloying and impurity elements on the specular reflectivity of aluminium, but the majority have used a fixed polishing time, and optimum conditions. The study of the specular reflectivity of aluminium after different times of chemical polishing gives valuable information relating to changes in surface morphology. It not only gives an indication of the maximum reflectivity obtainable in a particular solution and the time of polishing necessary to achieve it, but also, the duration of the maximum, which is particularly important commercially, since it is difficult to control the precise time of polishing on automatic and semi-automatic systems.

In all of the solutions studied both the 99.99% and the 99.5% aluminium showed a drop in reflectivity in the first 5 to 30 seconds of polishing. The surface at this time had a matt white etched appearance.

The solutions not containing dissolved copper produced a consistently poorer finish on the 99.5% aluminium than on the 99.99% aluminium. The 99.99% aluminium polished in the solution containing 6% nitric acid had a relatively high reflectivity, although this only lasted for a short time of polishing before falling. This solution, previously operated commercially has been superseded by solutions with one or a number of heavy metal additions(2,4,41,43,44) or other additions(2).

Solutions in the present study containing 1g/1 dissolved copper produced poor reflectivities on both the 99.99% and 99.5% aluminium, although the 99.99% aluminium produced a marginally better finish. Again the exception in these solutions was the solution containing 6% nitric acid. The 99.99% aluminium maintained a highly reflective surface for a duration of approximately two minutes whilst polishing. This time gives sufficient flexibility for commercial plants, and allows time for drainage, necessary to reduce dragout. The 99.5% aluminium had a higher reflectivity after polishing in the 6% nitric acid solution than the 99.99% aluminium. In addition it did not show the drop in reflectivity found on the 99.99% aluminium. Both of these observations are consistent with industrial experience, and are in agreement with Brace and Kape(41) who showed, by means of a Gardam grid arrangement, the loss in image clarity as the nitric acid was varied either side of 6%.

Wernick and Pinner(2) also found this variation in specular reflectivity on two aluminium alloys (Al/5.5%Zn, 1%Mg, and ¾%Cu, and 99.8% base 1%Mg). Brace and Kape(41) also reported an increase in brightness after polishing in a solution containing dissolved copper. Lattey and Neunzig(82) found a decrease in reflectivity as the percentage of impurities was increased, when using the Alupol IV and V baths, this was not found in the present study. Cooke and Spooner(63) also found a decrease in reflectivity as the amount of iron impurity was increased, but reported a slight increase in the case of some impurities (Si and Ti) up to a limited concentration and no change with others (Mg and Cu/Mn).

These results show a certain amount of variation for a given impurity and are all lower than those achieved in the present study. The authors also claim that copper produced a beneficial effect when present either in the alloy or in the solution. This is partially in agreement with the work in this study, although the presence of copper as an alloying element was not studied, the addition of copper to the solution, with 6% nitric acid, produced a considerable improvement in the specular reflectivity on the 99.5% aluminium, the reasons for this are discussed in more detail later.

### 3.6.2. Changes in Surface Morphology with polishing time in the absence of copper.

#### 3.6.2.1. 99.99% Aluminium

Chemical polishing can be seen as a sequence of events. In the first few seconds of polishing the surface of the aluminium is etched. Spherical etch pits form at random sites on the surface, Scratches and rolling lines are etched preferentially, either due to localised work hardening of the surface, which has been shown to increase the rate of formation of etch pits(83), or to defects in the air formed oxide caused by rolling. As the polishing time is increased the existing pits grow laterally and new pits nucleate and grow, until the surface is completely covered with pits. No evidence was found of grains of different orientation etching preferentially, as suggested by Kape(86). The side walls of these pits then present ridges of aluminium to the solution and will dissolve preferentially by the mechanisms proposed by previous authors(84). The levelling of these ridges is achieved after approximately 60 seconds polishing, and is followed by the formation of 'sub-micro patterns' of the type produced by a number of researchers both by chemical and electropolishing of aluminium, and will be discussed in more detail in a later section.

In addition to these patterns there were small protusions of aluminium present on the surface. In solution A (no nitric acid) the anodic reaction:

$$Al \rightarrow Al^{3+} + 3e^-$$

is balanced by the cathodic reaction:

$$2H^+ + 2e^- \rightarrow H_2$$

The evolution of hydrogen occurs on the surface of the aluminium. The gas forms bubbles on the surface which were sufficient in this solution to float a specimen weighing 12gms, out of the holder and on to the surface of the solution. The gas bubbles formed, whilst in contact with the aluminium, will prevent dissolution at the point of contact. This will render the point of contact inert with respect to the surrounding aluminium. Since the energy required for growth is less than that for the nucleation of a separate bubble, the one already present will become an electron acceptor, thus making the aluminium around it relatively anodic, and this leads to the formation of a circular groove that dissolves at a slightly more rapid rate. On detachment of the hydrogen bubble, when it has reached a critical size, the solution will dissolve the peak faster than the surrounding aluminium, and will provide a favourable site for the nucleation of a subsequent bubble. This process is repeated continuously.

Further polishing in a nitric acid free solution allows the different rates of dissolution of grains of different orientation to become more pronounced, causing a considerable drop in reflectivity.

The addition of 6% nitric acid to the solution has a pronounced effect on the changes in surface morphology with time. In the first instance the surface is entirely covered with etch pits after only 10 seconds polishing (this previously took 20 seconds). This implies a more rapid initial attack on the surface oxide and the underlying aluminium. Dilute nitric acid does attack aluminium, but only extremely slowly(25) but hot concentrated acid reacts as a non-ionised acid(2):

(1) $3HO.NO_2 + 2Al \rightarrow Al_2O_3 + 3HNO_2$

This type of reaction predominates in nitric acid containing polishing solutions and leads to 'nitrous fume' evolution by the reactions:

(2) $HNO_3 + HNO_2 \rightarrow 2NO_2 + H_2O$

(3) $2HNO_2 \rightarrow HNO_3 + 2NO + H_2O$

(4) $2NO + O_2 \rightarrow 2NO_2$

This would support the observation of a more rapid etching of the surface in the first few seconds of polishing. Wernick and Pinner(2) however, reported a reduction in weight loss of aluminium in solutions of this type as the nitric acid was increased up to 6%, but this applies to aluminium polished for a period of time, which would include the initial etch period and tend to give an average figure. Potential time determinations made in the present study (discussed in more detail in a later section) indicates a rapid rate of attack in the early stages of polishing, after which the rate is slower due to the passivation of the surface by the nitric acid, once polishing conditions are established. The passivating nature of the nitric acid is supported by the fact that after 180 seconds polishing the different rates of dissolution of grains of different orientation was not evident. The peaks of aluminium, found in the absence of nitric acid, were again found on the surface after polishing in this solution, although they were considerably smaller and did not show an annular ring. This is consistent with the observation that the physical size of the gas bubbles produced in this solution was smaller than those produced in the nitric acid free solution. As nitric acid is a strong oxidising agent and nascent hydrogen a strong reducing agent, it is not unreasonable to suppose that the hydrogen produced by the dissolution of the aluminium is rapidly oxidised by the nitric acid resulting in a relatively smaller bubble size and so reducing the size of the protrusions. Lattey(46) also believed that the presence of nitric acid reduced the over-potential of hydrogen discharge, thus allowing the reaction to proceed more smoothly. This would account for the absence of the annular groove which may also be prevented in part by the passivating nature of the nitric acid preventing preferential dissolution around the peak.

The prevention of the crystallographic dissolution, and the reduction in the size of the gassing defects are responsible for the improved specular reflectivity in this solution.

In solution C (20% nitric acid) the initial rate of etching appears similar to that found on the aluminium in the absence of nitric acid, although the etching at 20 seconds seems more superficial than found previously. The etched surface had been completely removed after 40 seconds polishing, but the presence of a number of scratches left on the surface would tend to indicate that the rate of dissolution is slower since all the surface scratches had been removed by this time in the previous solutions.

The protrusions of aluminium in the solutions containing 0 and 6% nitric acid were again present although the numbers were considerably less. In addition, the peaks that are present show pitting on the tip of the peaks. The reduction in the number of peaks could be explained by the increase in the amount of oxidising agent present reducing the hydrogen being evolved more rapidly and so reducing the number that reach a size capable of producing a defect. The presence of the pitting on the tip of the peaks is not easily explained. The dissolution of aluminium from the surface around the peaks will continue, albeit at a relatively reduced rate. The relatively fewer peaks associated with hydrogen evolution will have to account for a proportionately larger percentage of the total cathodic reaction. Furthermore, the greater profusion of nitric acid means that the hydrogen evolved at these points is oxidised considerably quicker, preventing the formation of gas bubbles, and the combination of these factors will lead to a breakdown of the passive film at these points. This theory is supported by the fact that copper deposits almost exclusively in these pits, (indicating their cathodic nature), in the solution containing dissolved copper, as discussed later.

The loss in specular reflectivity in this solution is partly due to the presence of gassing defects, but more to the undulating nature of the surface, and not etching(86).

### 3.6.2.2. 99.5% Aluminium

Both the etching and subsequent levelling of the surface is relatively rapid on the 99.5% aluminium in all three of these solutions. The surface is completely etched after 5 seconds polishing in solution A, and after 10 seconds in the other two solutions. Pitting due to the presence of inclusions was also apparent at this time of polishing. The majority of these inclusions were found to be iron rich. Titanium and silicon rich inclusions were also found, but did not show the same extensive surrounding pitting as the iron rich particles. This explains why Cooke and Spooner(63) did not find a decrease in reflectivity on the alloys they studied containing titanium and silicon, and why they did on those containing iron.

As the polishing time was increased the pitting around these iron rich inclusions became more extensive. Significant by their absence were the peaks of aluminium found on the 99.99% aluminium. The pitting associated with the iron rich particles could be due to one or a combination of two possible mechanisms. Since iron is more noble than aluminium it is likely to become an electron acceptor for electrons from the surrounding aluminium, thereby establishing a galvanic cell, and lead to preferential dissolution of the aluminium in the vicinity of the particle. An alternative or complementary mechanism involves the preferential evolution of hydrogen from the iron rich inclusions, a view supported by

Chatterjee and Thomas(65). Hydrogen is likely to evolve preferentially from these points for two reasons. The hydrogen evolution overpotential for iron is less than for aluminium(85), and as the particles dissolve at a slower rate than the matrix they present a rough protruding surface for the gas to nucleate on. Preferential evolution of hydrogen from these localised points will make the surrounding aluminium relatively anodic, and so produce a groove around the particle.

The different grain dissolution rates found on the 99.99% aluminium in this solution were not discernable on the 99.5% aluminium, due to the extensive pitting of the surface. The low specular reflectivity in this solution is quite clearly due to the pitting associated with the iron rich inclusions.

The addition of 6% nitric acid to the solution does not appreciably alter the etching process. It does, however, affect the iron rich inclusions, the majority of which are dissolved faster than the aluminium, leaving empty pits. As they are exposed to the solution they are responsible for pitting the surrounding aluminium, but are themselves attacked. Peaks of aluminium reappeared in this solution presumably because as the inclusions are being dissolved quicker there are now insufficient sites for gas nucleation and the remaining cathodic reaction is occurring on the aluminium surface, and producing gassing defects by the mechanism previously described. The loss in reflectivity in this solution is again due to pitting of the surface.

In the solution containing 20% nitric acid (solution C) the iron particles again dissolved at a much faster rate than the aluminium. The surface after 180 seconds polishing bears a resemblence to that of the 99.99% aluminium in the same solution, with additional pitting from the iron rich inclusions. Due to the nature of the pitting of the surface it was not possible to determine if peaks of aluminium were present on this surface or not.

### 3.6.3. Changes in surface morphology with polishing time in solutions containing copper

#### 3.6.3.1. 99.99% Aluminium

In solution D (no nitric acid) the etching and levelling process was more rapid than in the equivalent copper free solution. Previous authors(41,83,87) have found a decrease in the weight loss of aluminium polished in solutions containing dissolved copper. The increased rate of dissolution in this instance is likely, therefore, to be confined to the early stages of polishing.

Small copper deposits were found deposited at random sites on the surface, although they tended to deposit preferentially at defect sites (e.g. scratches) which is consistent with the more rapid rate of dissolution at these points and confirms the suppositions of Brace and Kape(41). The copper deposits were of two different sizes. The smaller were approximately 0.25μm. and the larger 1.5μm. After 120 seconds polishing the deposits had increased in size to 1.0μm. and 20μm. for smaller and larger respectively. The larger deposits at 5 seconds polishing may remain on the surface and act as sites for preferential deposition whilst the smaller deposits dissolve and redeposit again as relatively small particles. The larger copper deposits were responsible for pitting the surface by the same mechanism described for the pitting associated with iron rich particles. As the copper is more noble than iron one would expect the pitting to be correspondingly greater, and this is in fact the case. The concept that preferential hydrogen evolution from the copper deposits is in part responsible for the pitting is supported by the observation that the internal surface of the pits (with the copper dissolved out) is smooth., showing that there has been no breakdown in the polishing conditions, merely a localised increase in the rate of dissolution. Galvanic attack might be expected to produce an etched rough pit.

The aluminium polished in this solution showed other significant differences from the copper free solutions. Peaks of aluminium were not present on the surface since the hydrogen evolves preferentially from the copper deposits distributed over the surface, in the same way as had been found on the iron rich particles of the 99.5% aluminium in solution A.

Closer examination of the surface showed that the smaller copper particles tended to deposit on the ridges of the sub-micro patterns indicating the cathodic nature of the ridges relative to the aluminium between (as discussed in more detail in section 3.6.5).

Grains of different orientation were not found to dissolve at different rates in this solution. The deposited copper must provide a sufficiently even electrochemical potential over the surface to prevent any uneven grain dissolution.

The loss in reflectivity in this solution is clearly due to the pitting associated with the large copper deposits, and not, as in the solution on the same composition but not containing copper, due to gassing defects and uneven grain dissolution.

A solution of the type used in this work is used extensively commercially and contains 6% nitric acid (this figure is lower in solutions containing dissolved aluminium, e.g. approximately 4% in solutions with 40g/1 aluminium), and should produce a highly reflective surface with polishing times of 120 seconds and longer, on a range of bright trim alloys. This was found to be the case in the present study. The high degree of reflectivity is due mainly to the even way in which the copper is deposited. As the polishing time was increased the copper deposits increased in size from approximately 0.4μm. at 5 seconds polishing to approximately 1.5μm after 120 seconds polishing. No individual large deposits were formed and consequently no pitting was evident. The observation of the copper deposits as discrete particles refutes the theory of Brace and Kape(41) who believed that the surface of the aluminium was covered with copper to a thickness of several atomic layers. The authors also experienced difficulty in dissolving the deposited copper off the surface after brightening(86) and suggested that it was present as the oxide. No such difficulty was experienced in this study and the present investigation supports the theory proposed by Pinner(45) that the copper is deposited in its elemental state.

The sub-micro patterns visible under the relatively large copper deposits (Fig.3.70) shows that the formation of these patterns is independent of the copper deposition.

The nitric acid, as well as producing a surface film, has, in this solution, modified the copper deposition so that an even coverage is produced as is evident from the lack of any large particles. This is probably due to the nitric acid dissolving the deposited copper more rapidly than in the previous solution, thus preventing any large deposits from remaining on the surface for any length of time. The even coverage of copper also prevents gassing defects due to the abundence of sites for gas nucleation (which are removed after immersion in a 50% by volume nitric acid solution). Uneven grain dissolution is also prevented.

However, if an inordinate amount of nitric acid is present in the solution (as in solution F) this balance is upset. Very little copper is deposited on the surface and although the original etch pits have been levelled, new etch pits can be seen developing. After 40 seconds polishing grains of different orientation are dissolving at different rates. This was not found in solution C (20% nitric acid and no copper), and this uneven dissolution can therefore be attributed to the influence of the dissolved copper. Closer examination of the surface shows that the grains dissolving more rapidly are pitted and the pits contain very small copper deposits (approx 0.1μm). The slower dissolving grains show very few isolated deposits. The difference in rates of dissolution of the different grains becomes more pronounced with increase in the polishing time. The etch pits, where present, grow laterally with time and merge, with a corresponding increase in the amount of copper present on the surface in these regions. In this solution therefore, the nitric acid has considerably reduced the amount of copper deposited, and the amount deposited varies according to the orientation of the grains. There is, however, sufficient to prevent the formation of gassing defects. It is interesting to note, however, that the pits of Fig.3.84 containing copper bear a resemblance to the pitted peaks of aluminium formed in the solution of the same nitric acid content but with no dissolved copper (fig.3.45), and if this resemblence is a real effect then it supports the theory that the pits on these peaks are regions of relatively high rate of attack where a larger proportion of the cathodic reaction is occurring, than in solutions of a lower nitric acid content.

No evidence of sub-micro patterns was found on the surface after polishing in this solution, as in solution E. As the nitric acid content is increased the extent of these patterns is reduced, with or without dissolved copper. This is consistent with the theory that nitric acid has a passivating effect on the surface.

Loss of specular reflectivity in the solutions where the nitric acid content is too low or too high, is due to pitting and uneven grain dissolution respectively, and not simply due to etching as has been suggested(86).

### 3.6.3.2. 99.5% Aluminium

The changes in surface morphology with polishing time on the 99.5% aluminium were very similar to the 99.99% aluminium with one or two notable exceptions. The surface etching was quicker and the surface showed additional pitting, not associated with deposited copper, probably due to the iron rich inclusions. The sub-micro patterns found in the nitric acid free solution were of slightly larger dimensions than found on the 99.99% aluminium.

Copper was found to deposit preferentially on to the iron rich inclusions showing that they are cathodic relative to the aluminium. This supports the theory that the particles are evolving hydrogen preferentially. This preferential deposition also has the effect of reducing the amount of pitting associated with the iron rich particles. The reduction in localised dissolution may be due to the relatively larger total surface area of the deposited copper increasing the overall anodic area so that the pits formed are shallower. This was also found to be the case in the solution containing 6% nitric acid. In addition the iron rich particles do not dissolve as rapidly as they had in the absence of dissolved copper, and this leaves the particles standing proud of the surface. There is a limit to the size of the particle that will not cause pitting. This is in general agreement with the findings of Cooke and Spooner(63). The absence of any pitting around the titanium rich inclusions is due to the fact that their electrode potential is very similar to that of aluminium, and so there will not be the same galvanic couple as in the case of iron and copper. In addition titanium is relatively inert in these solutions (it is in fact used commercially as a jigging material with a considerable life), and consequently there is unlikely to be preferential hydrogen evolution.

The addition of 20% nitric acid to the solution produced the same changes in surface morphology as had been found on the 99.99% aluminium, with the exception of the iron rich inclusions. Figure 3.91 shows that these particles are in fact being dissolved and not simply undercut and dropping out of the surface. This figure also shows the absence of copper deposited on the iron. This means that after 120 seconds polishing, the surfaces unpitted on the 99.99% aluminium are now pitted by these inclusions.

The loss in reflectivity when the nitric acid is below 6% is due to pitting from the larger copper deposits and uneven grain dissolution with additional pitting due to the iron rich inclusions. At nitric acid concentrations above 6% the low reflectivity is due to extensive pitting caused by uneven copper deposition and the iron rich inclusions.

### 3.6.4. The incidence of Sub-Micro patterns

By using the high angle of incidence technique on the scanning electron microscope, sub-micro patterns were visible on the aluminium polished in a number of the solutions studied. The patterns found closely resembled those first described by Bucknell and Geach(49) and later by Cuff and Grant(57) and Bichsel(58) who used solutions not containing a dissolved heavy metal.

A clear orientation dependence was found, the patterns changing their dimensions and direction according to the orientation of the grain. It is perhaps relevant at this point to examine the surfaces of 99.99% and 99.5% aluminium etched in 20% hydrofluoric acid at room temperature for 10 minutes (Fig.3.115 and 3.116 respectively), which show clearly the size of the grains and on the 99.5% aluminium, show evidence of striations on certain grains. In addition to the grains showing patterns after chemical polishing, some grains were found that did not exhibit any patterns.

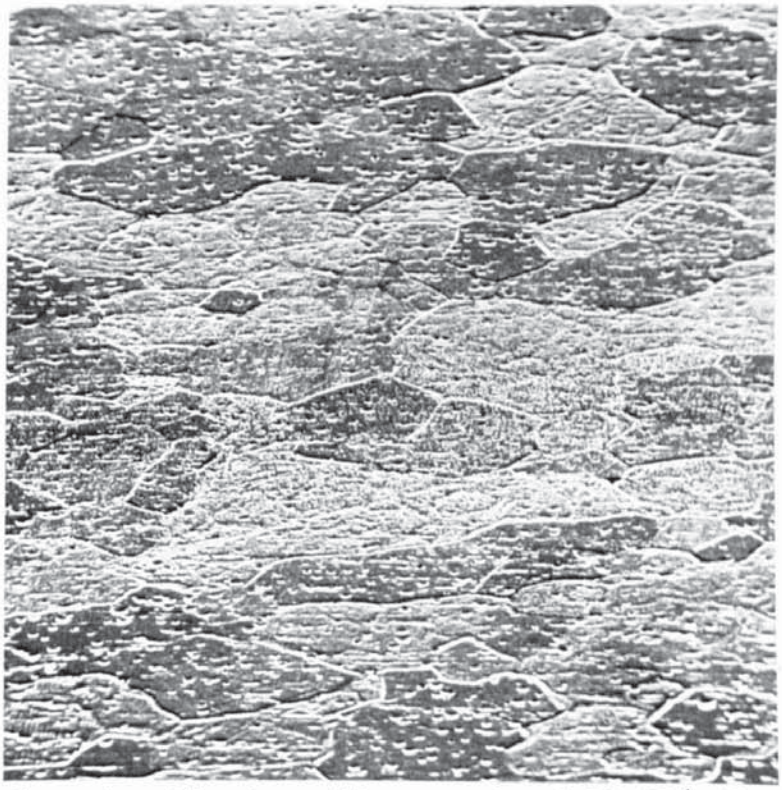


Fig.3.115. Scanning Electron Micrograph of 99.99% Al. etched in 20% HF. for 10 minutes. X 100.

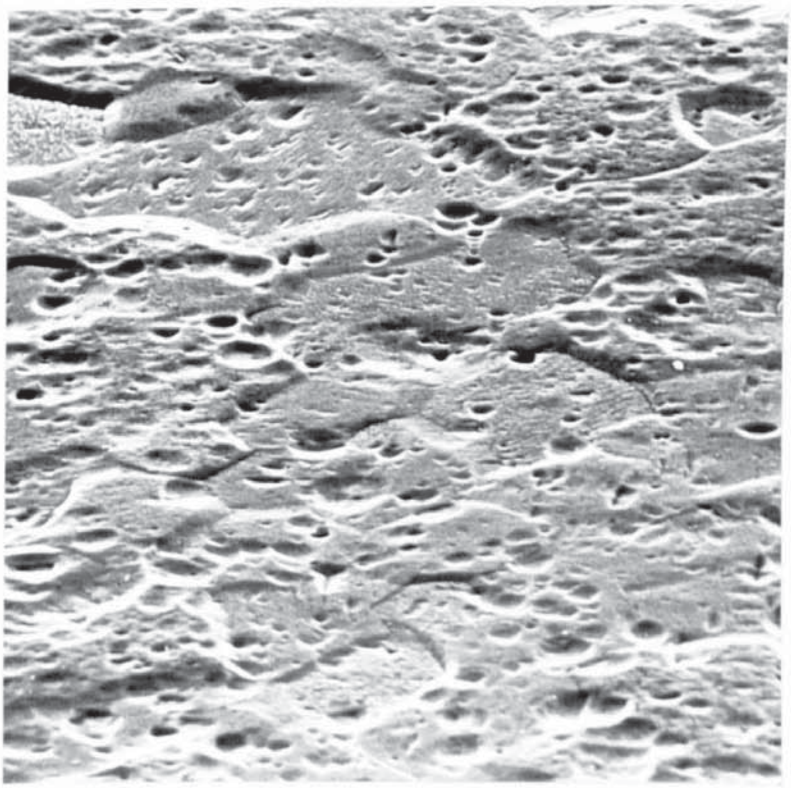


Fig.3.116. Scanning Electron Micrograph of 99.5% Al. etched in 20% HF. for 10 minutes. X 500.

This work, in support of others(57,58) refutes the suggestion of Hunter and Robinson(54), that these patterns are surface manifestations of sub-grain structures.

Cuff and Grant(57) believed that these patterns were surface manifestations of a three dimensional internal network of segregated impurity atoms, and that the ridges left were rich in these impurities and consequently cathodic in nature. The authors do not explain the mechanism of this segregation or on to which planes the segregation occurs. The hypothesis is also inconsistent with the observation, in the present study, of patterns lying underneath large amounts of deposited copper which act as cathodic sites in preference to the aluminium surface and would over rule any differences due to impurity segregation. In addition Welsh(52) found that the dimensions of the patterns altered with changes in the conditions of electrolysis.

Bichsel(58) suggested that the patterns found originated from the initial etched surface. The points of contact of the etch pits forming the ridges of the subsequent patterns. This however, does not explain how a relatively large etch pit network can evolve into a considerably smaller sub-micro pattern as found in the present study.

The micrographs in this investigation provide conclusive evidence that the patterns formed are composed of ridges and not furrows. The cathodic nature of the ridges is clearly indicated in Figs.3.111 and 3.112, where the copper has deposited preferentially along the ridges of the patterns. Figure 3.113 shows a grain with no discernable pattern, where copper has deposited as discrete islands.

The nitric acid was found to influence the dimensions of the surface patterns, an observation not previously reported. With no nitric acid the patterns had a large cell size. With 6% nitric acid the dimensions of the cells were smaller, and with 20% nitric acid no sub-micro patterns were visible.

This would tend to indicate that the nitric acid passivates the surface, eventually to the extent that the ridges are prevented from forming. This observation, and the fact that copper (at 2 + 4% nitric acid) deposits along the ridges or as isolated islands, supports the view$^{(1)}$ that the sub-micro patterns are surface manifestations of the internal crystal lattice structure.

### 3.6.5. Potential Time determinations

Evans$^{(85)}$ has pointed out some important features of potential time measurements. Potential measurements will give an indication of the surface state of a metal. If a metal with a porous film is placed in a liquid the potential will become more noble if the film is self healing, and the potential will become less noble if the film is not repaired and corrosion proceeds. In addition, a metal with a porous coating of a more noble metal will give a'compromise potential'. If the metal coating is more or less compact, the potential will be close to the potential of that metal, in the same liquid. Conversely if the coating is thin and considerably porous, the potential will be closely related to the underlying metal.

As the exact reference voltage of the calomel electrode at the temperatures used in this investigation is not accurately known, the results are expressed for comparative purposes, as the difference in millivolts, between the reference electrode and the aluminium specimen in the different solutions studied.

The aluminium immersed in the solutions studied showed a sudden surge in negativity in the first few seconds, corresponding to the etching of the surface and the removal of the air formed oxide. As the surface is levelled the potential gradually becomes less electronegative until a steady state is achieved. The initial surge in negativity may be due to a number of factors. One is the removal of the air formed oxide and it's replacement with a more noble polishing film. The scanning electron micrographs suggest that the rate of attack of the surface is faster in the first 30 seconds or so of polishing, with a gradual reduction as polishing conditions are established.

### 3.6.5.1. Solutions not containing copper

The rate at which the steady state is reached is relatively slower on the 99.99% aluminium than on the 99.5% aluminium, which is consistent with the observation that the etching of the surface of the latter is more rapid. In addition, the steady state potentials of the 99.99% aluminium were significantly more noble than the 99.5% aluminium due to the presence of the predominantly iron rich impurities present in the 99.5% aluminium.

As the nitric acid content was increased the potentials recorded became more noble, this is indicative of a more stable less ionically conducting film.

Brace and Kape(41) found a minimum weight loss on aluminium polished in these solutions at 6% nitric acid and a more rapid rate above and below this figure. With a higher rate of attack one would expect the potentials to become more electronegative due to the greater profusion of electrons left as the aluminium atoms dissolve and form positively charged ions. This was not in agreement with the present study. Since the system is in a state of dynamic equilibrium, increasing the amount of nitric acid will allow the cathodic reaction to proceed more efficiently and result in a net potential that is increasingly noble, despite the increased rate of aluminium dissolution.

### 3.6.5.2 Solutions containing copper

These solutions showed a similar initial negative surge in potential as the solutions not containing copper. The potentials recorded in these solutions were all significantly more noble than in the copper free solutions, due to the presence of copper deposited on the surface of the electrodes. In addition the change in steady state potentials in the solutions from 8% nitric acid to 20% was less than in the corresponding solutions not containing copper. That is to say, on the 99.99% aluminium the difference in steady state potentials from nitric acid contents of 8% to 20% was -0.30V as opposed to a difference of -0.11V for the copper containing solutions, (the 99.5% aluminium gave a similar difference). The presence of copper deposited on the surface will make the electrode give a more noble 'compromise potential'. As the nitric acid content is increased the amount of copper deposited on the surface is reduced, the surface film becomes more passive, and these factors lessen the differences in potential recorded.

Two solutions (2% and 4% nitric acid) exhibited a potential cycling effect. After the initial surge in negativity the potential approached a steady state potential, at which point there is a sudden surge to a more noble potential, and then a rapid return to a potential closer to one that might be extrapolated from potentials of the solutions of higher and lower nitric acid contents. Scanning electron microscope examination of the surface showed that at the most noble potential in the cycle the surface of the aluminium was extensively covered with copper. These results bear a resemblance to those obtained by Dmitriev(47), although his results can be criticised in the light of the results from the present work. In using 100ml of solution and a specimen surface area of 9cm$^2$ with polishing times up to 200 minutes there will be a considerable drop in the nitric acid content during polishing. No mention of nitric acid additions to compensate for this loss was made by the author. In addition he does not take into account the effect of dissolved aluminium which will significantly affect the potential during polishing

Dmitriev attributes the potential cycle to changes in the electrochemical properties of the 'film', which leads to changes in the conditions for the dissolution of the oxide film. The author concludes that the best polishing is achieved in the fresh solution, this is not suprising since the nitric acid concentration will be correct at this time.

The present study shows that the potential cycle is due to sudden extensive deposition of copper on the surface of the aluminium electrode. In the solution with no nitric acid, dissolution of the deposited copper is relatively slow, and this has been shown to lead to isolated large deposits. In the presence of a relatively low nitric acid concentration (2%) dissolution of the copper deposits is more rapid, but more importantly, the mode of copper deposition is such that the surface is covered with a large number of small deposits that provide numerous sites for preferential deposition of copper to such an extent that the deposition rate over the whole surface exceeds that of the dissolution rate. Eventually the surface will be covered with sufficient copper to register a potential close to that of pure copper in these solutions. This coverage of copper then alters the reactions occuring since the electrode is now essentially a copper electrode. This leads to a rapid dissolution of the copper until sufficient is removed for aluminium dissolution to become the predominate reaction, and so the potential returns to a more negative value and the cycle is repeated.

The 99.5% aluminium showed a longer interval between the noble surges in potential, particularly in the 4% nitric acid solution. This indicates that the copper deposition/dissolution equilibrium is maintained at a steady state level for a longer period of time before sufficient copper has plated out onto the surface to register a potential close to that of copper. This may be due to the fact that, as the 99.5% aluminium is less noble than the 99.99% aluminium more copper must be deposited before the electrode reaches the point at which it's potential is close to that of pure copper (in this solution).

The potential cycle does not occur in solutions containing 6% nitric acid and more, as the nitric acid not only prevents the deposition of such large amounts of copper, but also dissolves the copper from the surface sufficiently rapidly to prevent the conditions necessary for the potential cycle.

The potential cycle can, therefore, be attributed to the deposition of a considerable quantity of copper onto the surface, and it's subsequent redissolution, and not changes in the underlying surface film(47). It is also interesting to note that the samples after producing these potential cycles all had a good polished surface (judged by eye), although not to the same specularity of the correct nitric acid contentration.

### 3.6.6 The existence of a surface film

The presence of a surface film after chemical polishing has been shown by a number of different techniques. An attempt was made in this investigation to determine the thickness, composition and changes in composition with depth of the surface film.

Experiments using the energy dispersive x-ray analysis facilities on the scanning electron microscope revealed some features of the surface film. Firstly , that there were appreciable amounts of phosphorus and sulphur present in the surface film, and secondly that the distribution of these elements was not even over the surface. This suggested that the surface film was heterogeneous and composed of phosphates and sulphates of aluminium. The results also showed an apparent decrease in the amount of phosphorous present after 30 seconds of polishing (Fig.3.114), after which the amount of phosphorus detected rose with increased polishing time. The drop in phosphorus counts at 30 seconds may not in fact be a real effect, as the etched surface at this time may prevent a proportion of the phosphorus x-rays from escaping from the surface and thereby reduce the number of counts. The results of the x-ray analysis also indicated that the surface film may have been as much as 1000A thick, due to the relatively large amounts of phosphorus and sulphur detected.

The E.S.C.A. results, however, showed that the x-ray results on their own could be misinterpreted. The phosphorus and sulphur detected was in fact found to be only adsorbed onto the surface layers of the film. This is comparable with results obtained by Olefjord(32) who found phosphorous and sulphur on the outer layer of the film produced by electropolishing stainless steel in a phosphoric/sulphuric acid based solution.

The film was found to be essentially an oxide film, although copper (present in the 99.99% aluminium in solid solution to the extent of only 0.002% by weight) is preferentially incorporated in the film. Previous authors(28,29) have suggested that the film was of an oxide type (although it is not clear from these experiments whether the film was formed during polishing or subsequent preparative operations). Others(61) have suggested that the film is in fact a 'compact' or 'solid' film, being either a contaminated oxide type or consisting of products of dissolution(30).

Estimation of the precise thickness of the film formed in chemical polishing is subject to a number of possible errors. The surface of the samples studied was not flat and the area examined was approximately Imm and will, therefore, give an average value regardless of local variations. The data for determining film thickness in this instance is derived from figures for the pure oxide(80), and not one that is ionically conducting, possibly porous(31,60) and contaminated with atoms of other elements of considerably higher atomic weight.

The relatively high figures obtained from sample 5 (table 3.5) indicating a film thickness of up to 1200Å are probably due to the etched nature of the surface of this sample. Argon ion milling will remove oxide and metal from the top of the ridges of the etch pits, leaving oxide present at the bottom of the pits, which will on subsequent analysis, reveal the presence of oxide which would have been removed by the ion milling had the surface been flat.

In addition, attempts to examine cross-sections of the film by ultramicrotomy (a technique capable of showing anodic films 400Å thick) proved unsuccessful.

# CHAPTER 4

# THE INFLUENCE OF SULPHURIC ACID AND BENZOTRIAZOLE

## 4.1 Introduction

Little mention has been made in the literature of the effect on the surface morphology of aluminium of increasing the amount of sulphuric acid present in phosphoric acid based solutions. It has generally been assumed to be a cheap diluent(87), or an addition that produces a bright etch type of solution(2). The addition of sulphuric acid to these solutions is of great industrial importance, which is easily appreciated when one compares the price of the two acids. Ortho-phosphoric acid costs £0.52p per litre, and sulphuric acid £0.07p per litre (1975 price).

It is known(88) that a solution operating at a low phosphoric to sulphuric acid ratio has been marketed by Albright and Wilson Ltd., and has been accepted as giving as good a finish as the higher ratio solutions normally used.

In the original Albright and Wilson work(88) increasing problems with transfer etch were experienced as the acid ratio was reduced below about 3:1. Transfer etch occurs on the aluminium during transfer from the polishing tank to the next treatment stage (usually a water rinse) on automatic and semi-automatic plants with transfer times between 30 and 60 seconds. The loss in specular reflectivity that occurs during relatively long transfer times takes the form of an irremovable surface film on the aluminium. This problem has now been overcome by the addition of one of a number of organic compounds as described in the British Patent application 42902/75, Benzotriazole (B.T.A.) being a typical additive.

The work in this chapter was to elucidate the effect of increasing the percentage of sulphuric acid in these solutions, to explain the mechanism of transfer etch, and the mechanism by which the B.T.A. inhibits the transfer etch.

Solutions approximating to those given in examples 1 and 2 of the above patent have been compared with and without B.T.A.

## 4.2 Specular Reflectivity Results

### 4.2.1 Solution G (58.2% by vol. $H_3PO_4$;35.8% $H_2SO_4$;6% $HNO_3$)

The specular reflectivity for samples of 99.99% aluminium and 99.5% aluminium polished in solution G (table 2.2) for 5,10,20,40,50,60, 90,120,150,180 and 240 seconds are illustrated in Fig.4.1. The 99.5% aluminium showed excellent specular reflectivity after polishing in this solution. The 99.99% aluminium did not achieve the same degree of reflectivity however.

### 4.2.2. Solution H (as above with 2.8g/1 B.T.A.)

The specular reflectivity of the 99.99% aluminium greatly improved in this solution, to match the reflectivity achieved by the 99.5% aluminium in solution G. The 99.5% aluminium in this solution gave a similar reflectivity to that achieved in solution G, (Fig.4.2).

### 4.2.3. Solution J (47.0% (by vol.) $H_3PO_4$;47.0% $H_2SO_4$;6% $HNO_3$)

This solution produced a poor finish on both the 99.99% and 99.5% aluminium (Fig.4.3). In contrast to solution G, the 99.99% aluminium produced the slightly better finish.

### 4.2.4 Solution K (as above with 10g/1 B.T.A.)

Additions of benzotriazole were made to the solution in steps of o.5g/1 until no further increase in reflectivity was achieved. 10g/1

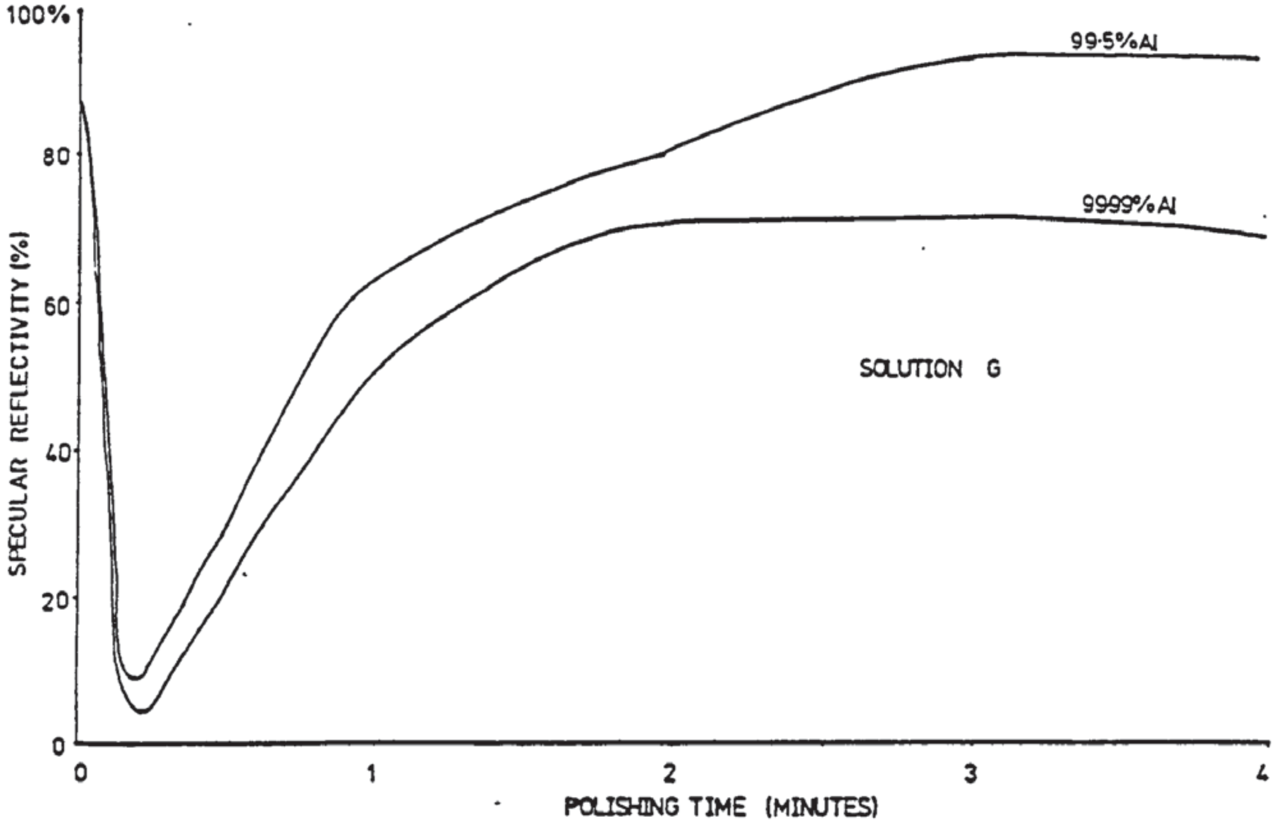


Fig.4.I. Specular Reflectivity vs. Polishing Time

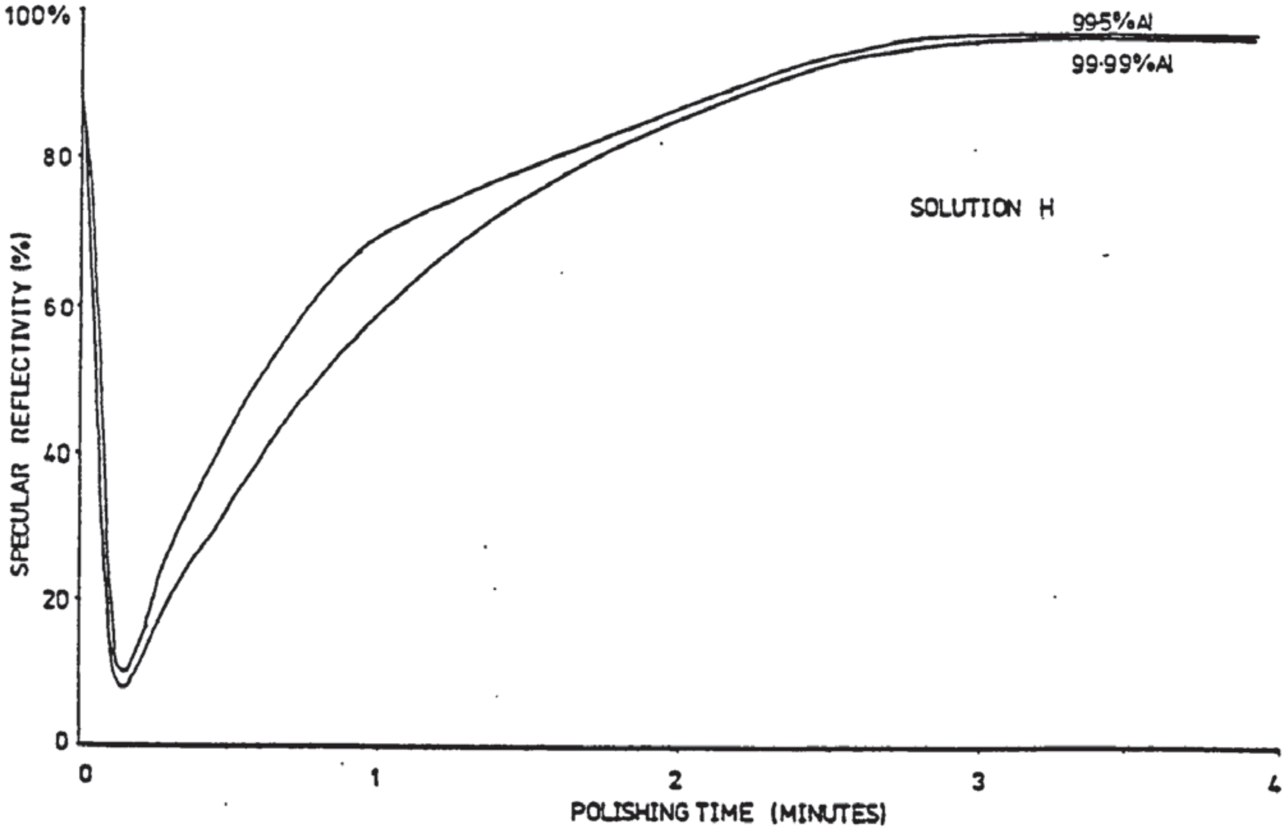


Fig.4.2. Specular Reflectivity vs. Polishing Time

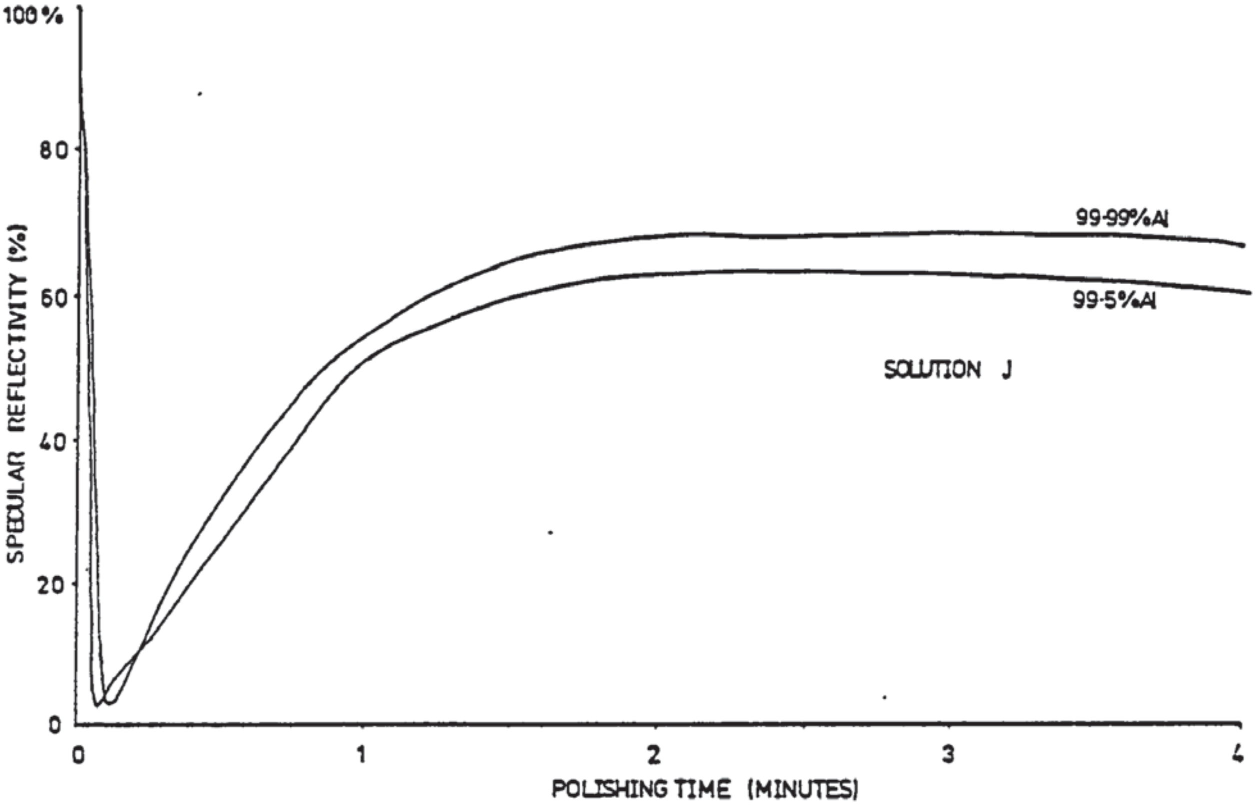


Fig.4.3. Specular Reflectivity vs. Polishing Time

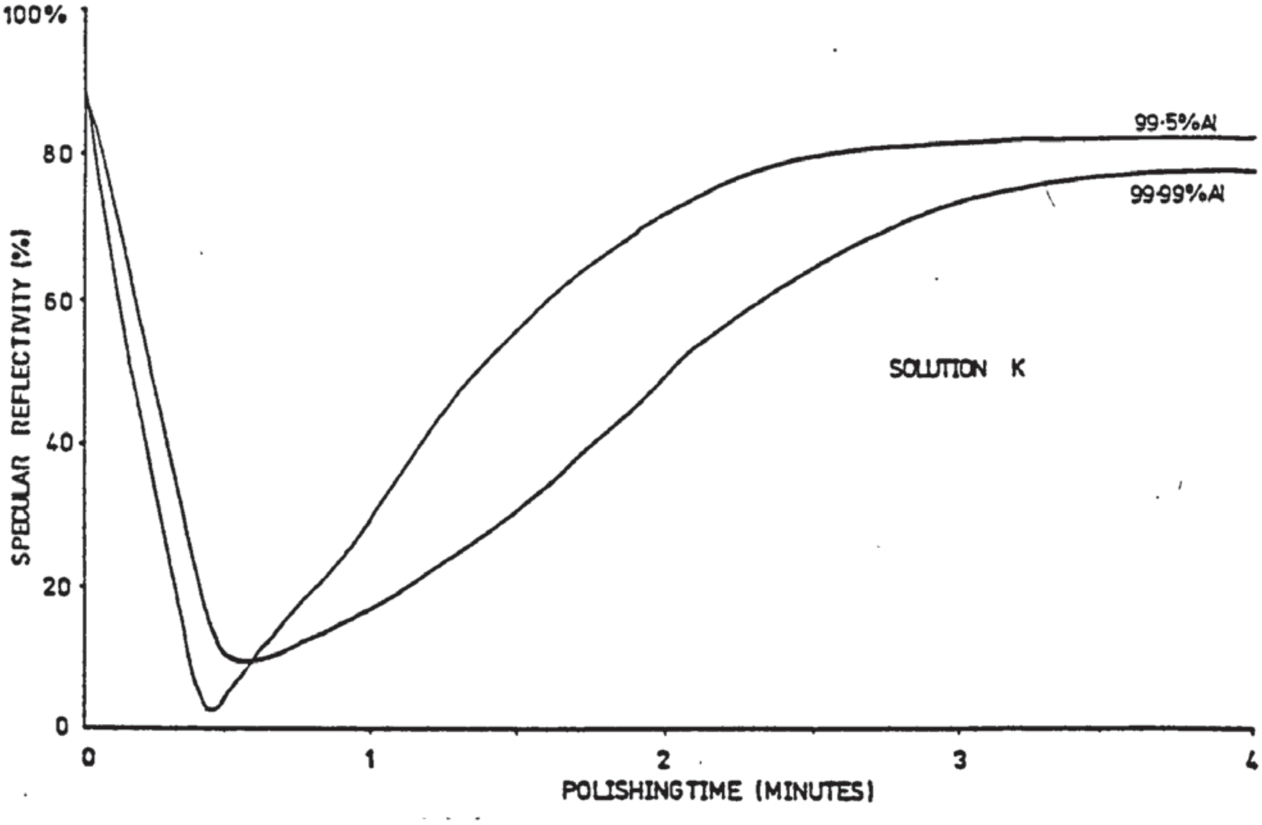


Fig.4.4. Specular Reflectivity vs. Polishing Time.

of B.T.A. was found to be the optimum. The 99.5% aluminium gave the highest reflectivity, and a higher reflectivity than the 99.99% aluminium (Fig.4.4). The results were generally lower than would be acceptable commercially as they were appreciably lower than those produced in solution H.

### 4.3. The effect of extended drain time on the Specular Reflectivity

As the 99.99% aluminium produced a low specular reflectivity in solution G even with 0 seconds drain time, only the 99.5% aluminium was studied in this section.

Specimens of 99.5% aluminium 5cm x 10cm were polished in solution G for three minutes, and were held above the solution for times of 5,10,20 40 and 60 seconds to drain, they were then rinsed in deionised water and then acetone, and dried in air.

After approximately 5 seconds a vigorous reaction occured, on the surface which continued for 40 seconds producing a white foam. During this reaction nitric oxide was evolved. As the drain time was extended the amount of copper deposited on the surface increased. Removal of this copper in a 50% (by vol.) nitric acid solution left a bluish-white film on the surface, which could not be removed.

As the drain time was increased the image clarity decreased (Fig.4.5)

### 4.4 Scanning Electron Microscopy

#### 4.4.1. Solution G (1.6:1 ratio $H_3PO_4$:$H_2SO_4$,no B.T.A.) 99.99% Al.

In the early stages of polishing the surface had the same etched appearance as had been found in previous solutions. There was little evidence of deposited copper after 10 seconds polishing (Fig.4.6). Structures, relatively rich in sulphur, were visible on the surface after 30 seconds polishing (Fig.4.7 & 4.8). Polishing for 60 seconds produced a change in the morphology of these structures (Fig.4.9). The aluminium

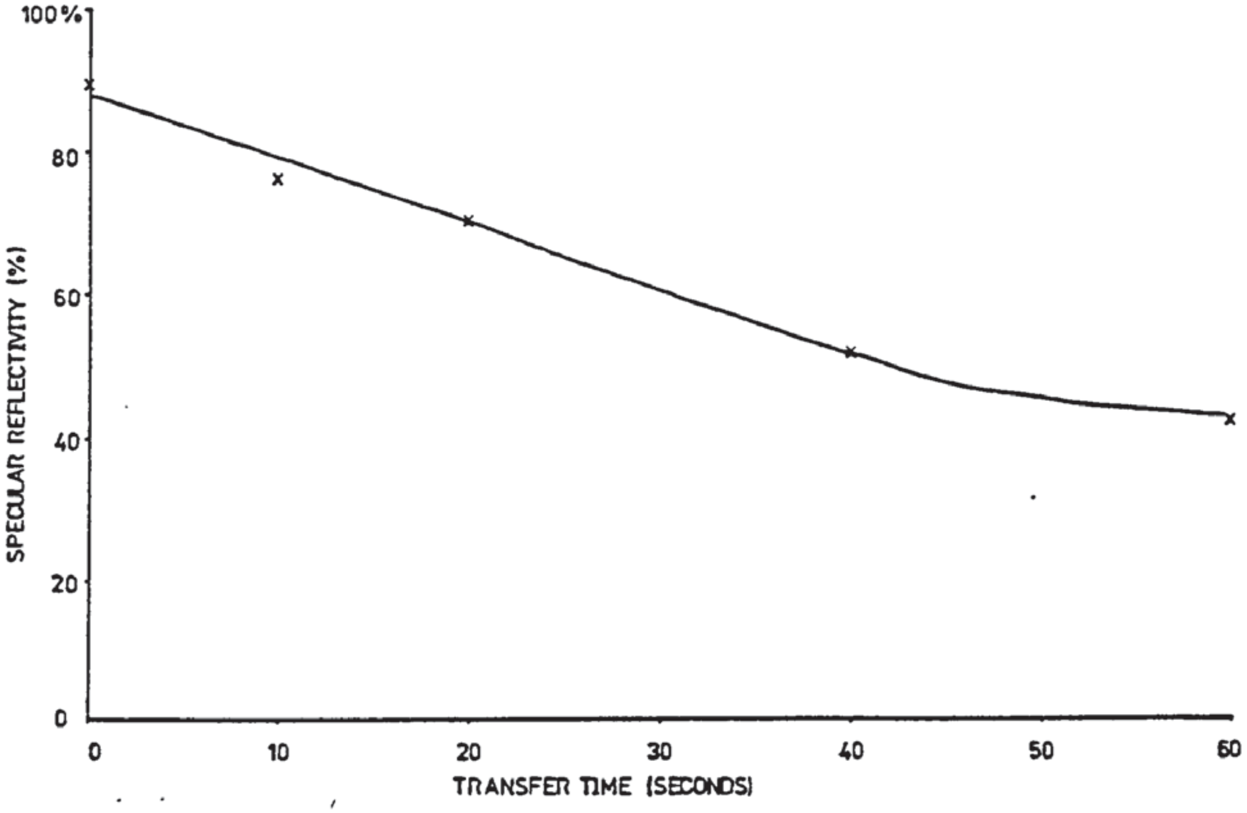


Fig.4.5. Specular Reflectivity vs. Specimen Transfer Time for 99.99% Aluminium in Solution G.

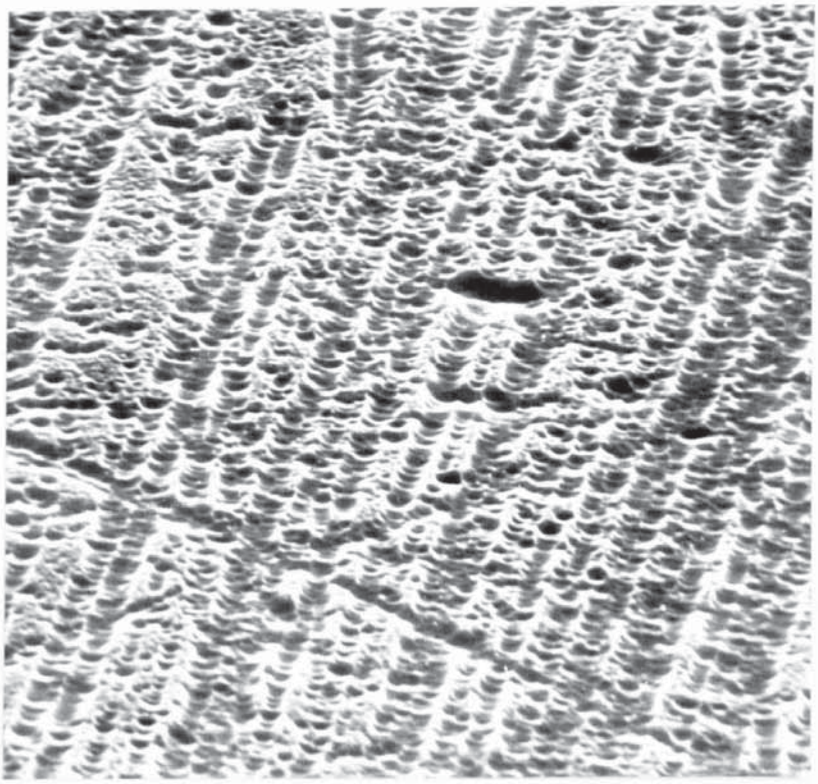


Fig.4.6. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution G for IO seconds. X 2000.

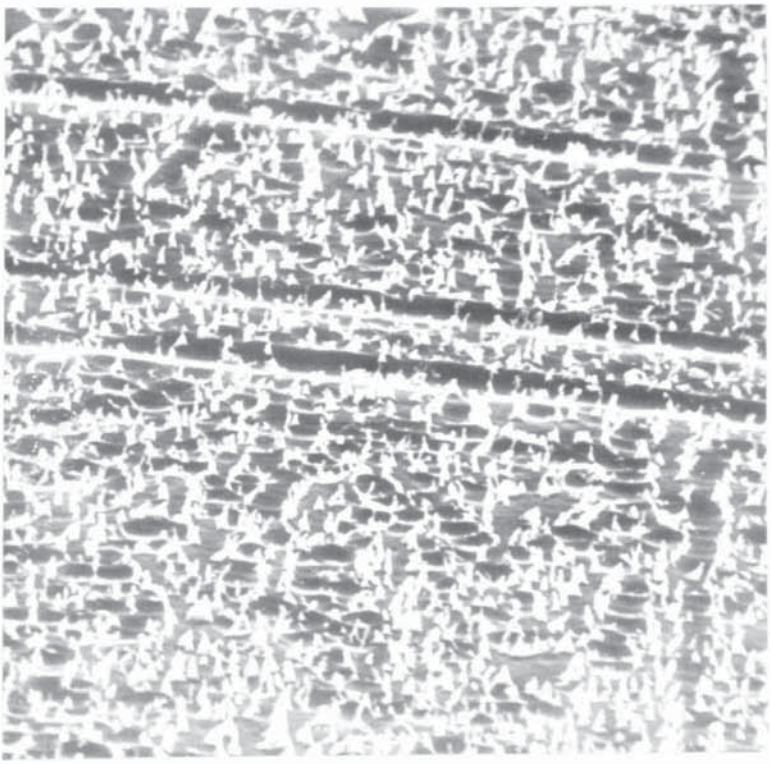


Fig.4.7. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution G for 30 seconds. X 2000.

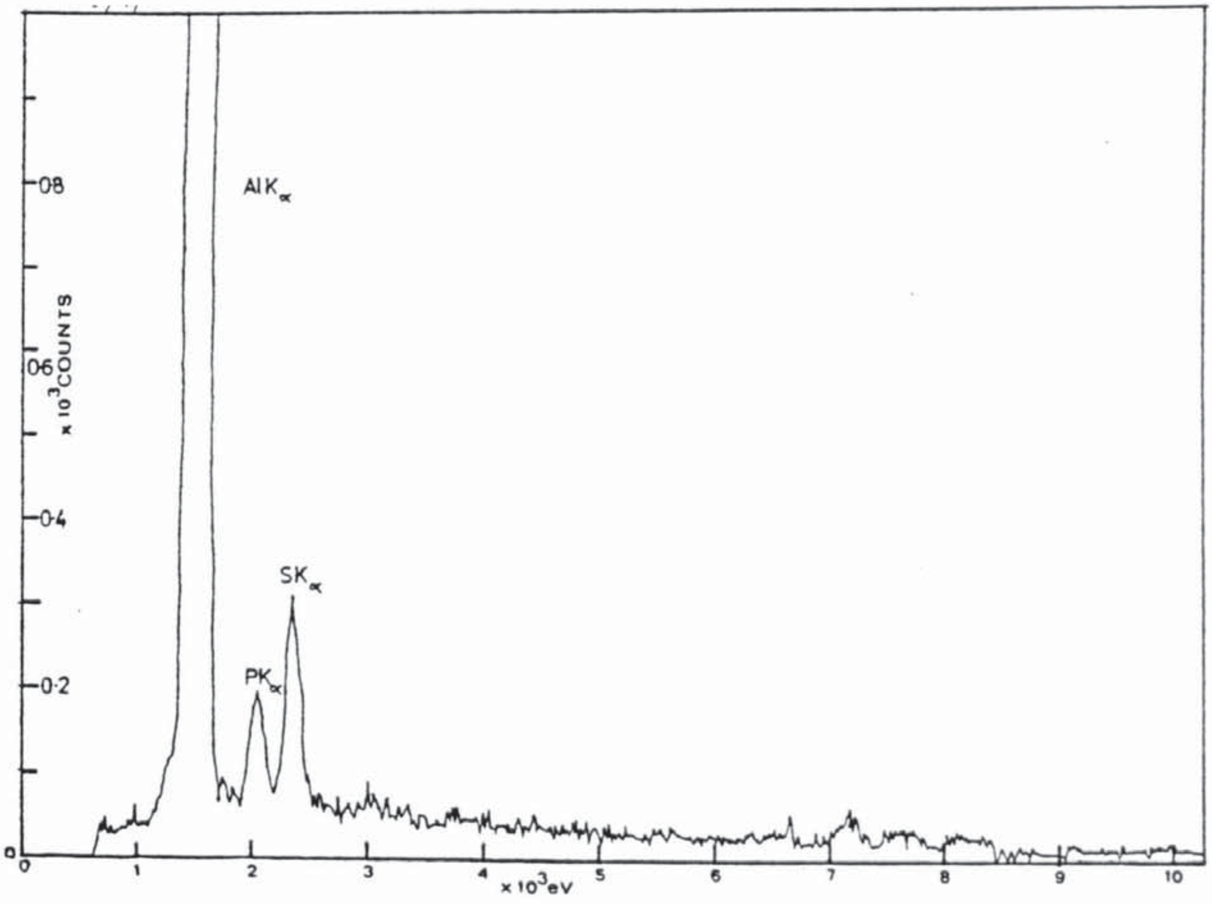


Fig.4.8. 'Kevex' x-ray analysis of the surface structures in Fig.4.7. above.

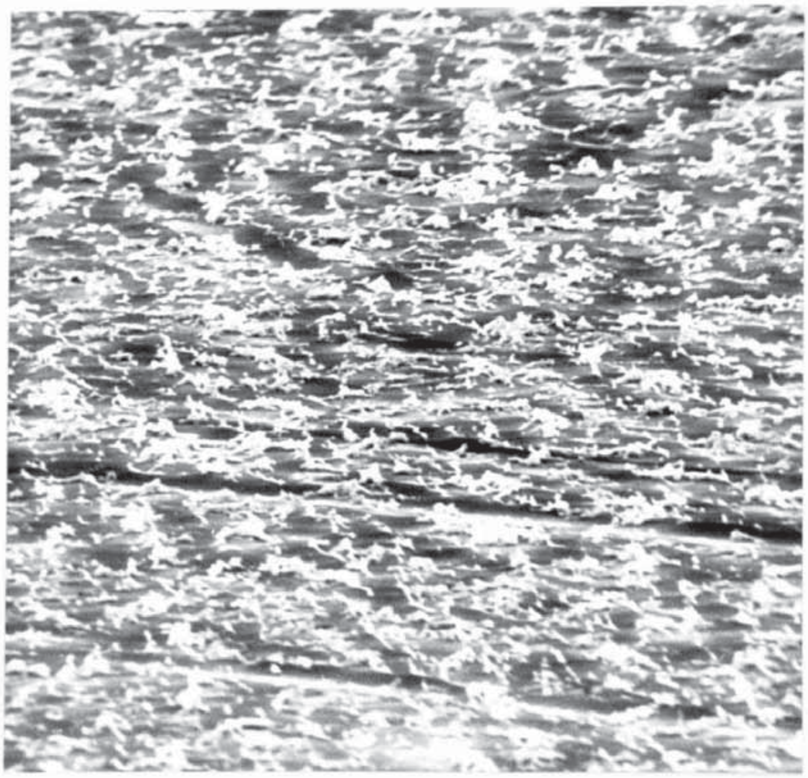


Fig.4.9. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution G for 60 seconds. X 2000.

had been levelled after 120 seconds polishing, and the structures found on the surface had accumulated into relatively localised clumps (Fig.4.10). Copper was detected on this surface (Fig.4.11). There was no change in surface morphology with further polishing. Removal of the deposited copper in a 50% (by vol.) nitric acid solution left a copper-free surface, a large percentage of which was covered with the structures found on the earlier samples (Fig.4.12).

### 4.4.2 Solution G (1.6:1 ratio $H_3PO_4$:$H_2SO_4$, no B.T.A.) 99.5% Al.

The 99.5% aluminium in this solution exhibited the same changes in surface structure as it had in solution E. The surface after 180 seconds polishing and with the deposited copper removed in a 50% (by vol) nitric acid solution (Fig.4.13) was free from any serious defects, although some pitting is visible, it was not sufficient to cause a significant loss in image clarity.

### 4.4.3. Solution H (1.6:1 ratio $H_3PO_4$:$H_2SO_4$, & 2.8g/l B.T.A.) 99.99% Al.

Fig. 4.14 shows the surface after 180 seconds polishing in this solution. Earlier samples had shown the same changes in surface morphology as had been found in solution E. The difference after 180 seconds polishing in this solution was the presence of relatively large isolated deposits of copper on the surface with no preferential dissolution in their vicinity, which had been the case in solution D (no nitric acid & 1g/l Cu).

Removal of this deposited copper in a 50% (by vol.) nitric acid solution (Fig.4.15) revealed a comparatively defect free surface. Some undissolved copper remained on the surface.

### 4.4.4. Solution H (1.6:1 ratio $H_3PO_4$:$H_2SO_4$,& 2.8g/l B.T.A.) 99.5% Al.

The changes in the surface structure in this solution appeared identical to those in solution G.

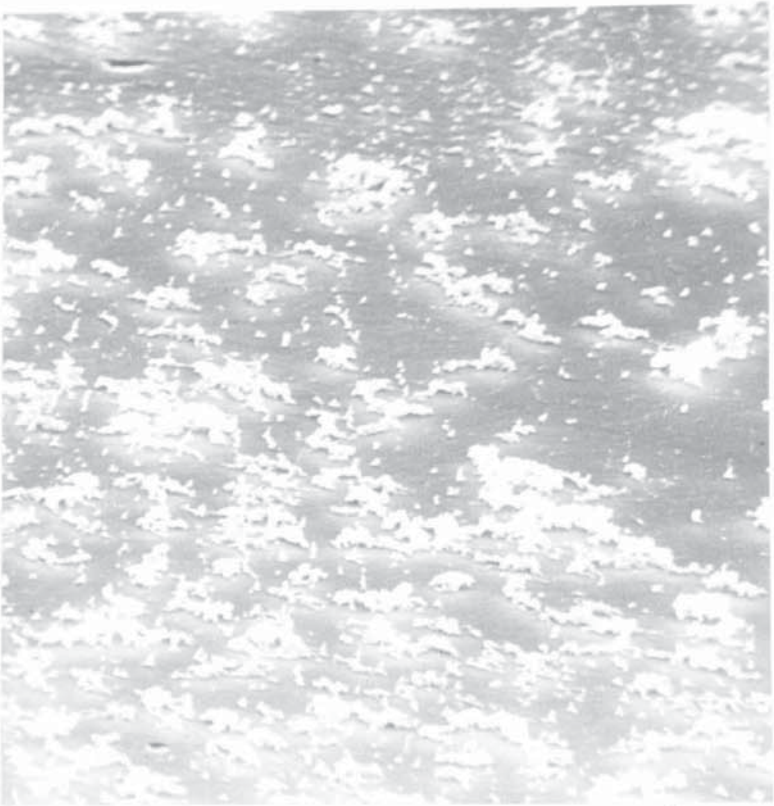


Fig.4.I0. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution G for I20 seconds. X2000.

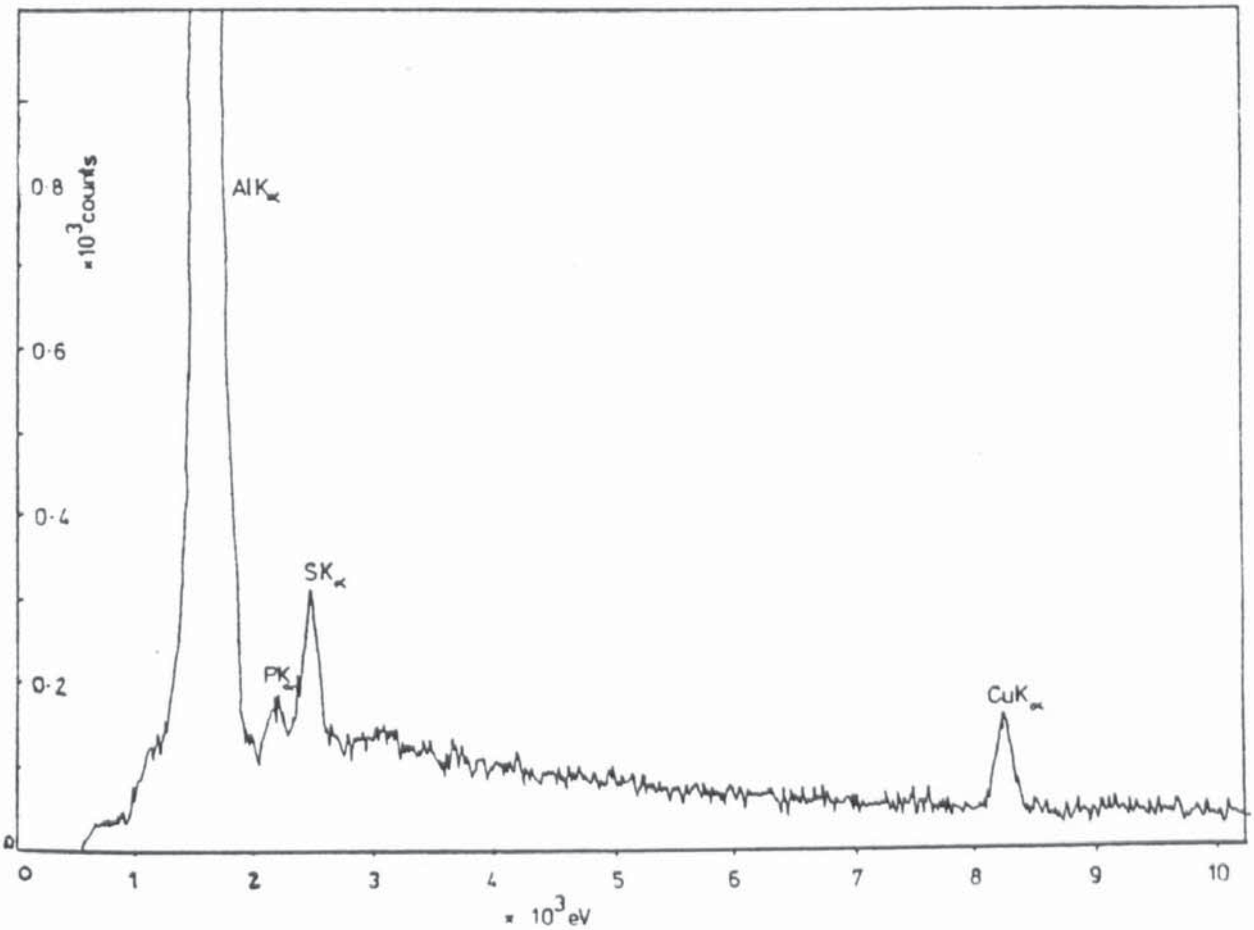


Fig.4.II. 'Kevex' x-ray analysis of the surface in Fig.4.I0 above.

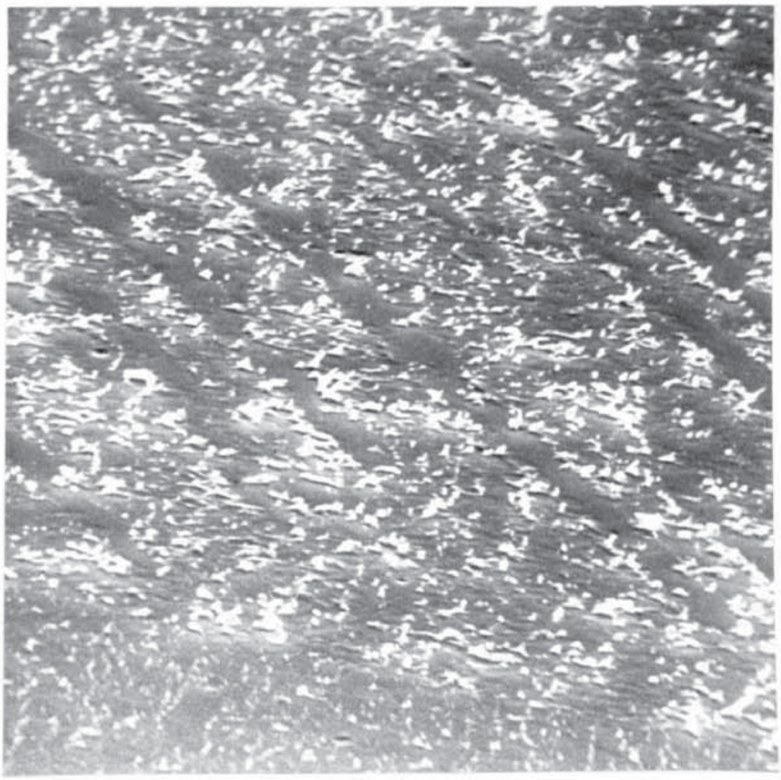


Fig.4.I2. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution G for I20 seconds. X 2000.

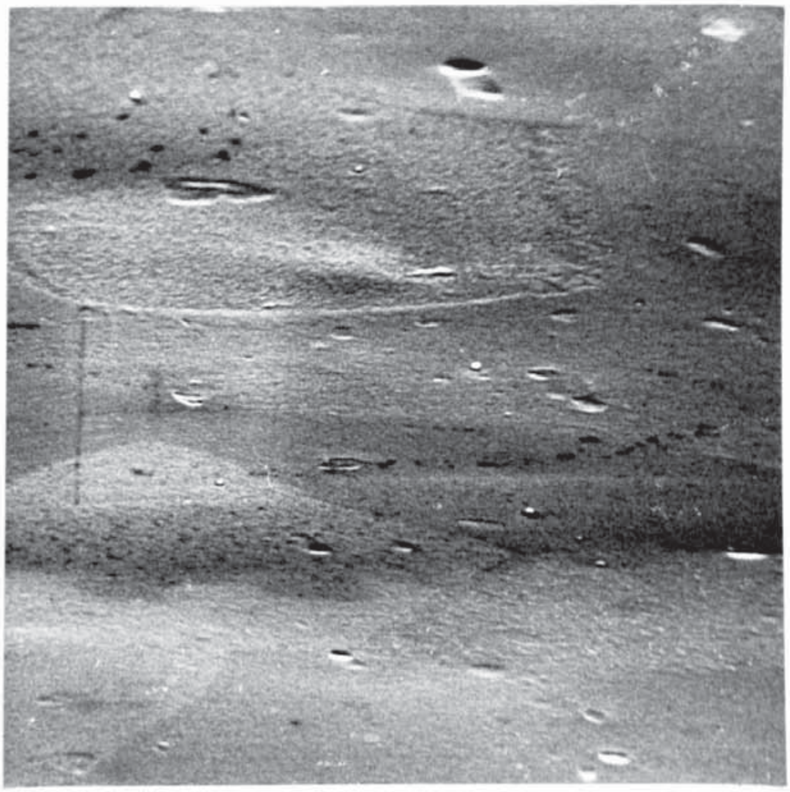


Fig.4.I3. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution G for I80 seconds, with the deposited copper removed. X 2000.

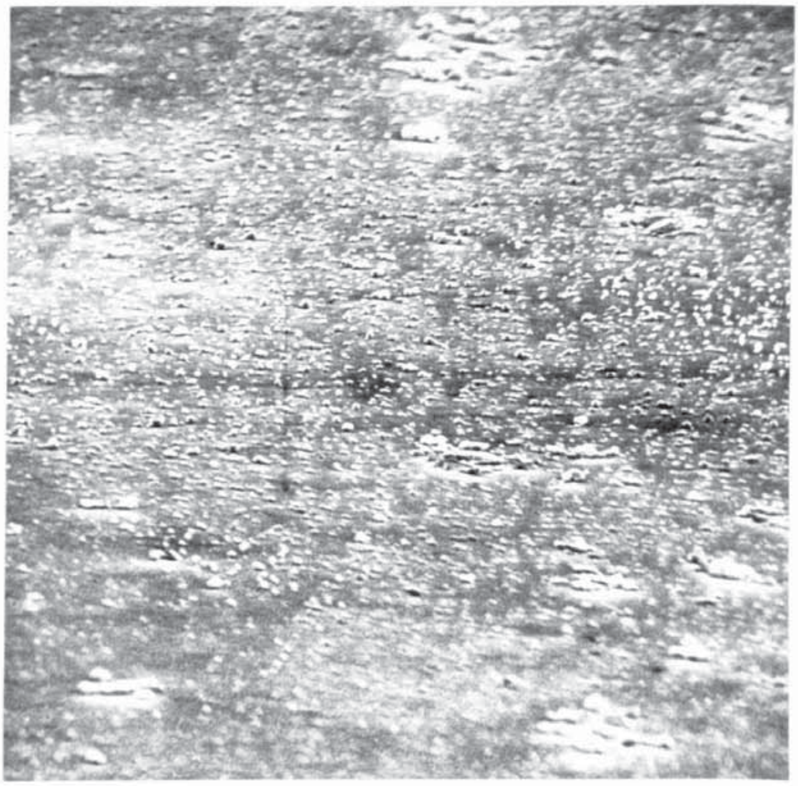


Fig.4.I4. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution H for I80 seconds. X 2000.

Fig.4.I5. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution H for I80 seconds, and after immersion in a 50%(by Vol.) nitric acid solution. X I0,000.

### 4.4.5. Solution J (1:1 ratio $H_3PO_4$:$H_2SO_4$,& no B.T.A.) 99.99% Al.

The surface after 60 seconds polishing in this solution was still considerably etched, and had the same type of structures found on 99.99% Al. in solution G, although in this instance the amount was less (Fig. 4.16). No copper was detected on the surface at this time of polishing. Polishing for 180 seconds levelled the etched surface (Fig.4.17). The surface structures were now grouped into distinct regions, which had deposited copper, and a relatively large amount of sulphur (Fig.4.18). Although it was not possible to distinguish the copper deposits on the surface Figs. 4.19 & 4.20 show the surface of one of these regions before and after the removal of the copper in a 50% (by vol) nitric acid solution.

### 4.4.6 Solution J (1.1 ratio $H_3PO_4$:$H_2SO_4$, no B.T.A.) 99.5% Al

The surface of the 99.5% aluminium after 30 seconds polishing (Fig.4.21), was quite different from the 99.99% aluminium. The surface had a large number of pyramidal shaped structures whose size and separation depended on the grain orientation. Analysis of one of the larger structures on the right of Fig.4.22 gave a high sulphur count. After 60 seconds polishing the extent of the coverage of these structures had decreased (Fig.4.23). The surface after a further 180 seconds polishing (Fig.4.24) had a levelled appearance with some evidence of pitting. The surface sulphur rich structures were now more or less structureless and did not cover all of the surface (Fig.4.25). Analysis of one of the larger particles revealed the presence of copper with the sulphur. Removal of the copper in a 50% (by vol) nitric acid solution showed that the deposited copper accounted for few of the surface structures (Fig.4.26).

### 4.4.7 Solution K (1.1 ratio $H_3PO_4$:$H_2SO_4$, & 10g/1 B.T.A.) 99.99% Al.

The etching stage in this solution was considerably extended, as

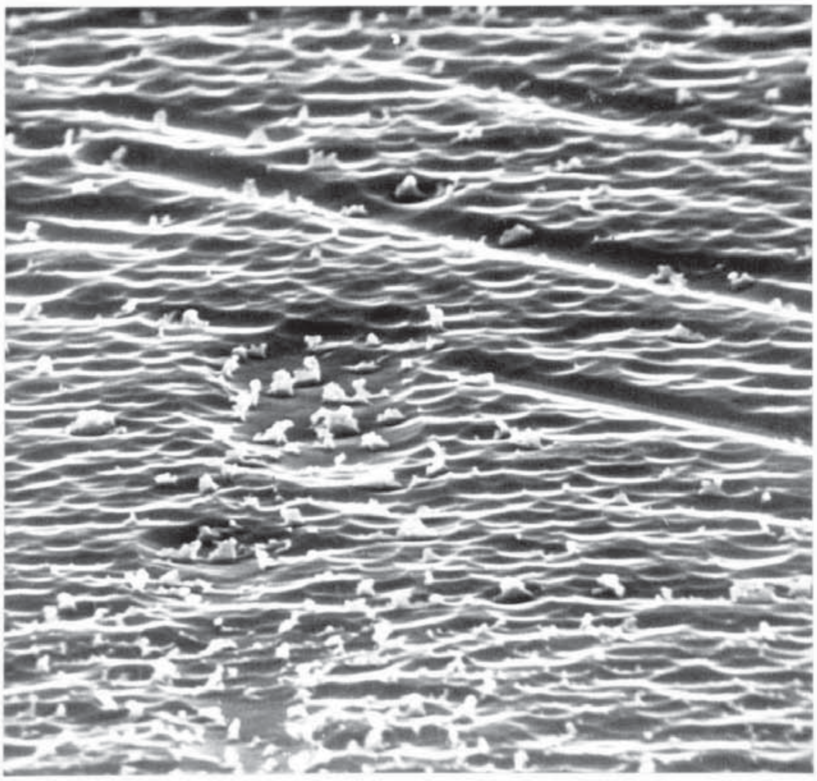


Fig.4.16. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution J for 60 seconds. X 2000.

Fig.4.17. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution J for 180 seconds. X 1000.

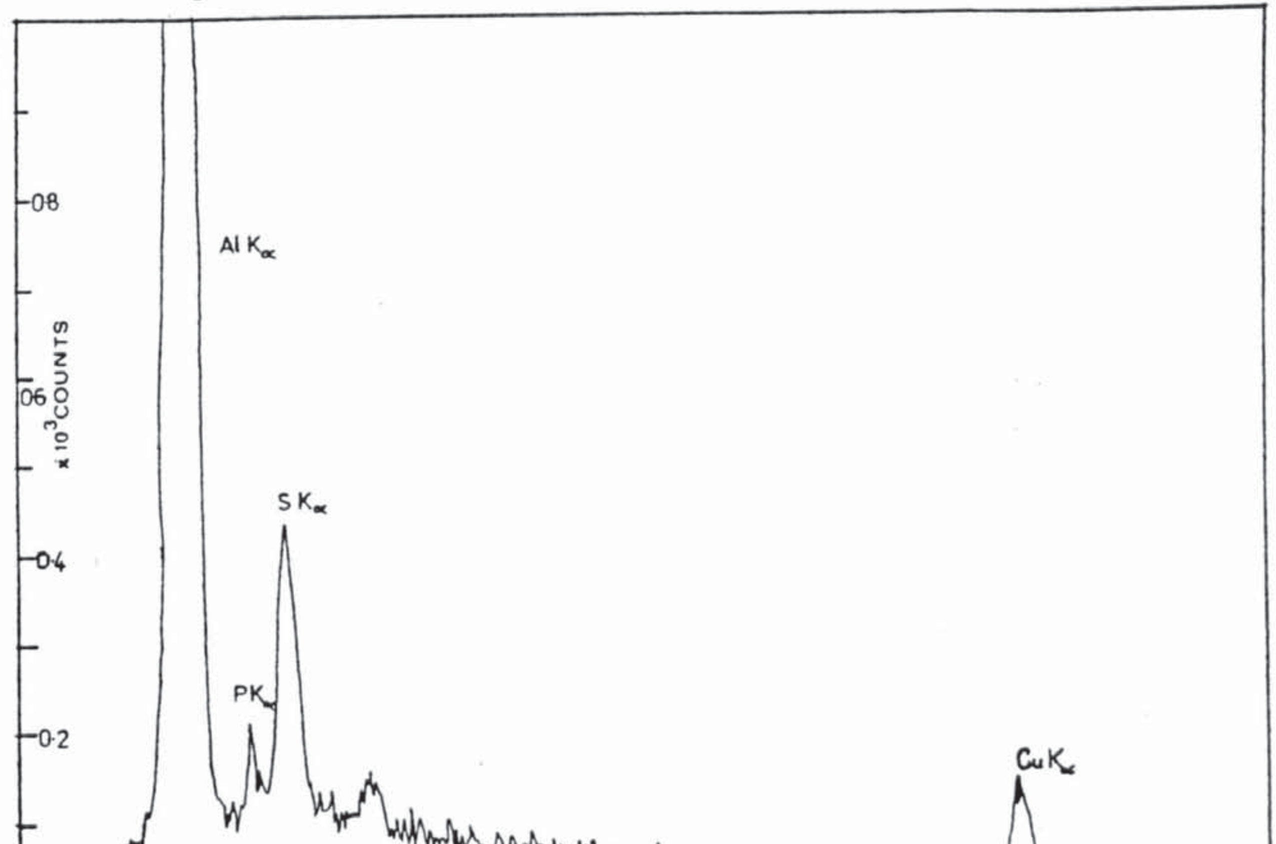


Fig.4.18. 'Kevex' x-ray analysis of the particles in Fig.4.17. above.

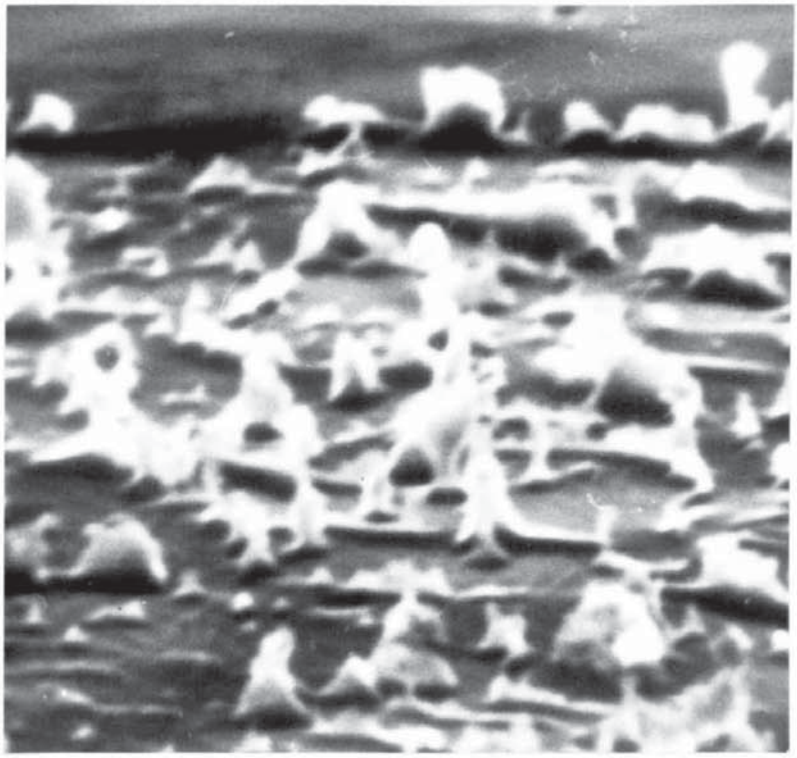


Fig.4.I9. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution J for I80 seconds. X I0,000.

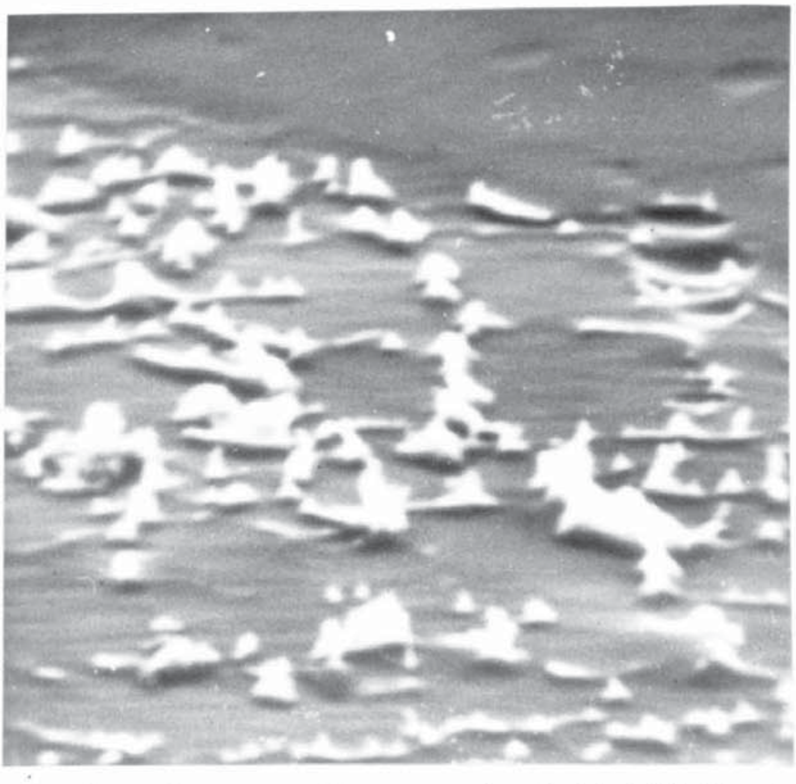


Fig.4.20. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution J for I80 seconds, with the deposited copper removed. X I0,000.

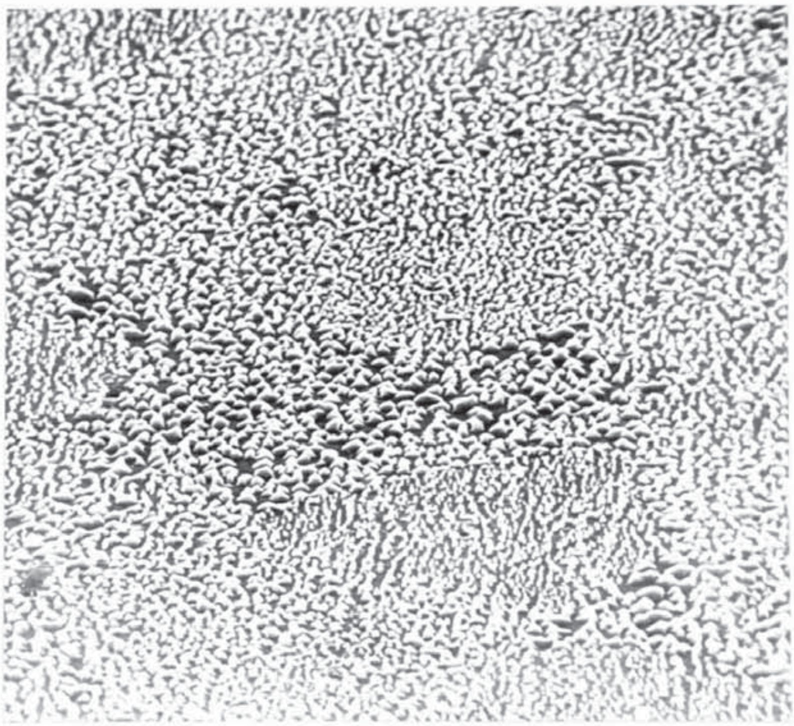


Fig.4.2I. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution J for 30 seconds. X 1000.

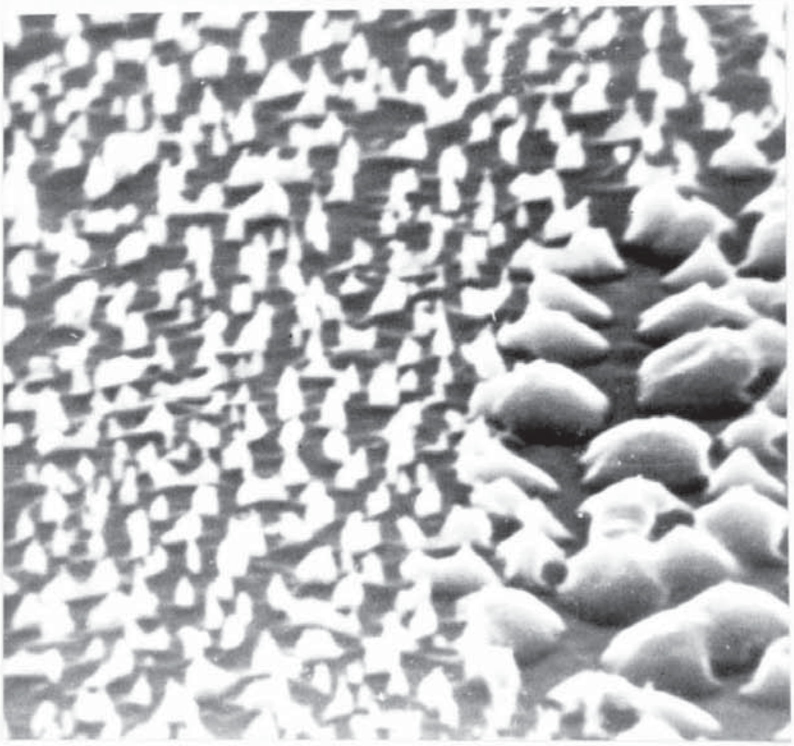


Fig.4.22. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution J for 30 seconds. X 5000.

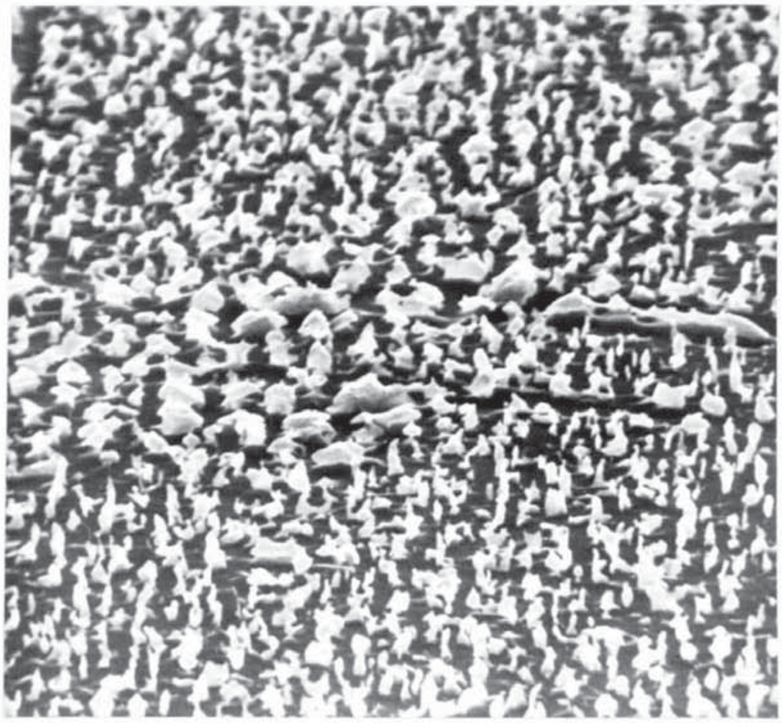


Fig.4.23. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution J for 60 seconds. X 5000.

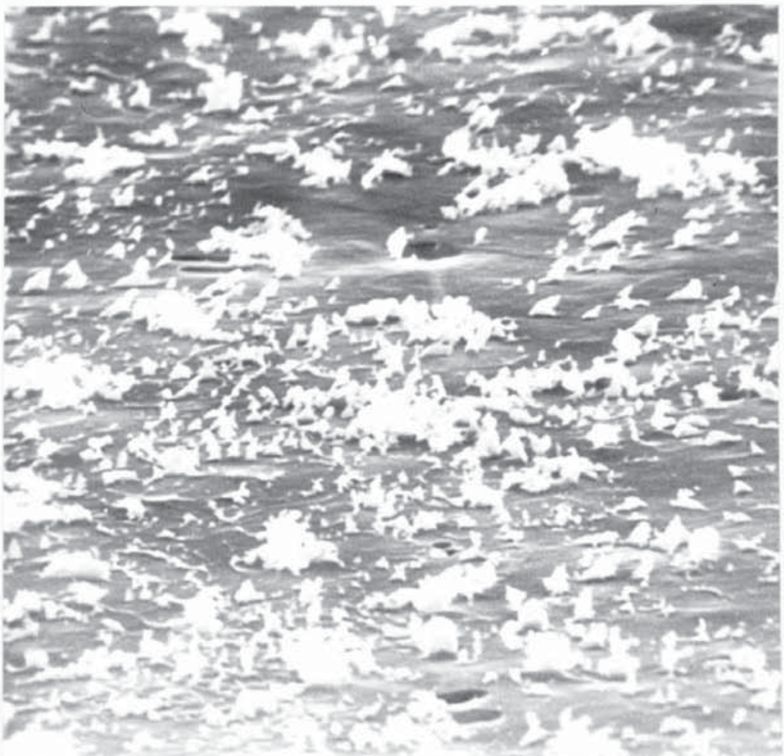


Fig.4.24. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution J for 180 seconds. X 2000.

Fig.4.25. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution J for 180 seconds. X 2000.

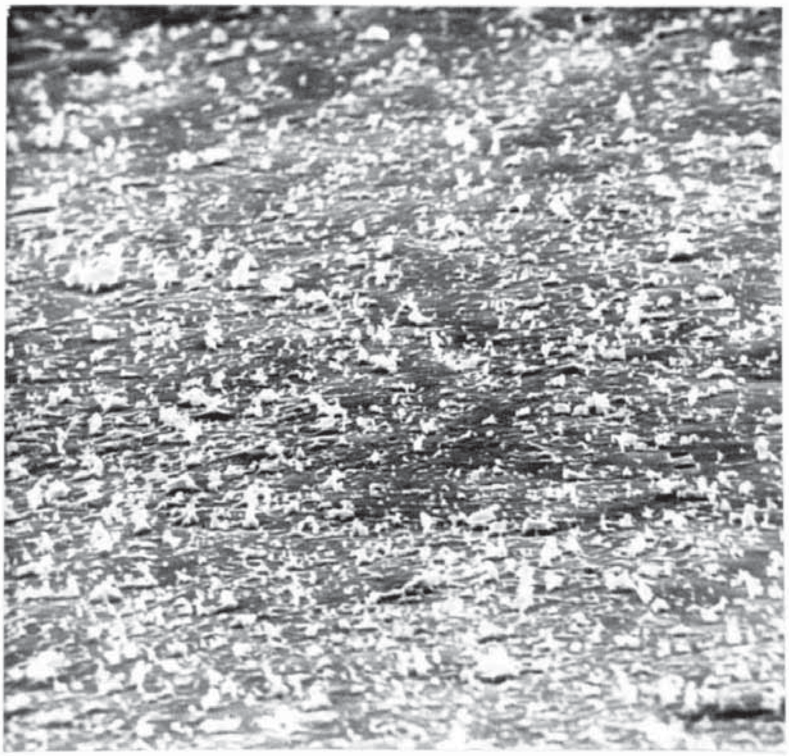


Fig.4.26. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution J for 180 seconds. X 1,100.

can be seen in Fig.4.27, which shows the surface after 60 seconds polishing. Even after 180 seconds polishing (Fig.4.28) the etched network had not been levelled. In addition to this, very little copper was detected, but no evidence of the sulphur rich structures present on the aluminium in the previous solution H, containing benzotriazole, was found.

### 4.4.8 Solution K (1:1 ratio $H_3PO_4$:$H_2SO_4$, & 10g/l B.T.A) 99.5% Al.

The addition of 10g/l benzotriazole to this solution considerably reduced the incidence of the pyramidal structures found after 30 seconds polishing in the solution not containing bezotriazole, (Fig.4.29). With 60 seconds polishing (Fig.4.30), the last remaining traces of these structures had disappeared. Copper deposition was evident along the ridges of sub-micro patterns (Fig.4.31). The copper deposition after 180 seconds polishing did not however remain as evenly dispersed small deposits, but grew to form localised large particles, (Fig.4.32). These large copper deposits had not caused preferential dissolution in their vicinity. Removal of the copper in a 50% (by vol) nitric acid solution revealed a fairly even surface although there was some pitting due to iron rich inclusions (Fig.4.33), and the sub-micro patterns were relatively coarse.

### 4.4.9 The effect of extended transfer time on surface morphology

The effect on specular reflectivity of an extended drain time has been shown in Fig.4.5. The reflectivity drops quite significantly after 10 seconds draining to a commercially unacceptable level. This had been assumed to be due to an etching of the surface attributable to the large amounts of copper deposited onto the surface during the transfer. The amount of copper on the surface after the specimens had been rinsed in de-ionised water was noticably greater as the drain time was increased.

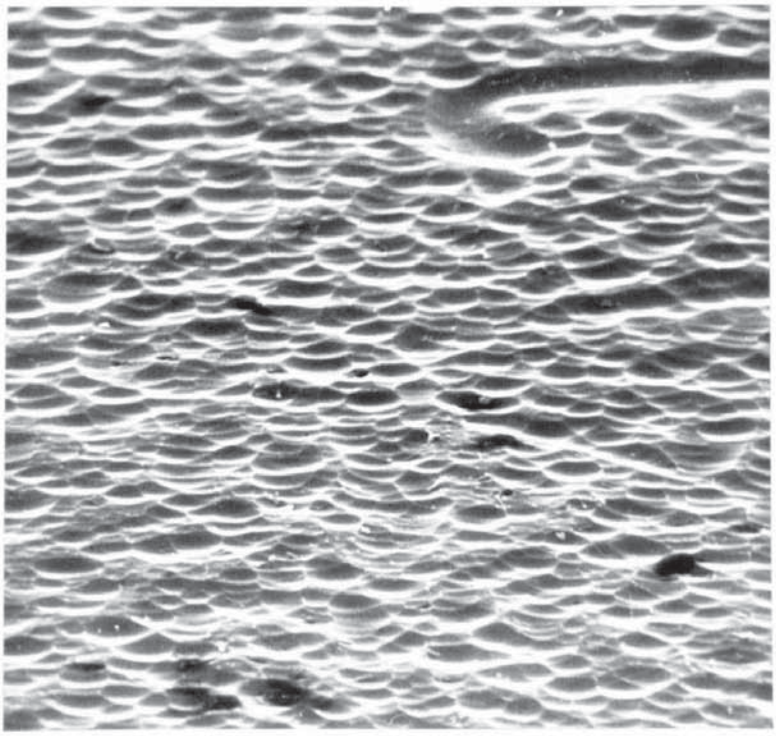


Fig.4.27. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution K for 60 seconds. X 2,400.

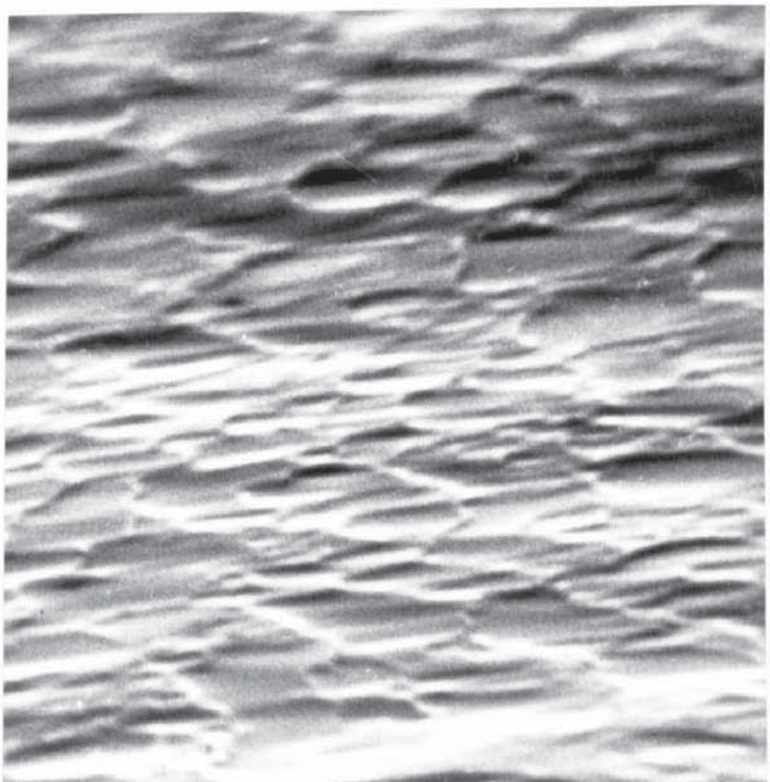


Fig.4.28. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution K for 180 seconds. X 12,000.

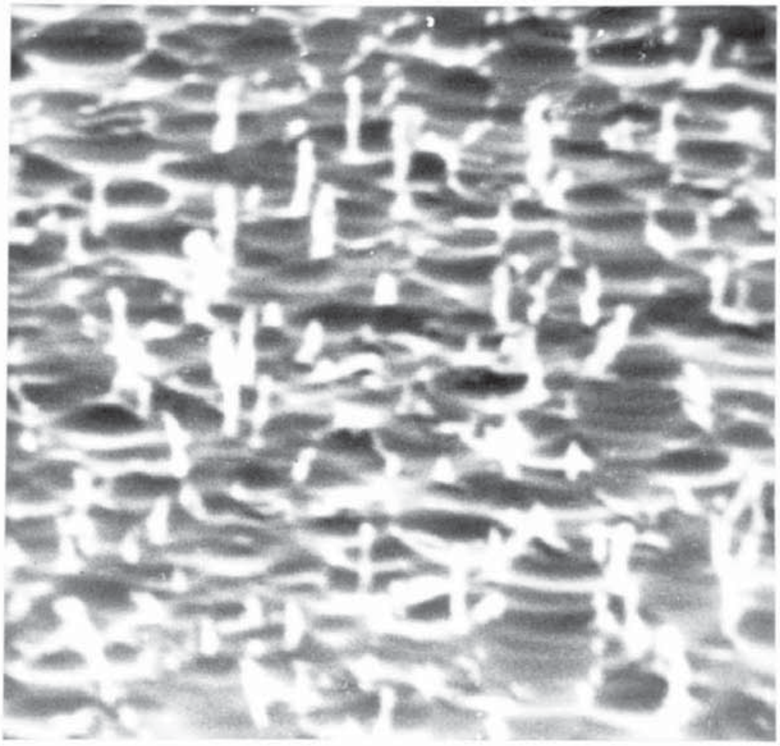


Fig.4.29. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution K for 30 seconds. X 10,000.

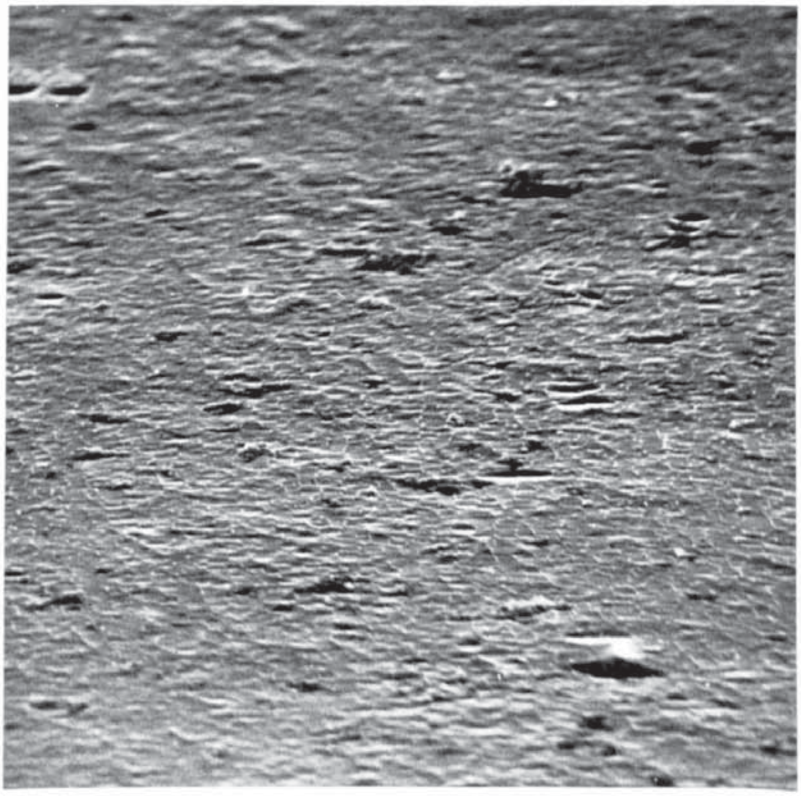


Fig.4.30. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution K for 60 seconds. X 2000.

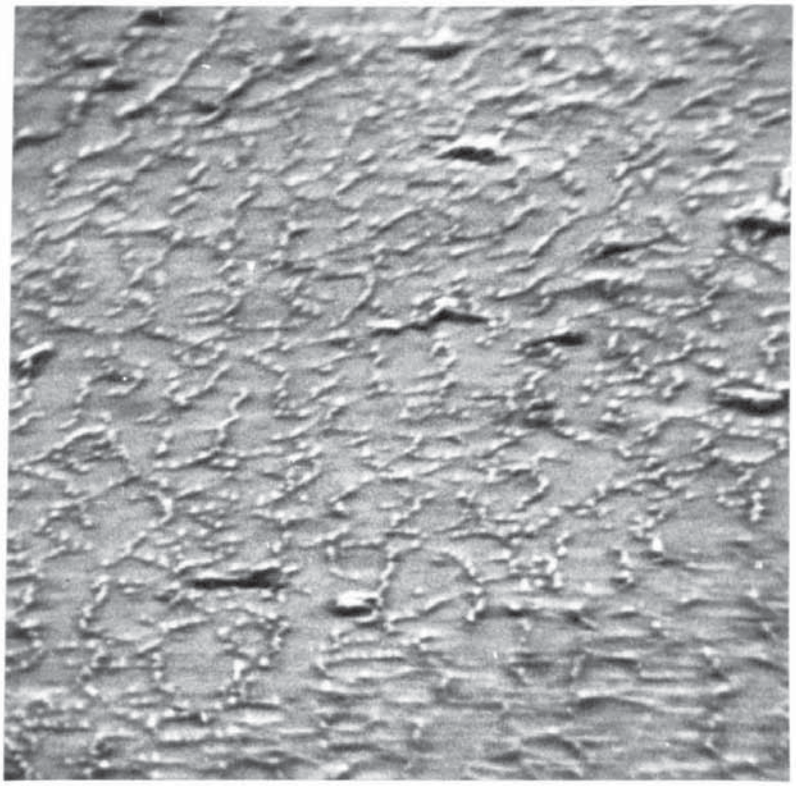


Fig.4.3I. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution K for 60 seconds. X 5000.

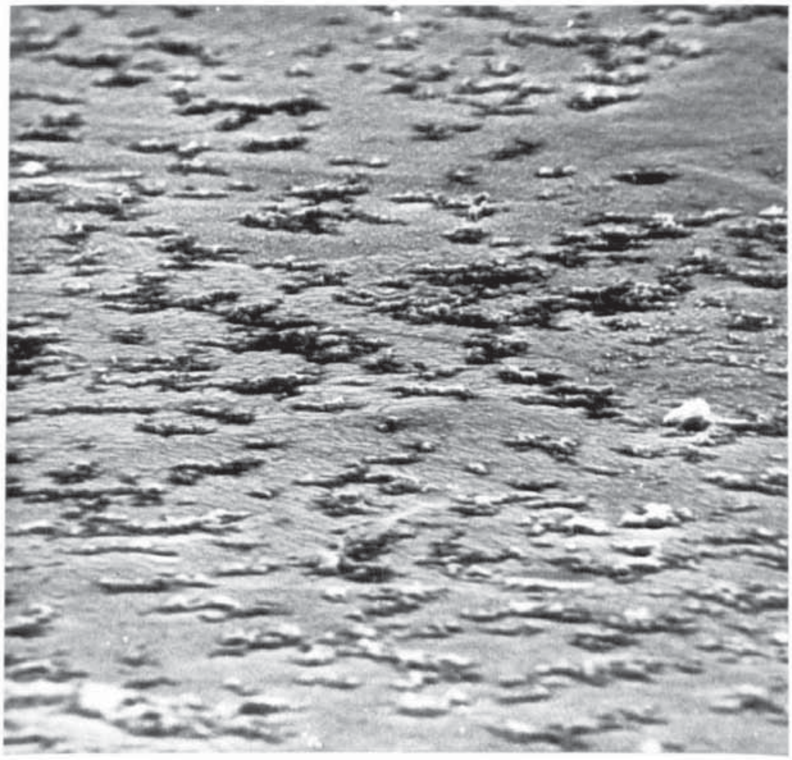


Fig.4.32. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution K for I80 seconds. X 2000.

Fig.4.33. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution K for 180 seconds, with the deposited copper removed. X 5000.

Figs.4.34 to 4.37 are scanning electron micrographs of the surface after 10,20,40 and 60 seconds draining, respectively, and show this increase in copper deposition. The top region of the panels drained more rapidly than the lower regions and did not show the same extensive copper deposition (Fig.4.38).

The removal of the copper in a 50% (by vol) nitric acid solution revealed structures on the surface (Fig.4.39) similar to those found on the 99.5% aluminium after polishing in solution J (1:1 ratio phosphoric acid to sulphuric acid and no B.T.A), for 30 seconds. The structures formed in this instance were also found to be relatively rich in sulphur (Fig.4.40). The region at the top of the specimen with relatively little deposited copper showed considerably fewer of these structures (Fig.4.41).

The addition of 2.8g/l of B.T.A. into the solution significantly reduced the amount of copper deposited on the surface during transfer. Fig.4.42 shows the surface after 3 minutes polishing and 60 seconds draining, and exhibits this reduction in copper deposition. A similar sample with this copper removed (Fig.4.43) reveals the absence of any surface features, apart from some pitting due to the influence of the predominantly iron rich intermetallic particles.

## 4.5 Potential Time Determinations

As the work in this chapter was concerned mainly with development of an existing commercial solution, the range of the variables studied in this section was limited to those pertaining more closely to commercial conditions. Consequently the potential time determinations were limited to a shorter range of nitric acid concentrations, and all the solutions contain dissolved copper. Figs. 4.44 and 4.45 show the potential time determinations for 99.5% aluminium polished in the solutions listed in table 4.1 below:

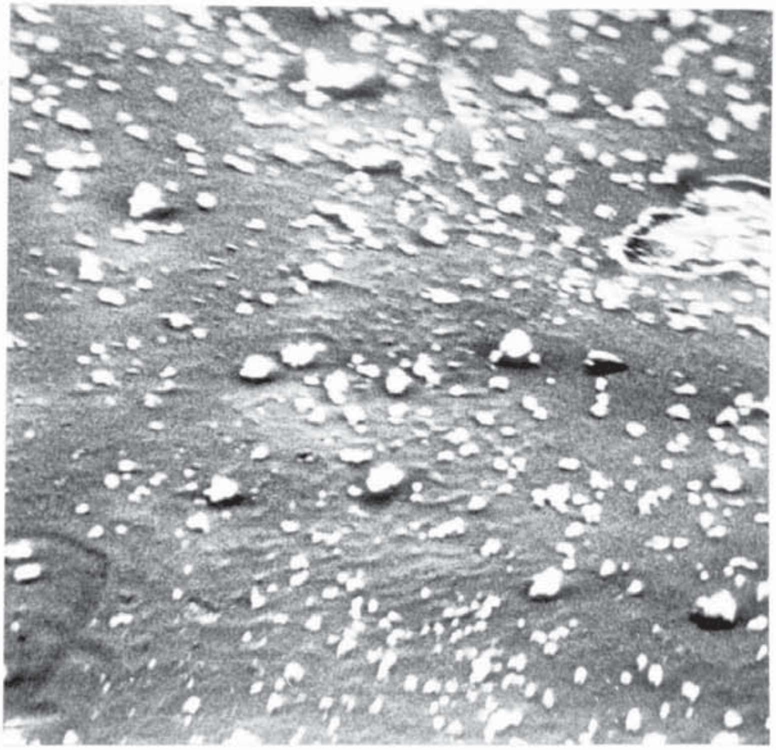


Fig.4.34. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution G for 3 minutes and drained for I0 seconds prior to rinsing in water. X 5000.

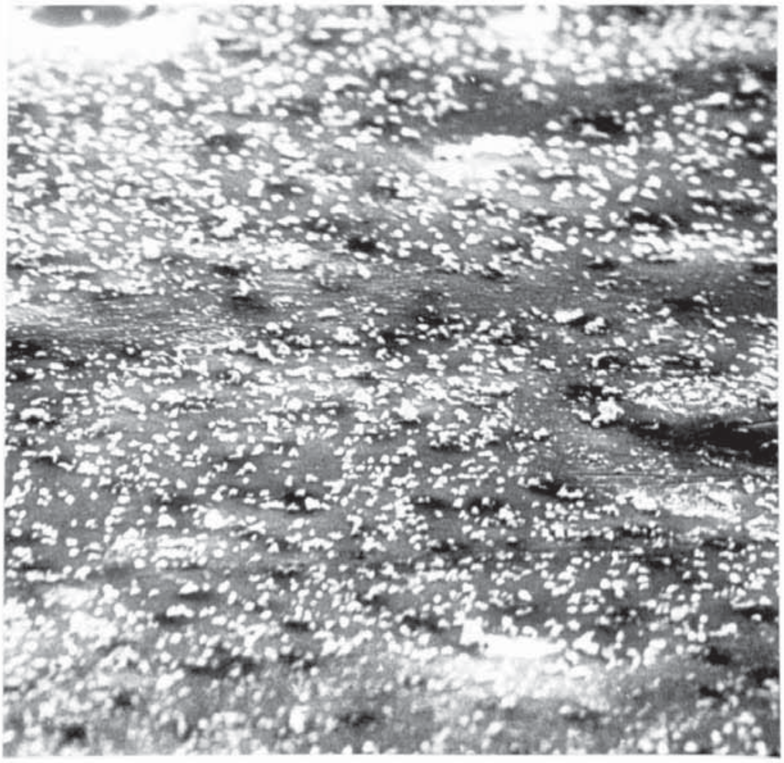


Fig.4.35. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution G for 3 minutes and drained for 20 seconds prior to rinsing in water. X 2000.

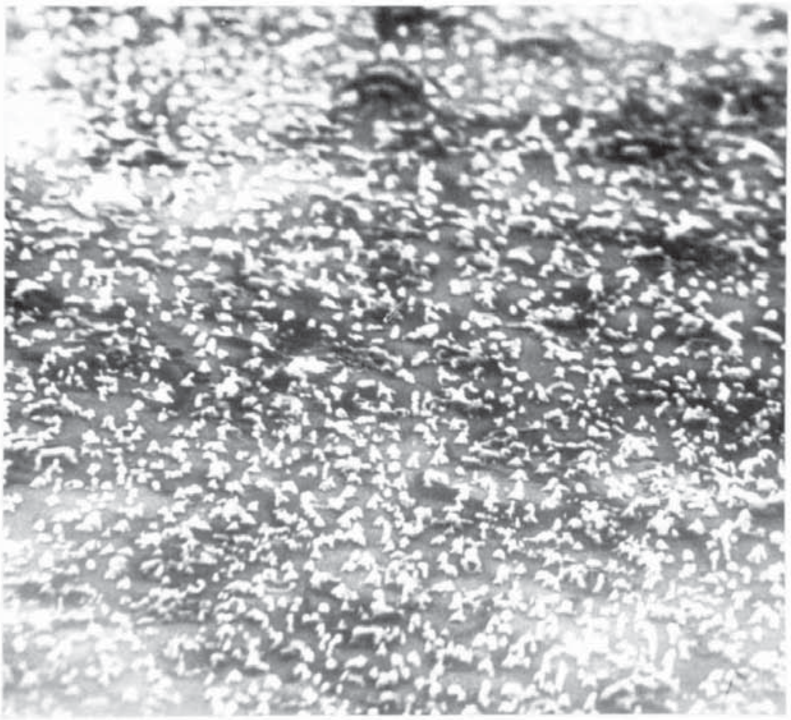


Fig.4.36. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution G for 3 minutes and drained for 40 seconds prior to rinsing in water. X 2000.

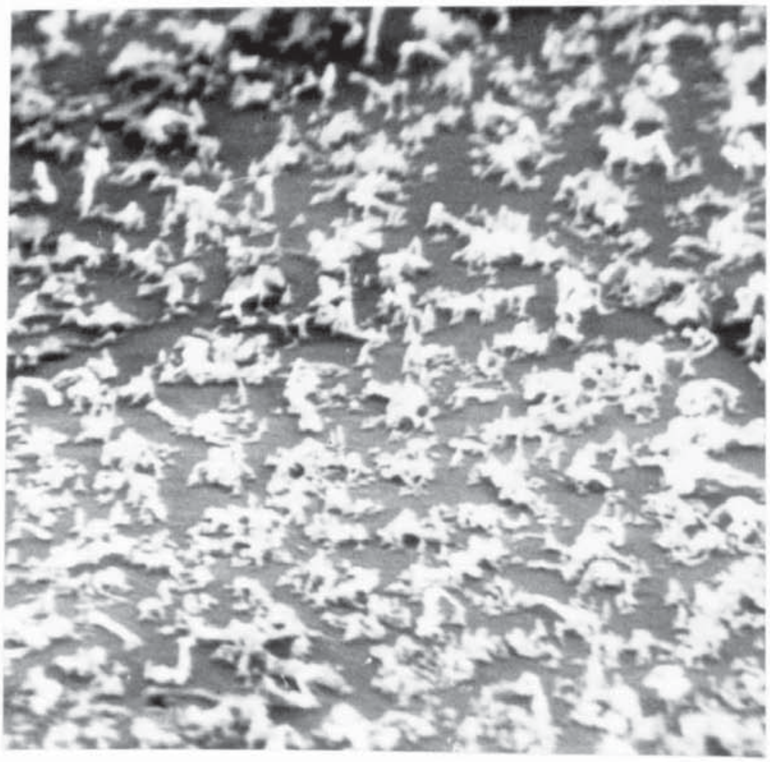


Fig.4.37 Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution G for 3 minutes and drained for 60 seconds prior to rinsing in water. X 5,500.

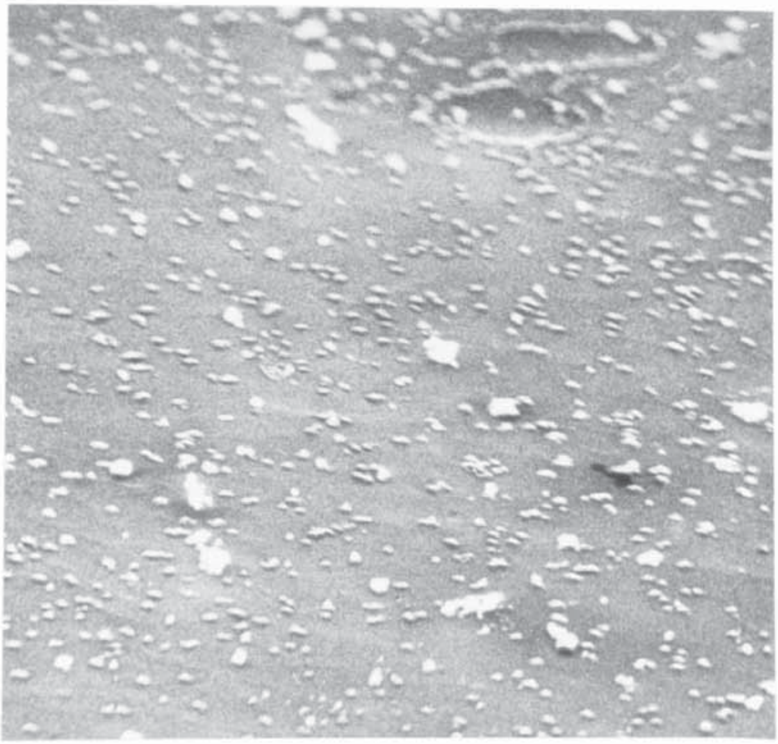


Fig.4.38. Scanning Electron Micrograph of the top region of the same specimen as shown in Fig.4.37. X 5000.

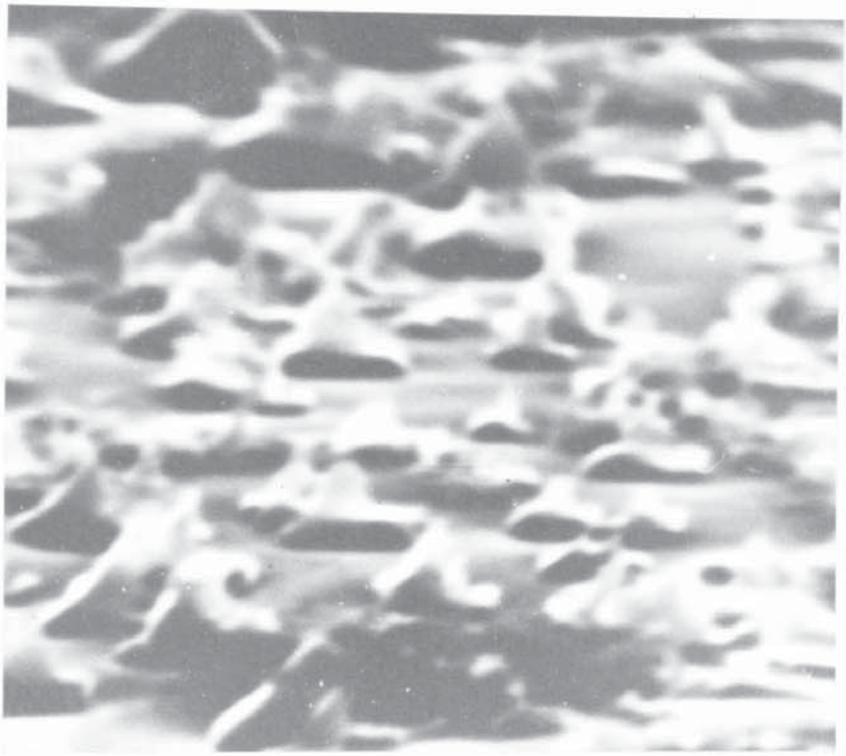


Fig.4.39. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution G for 3 minutes and drained for 60 seconds prior to rinsing in water, with the deposited copper removed. X 10,000.

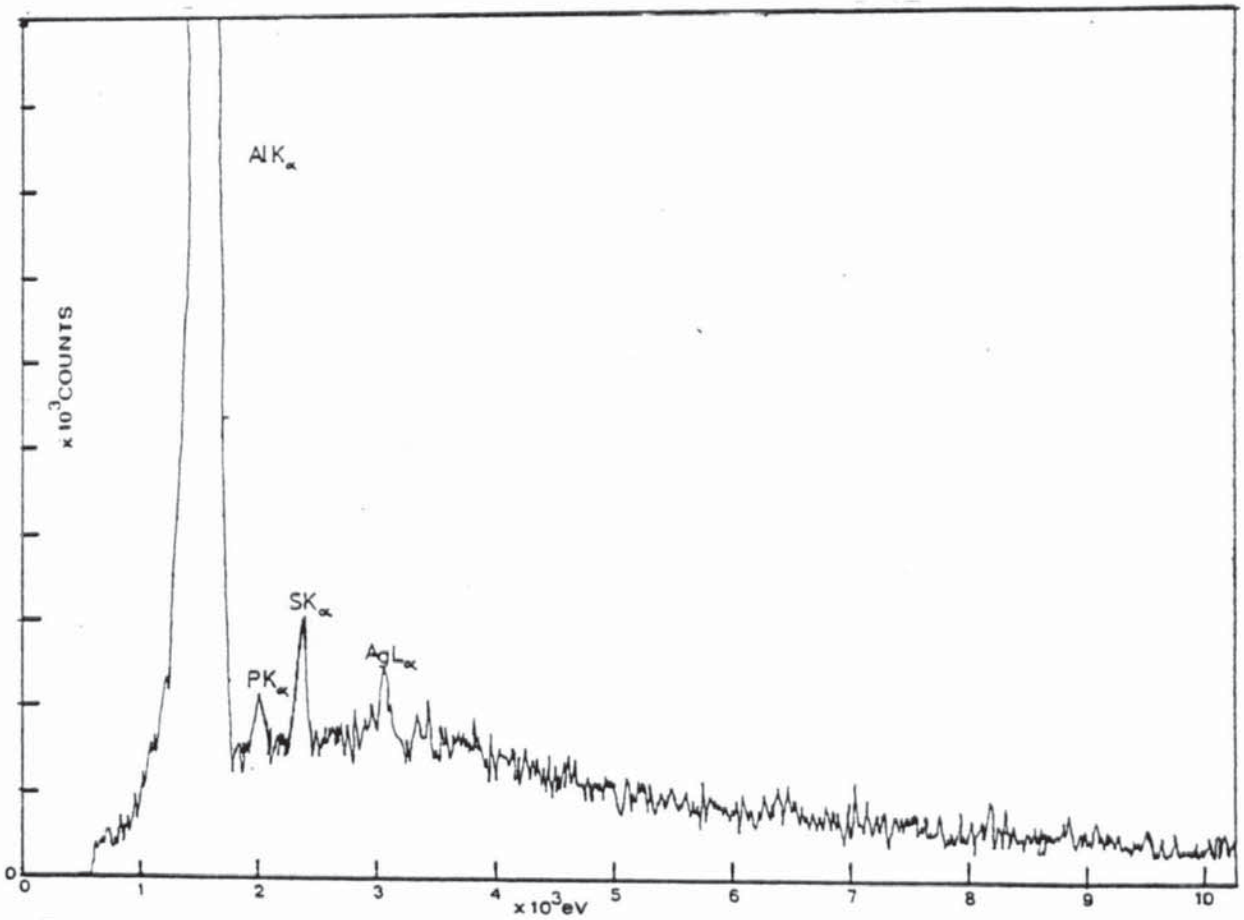


Fig.4.40. 'Kevex' x-ray analysis of the surface structures in Fig.4.39 above.

Fig.4.4I. Scanning Electron Micrograph of the top of the same specimen as shown in Fig.4.39. , with the deposited copper removed. X 2000.

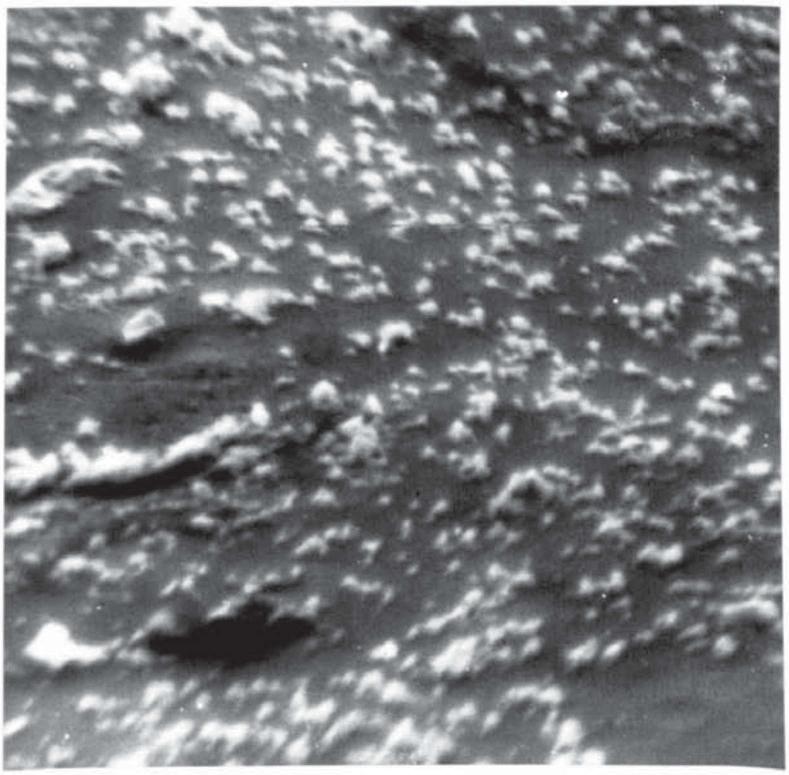


Fig.4.42. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution H for 3 minutes and drained for 60 seconds prior to rinsing in water. X 5000.

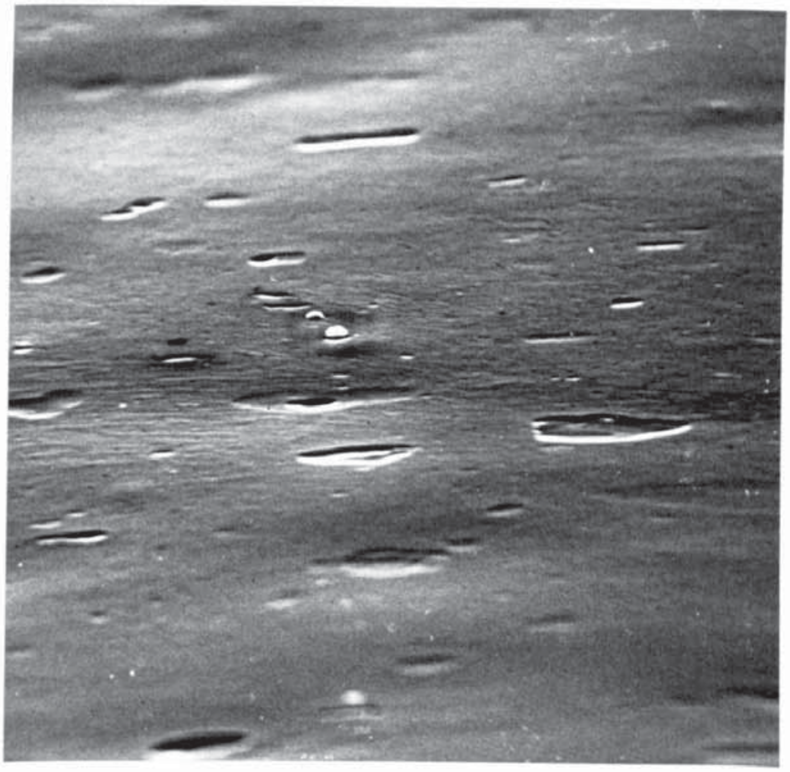


Fig.4.43. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution H for 3 minutes and drained for 60 seconds prior to rinsing in water (with the copper removed). X 2000.

TABLE 4.1

| Solution | Phosphoric acid (S.G.I.75) | Sulphuric acid (S.G.I.84) | Nitric acid (S.G.I.5) | Copper |
|---|---|---|---|---|
| I | 60.7% (by vol) | 37.3% (by vol) | 2% (by vol) | 1g/l |
| II | 59.5% | 36.5% | 4% | 1g/l |
| III | 58.2% | 35.8% | 6% | 1g/l |
| IV | 57% | 35.0% | 8% | 1g/l |
| V | 55.7% | 34.3% | 10% | 1g/l |
| VI | 54.5% | 33.5% | 12% | 1g/l |

The steady state and surge potentials of the aluminium electrodes in the above solutions are given in Table 4.2 below:

TABLE 4.2

| Solution | Initial Surge Potential (w.r.t. S.C.E) | Steady State Potential (w.r.t. S.C.E) |
|---|---|---|
| I | -0.62V | -0.48V |
| II | - | - |
| III | -0.44V | -0.34V |
| IV | -0.40V | -0.33V |
| V | -0.375V | -0.30V |
| VI | -0.35V | -0.28V |

The potentials all dropped sharply initially and then rose to a more noble steady state potential. As the percentage of the nitric acid in these solutions was increased the initial fall and steady state potentials recorded became more noble (Fig.4.46), in the same manner as in solutions 1-9 and 10-18 (section 3.4). These solutions do, however, exhibit certain differences from the higher phosphoric acid containing solutions. The

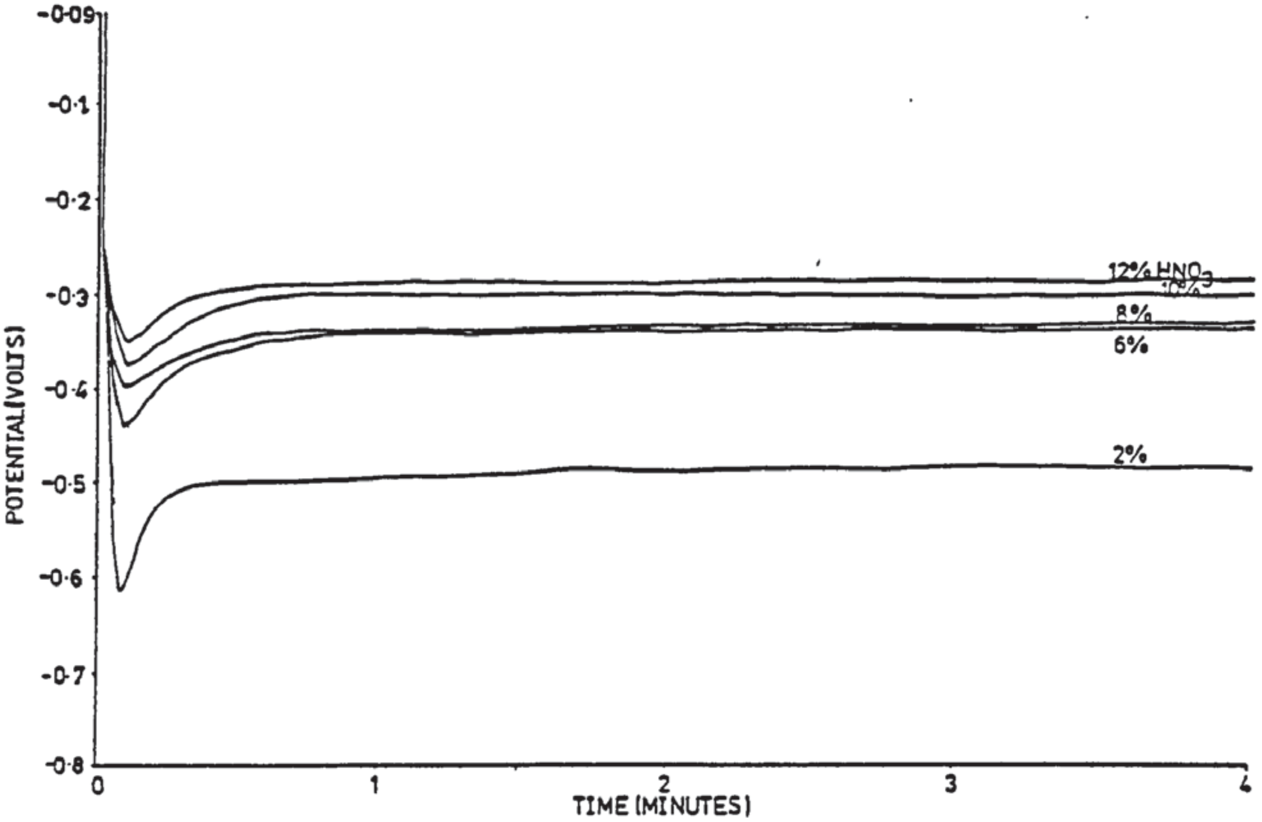


Fig.4.44. Potential vs. Time of 99.5% Al. in solutions I–VI, (Table 4.I.).

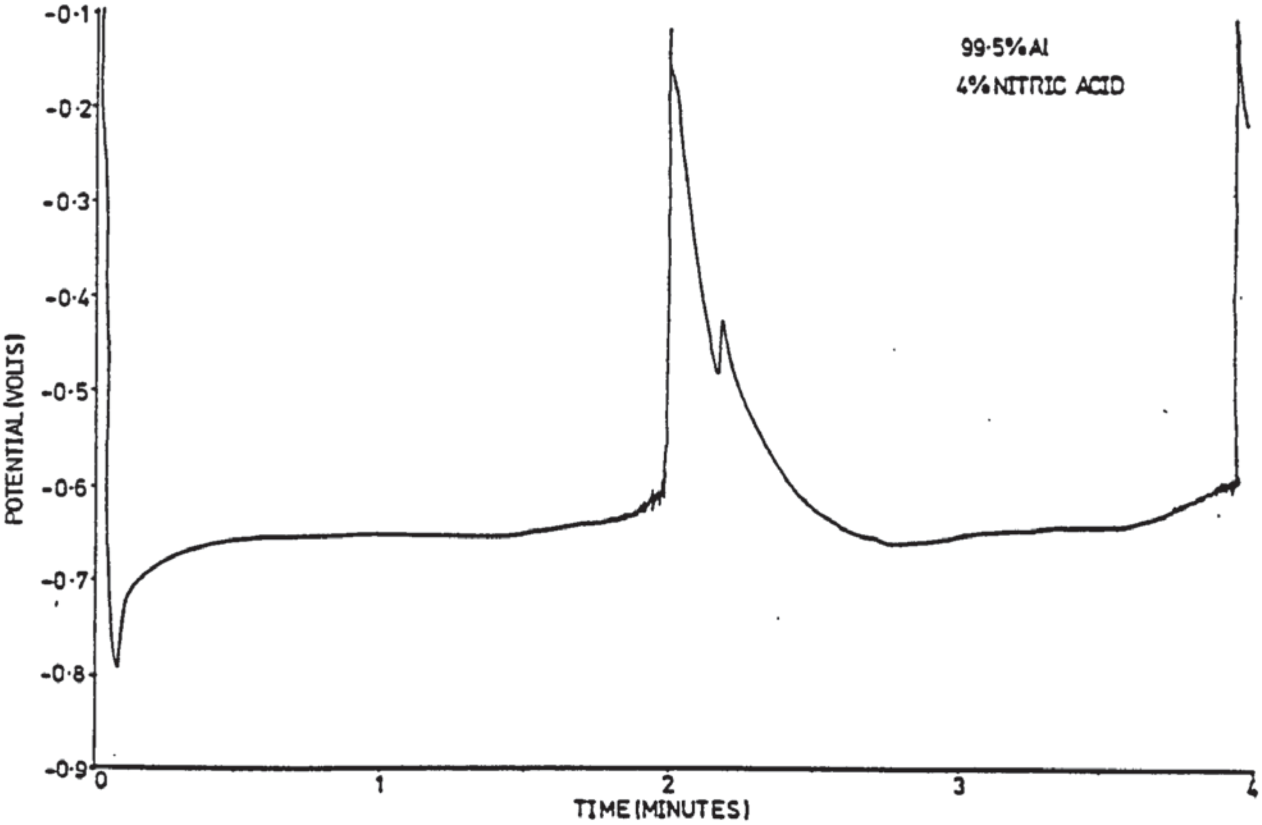


Fig.4.45. Potential vs. Time of 99.5% Al. in solution II, (Table 4.I.).

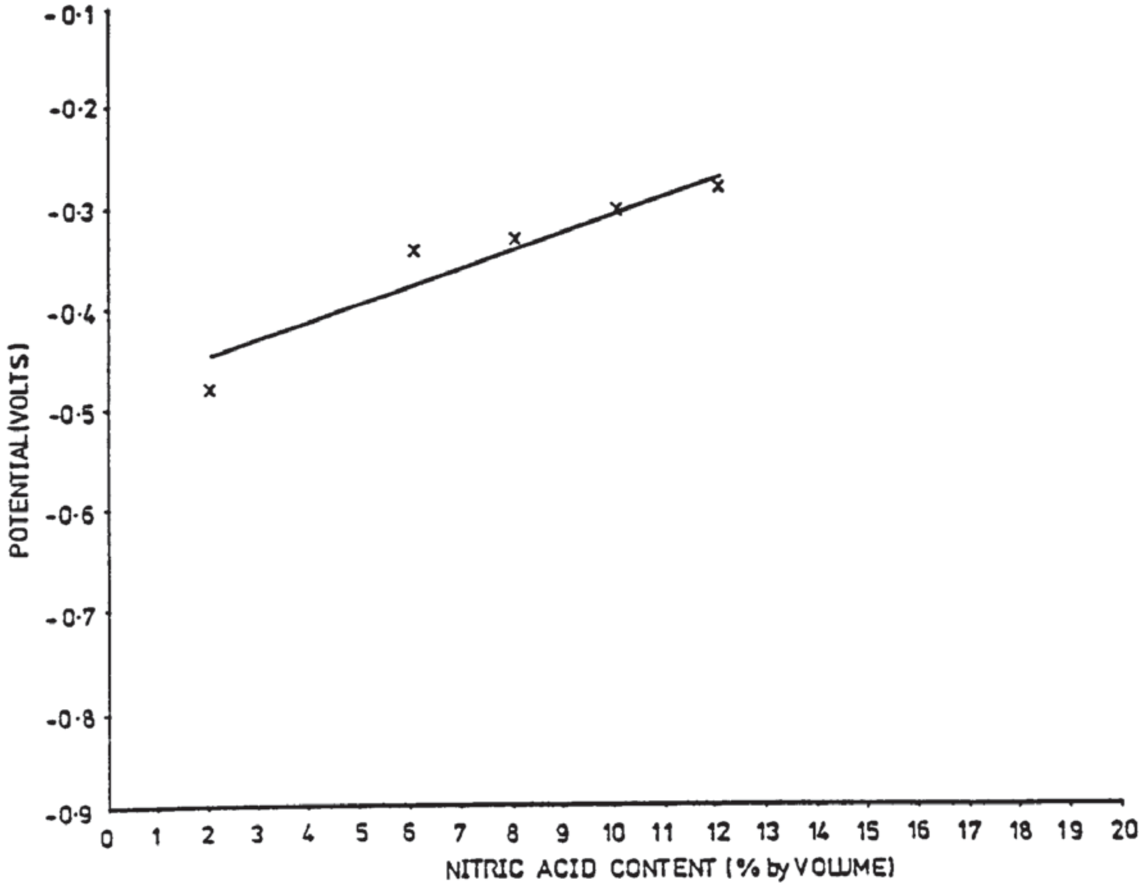


Fig.4.46. Steady State Potentials vs. Nitric acid content, of 99.99% aluminium in solutions I to VI, (table 4.I.).

potentials, for a given nitric acid content, were more noble in these solutions and the potential cycle only occured at one nitric acid concentration (4%). At 4% nitric acid, once the aluminium electrode had been immersed in the solution the potential remained at a constant value for a longer period of time before the first noble surge. Once at this noble potential, it also took longer to return to the more negative potential. The period between noble surges in potential was longer than in previous solutions.

The addition of 2.8g/l B.T.A in solution H produced no significant differences in the potentials recorded with the exception that no potential cycle occurred at any of the nitric acid concentrations studied.

## 4.6 Discussion

### 4.6.1 Specular Reflectivity

Solutions G to K were compared with solution E (77.5% by vol. phosphoric acid; 16.5% sulphuric acid and 6% nitric acid with 1g/l dissolved copper) as this solution is widely used in industry and produces an excellent finish on a range of aluminium alloys$^{(2)}$.

The high reflectivity produced on the 99.5% aluminium in solutions G and H is in accordance with industrial experience, as these solutions have both been used successfully on a commercial scale. The 99.99% aluminium did not however, achieve a high specular reflectivity in solution G. Initially this was thought to be due to the fact that far less copper was deposited on the surface (evident after rinsing in de-ionised water) after polishing in this solution than in solution E.

The addition of 2.8g/l of B.T.A. into the solution (solution H) did not alter the amount of deposited copper but did improve the reflectivity of the 99.99% aluminium to match that achieved by the 99.5%

aluminium in both solutions.

Aluminium polished in all four solutions required a longer period of polishing before the maximum reflectivity was achieved. In solution E this time was approximately 90 seconds, and in solutions G, H and K 180 seconds was required to produce the maximum reflectivity. This may be due to the more extensive etching of the surface in the initial stage of polishing, or to a slower rate of levelling of the etched surface.

Solution J produced a poor finish on both 99.99% and 99.5% aluminium. The addition of 10g/l of B.T.A. to this solution (solution K) increased the maximum reflectivity obtained with this particular acid combination, but not to a commercially acceptable level. In a commercial situation drag out from the solution would necessitate the addition of as much as 15g/l B.T.A. to maintain a level of 10g/l, which would overrule any advantages gained by the addition of the sulphuric acid.

Aluminium polished in Solution G, when first operated on an industrial scale using automatic and semi-automatic plants, with transfer times of 30 to 60 seconds, from the polishing tank to the rinse tank, suffered from a loss in reflectivity. This was also found to be the case in the present study. Significantly larger amounts of copper were evident on the surface as the transfer time was increased, and it was originally thought that this copper was responsible for local galvanic attack of the surface and, therefore, the loss in image clarity although as shown later a different mechanism occurs. Accordingly a copper inhibitor capable of remaining stable in these solutions was sought. The addition of 2.8g/l B.T.A was found to be sufficient to prevent any loss in image clarity with transfer times up to 60 seconds.

### 4.6.2 Influence of Sulphuric acid

### 4.6.2.1. Solution G

Increasing the percentage of sulphuric acid in this solution reduced the amount of copper deposited on the surface of the aluminium. The changes in surface morphology were essentially the same as found in the previous solutions. Etching of the surface was followed by levelling of the etch pits until a flat surface was produced. However, in the case of the 99.99% aluminium, sulphur rich structures with an orientation dependence, were found on the surface after polishing. These remained on the surface after the deposited copper had been removed in a 50% (by vol) nitric acid solution. It was these structures that were responsible for the loss in specular reflectivity, and not gassing defects, that had been suspected due to the reduced amount of deposited copper. The 99.5% aluminium had more deposited copper and did not have any gross surface features when the deposited copper had been removed. and consequently had a high specular reflectivity.

### 4.6.2.2 Solution J

When the sulphuric acid content was increased to a 1:1 ratio with the phosphoric acid, the amount of copper that was deposited on the surface was further reduced on the 99.99% aluminium, but the incidence of the sulphur rich structures was more or less the same, except that they tended to be confined to certain regions leaving other areas unaffected. The 99.5% aluminium showed a considerable change in this solution from solution G. The surface after 30 seconds polishing was entirely covered with orientation dependent pyramidal shaped structures rich in sulphur. The extent of these structures was reduced with further polishing, but were more extensive than the 99.99% aluminium, and this led to a lower specular reflectivity.

The relatively smaller amount of deposited copper in these solutions was not found to be a problem since sufficient was being deposited to prevent gassing defects. The low specularity of the 99.99% and 99.5% aluminium polished in this solution is due to the presence of irremovable sulphur rich surface structures.

Aluminium phosphate is virtually insoluble in water at 100°C but is soluble in sulphuric acid, however, aluminium sulphate is very soluble in water. A number of reactions may occur in these solutions to varying extents. If one considers the reactions between aluminium and phosphoric and sulphuric acids on their own:

(1) $2Al + 2H_3PO_4 \rightarrow 2AlPO_4 + 3H_2$

(2) $2Al + 3H_3PO_4 \rightarrow Al_2(H_2PO_4)_3 + {}^3/_2H_2$

(3) $2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2$

(4) $Al + 2H_2SO_4 \rightarrow Al(HSO_4)_3 + H_2$

In solution E where there is considerably more phosphoric acid than sulphuric acid, reactions (1) and (2) will tend to predominate. However, in solution J there is the same amount of the two acids. This will mean that the likelihood of reactions (3) and (4) occurring is increased. As aluminium sulphate has considerable water of crystalisation

(5) $Al_2(SO_4)_3 + \text{Free water} \rightarrow Al_2(SO_4)_3.18\ H_2O$

reaction (5) in conjunction with reaction (3) and (4) will tend to produce a solution deficient in free water, particularly at the aluminium/ solution interface. This leads to the precipitation of an insoluble sulphur containing, aluminium salt on the surface. Scanning electron micrographs in the previous section had indicated that the rate of reaction was faster in the first 30 seconds or so of polishing. This would explain the profusion of aluminium sulphate on the surface of the 99.5% aluminium after 30 seconds polishing as at 30 seconds polishing there will be a deficiency of free water at the aluminium/ solution interface for the solvation of the aluminium sulphate being produced. The reduction of the dissolution rate with further polishing will allow these structures to be dissolved, to a limited extent.

In view of these results the water content of solution G was deliberately allowed to fall well below the recommended optimum, the nitric acid was adjusted to the optimum and a sample of 99.5% aluminium was polished for 3 minutes. The surface (Fig.4.47) showed very similar structures to those at the recommended optimum water content of solution J. Consequently, solution J was successively diluted with water from the optimum in an attempt to prevent the formation of these surface structures. (A dilution of 7% was necessary to achieve a reduction in the incidence of the structures). The 99.5% aluminium did show a slight lessening (fig. 4.48), and the 99.99% aluminium did eventually have a surface free from these structures, but the surface now had gassing defects due to the complete absence of deposited copper (Fig.4.49) and showed an etched surface.

### 4.6.3 Influence of Benzotriazole

Benzotriazole is well known as a corrosion inhibitor for copper(68, 69,70,71,72,73). However, its use in hot concentrated mixed acids has not previously been reported. The profusion of copper on the surface of aluminium after long transfer times indicated that copper was responsible for the loss in image clarity. The addition of B.T.A. to solution G (solution H) was successful in preventing any loss in specularity during transfer times of up to 60 seconds. However, in solution G 99.99% aluminium produced sulphur rich in insoluble reaction products on the surface., which the addition of B.T.A. prevented. This is not a consequence of the action of copper, since approximately the same amount of deposited copper was evident with or without the B.T.A. Consequently the B.T.A. appears to modify the solution characteristics in some way.

The combination of the three acids, phosphoric, sulphuric and nitric, in their concentrated forms, produces a complex solution in which the precise nature of the individual species is uncertain.

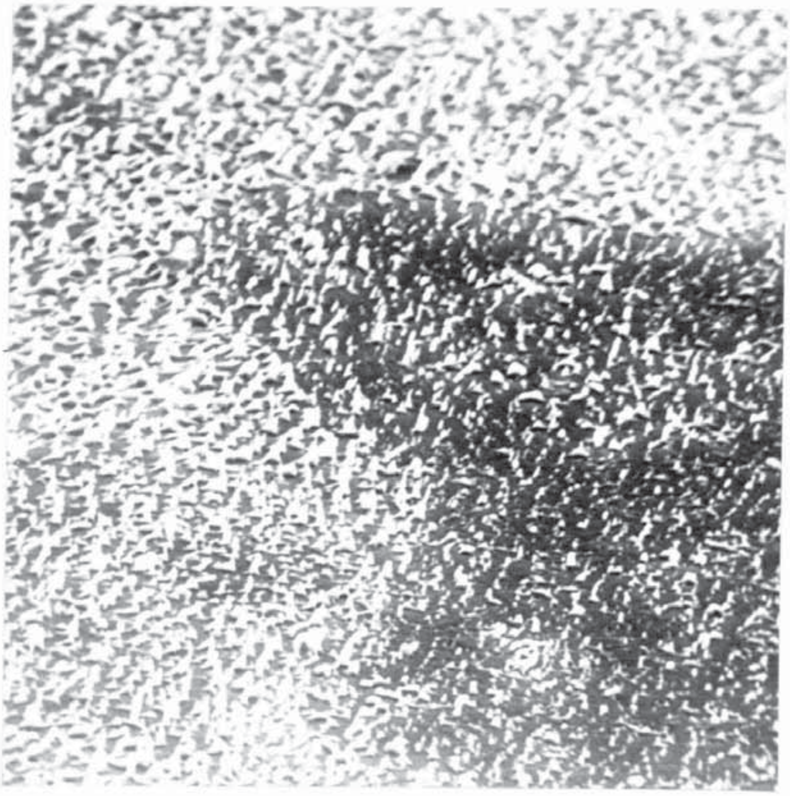


Fig.4.47. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution G, with a low water content, for 3 minutes. X 2000.

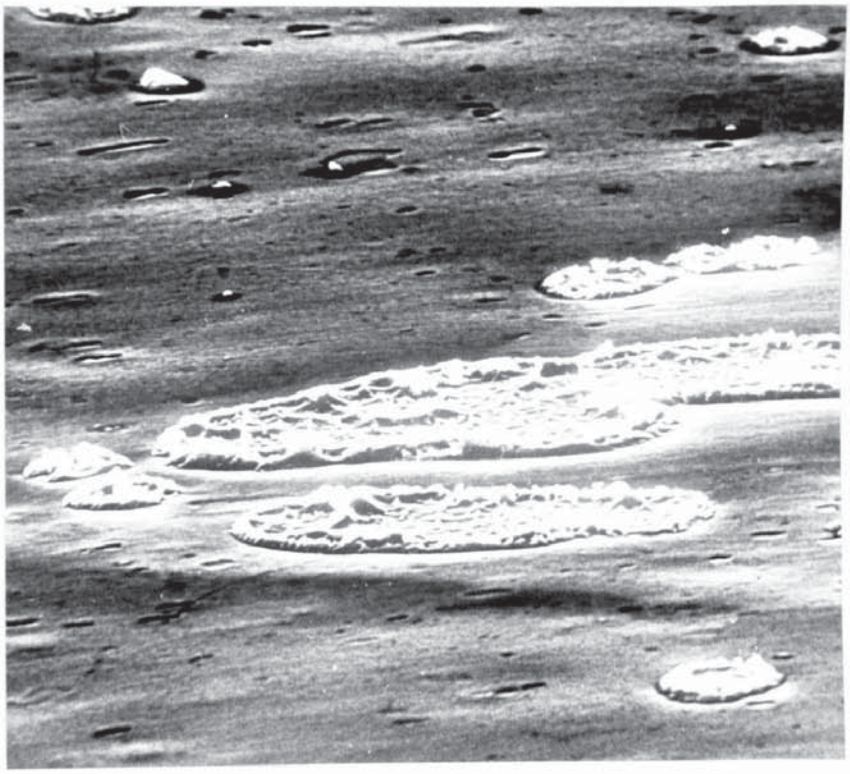


Fig.4.48. Scanning Electron Micrograph of 99.5% Al. Chemically polished in solution J (diluted by 7%) for 3 minutes . X 2000.

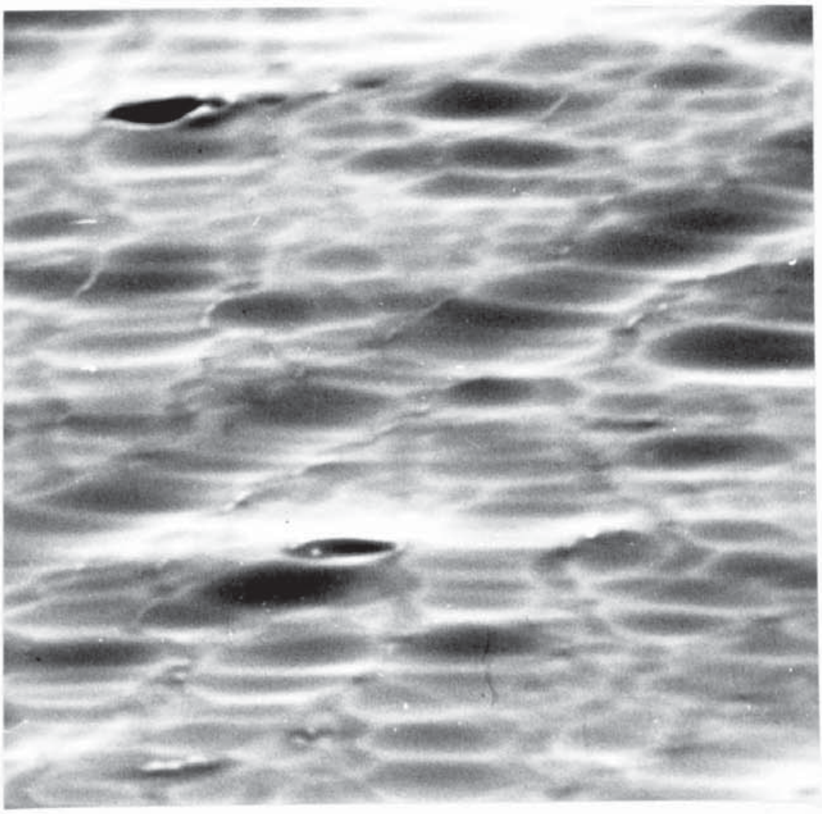
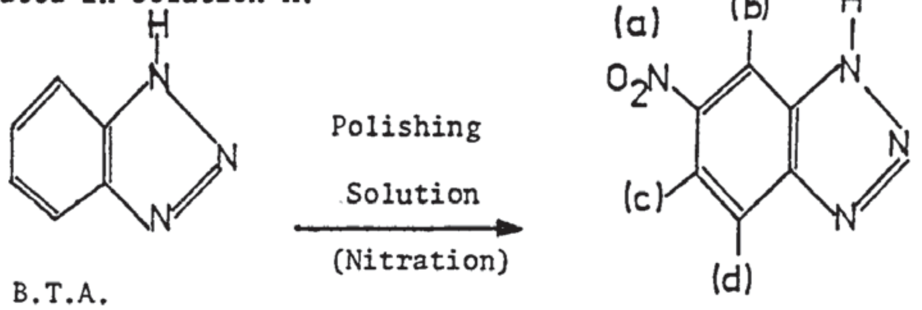


Fig.4.49. Scanning Electron Micrograph of 99.99% Al. Chemically polished in solution J (diluted by 7%) for 3 minutes. X 5000.

B.T.A. has been found, from nuclear magnetic resonance spectroscopy, to be nitrated in solution H.(88)



B.T.A.

The nitro group is substituted in <u>one</u> of the positions (a),(b),(c) or (d). The B.T.A. was also found to be stable in these solutions. It is difficult to determine the precise mode of action of the B.T.A. but certain features are evident. When present in solution K at 10g/l the B.T.A. reduces the rate of levelling as can be seen from the fact that the etched surface of the 99.99% aluminium in this solution is not removed. This slowing of the rate of levelling of the surface may not be the only mechanism operating. The B.T.A. may also be forming a complex with the aluminium sulphate and so producing a soluble product. The B.T.A. may become adsorbed onto the surface of the copper(68,69,70) deposits on the surface of the aluminium and reduce the rate of dissolution, although at a concentration of 10g/l of B.T.A. the amount of deposited copper is considerably reduced, particularly on the 99.99% aluminium.

### 4.6.4 Potential Time Determinations

As less copper was deposited on the surface of the aluminium in these solutions, one might expect the potentials recorded to be more electronegative than in the solutions containing more phosphoric acid and showing more deposited copper. However, this was not found to be the case. After an initial fall the potential reached a steady state potential that was more noble than had been found in the previous solutions. However, this is in agreement with the observation that the length of polishing time required to achieve the maximum reflectivity was longer than in the higher phosphoric acid containing solutions, which indicates that a slower rate of dissolution is responsible for the relatively noble steady state potentials.

The potential cycle recorded was also different from the previous solutions. In the first instance no potential cycle was recorded at a nitric acid concentration of 2%. This is likely to be due to the slow deposition of isolated large copper deposits, and their equally slow dissolution, as had been the case in solution D.

At 4% nitric acid a potential cycle was recorded that had two significant differences from the corresponding solution with more phosphoric acid. The copper deposition rate was slower since the interval between the noble surges in potential was longer. Secondly, the time taken for the potential to return to the more negative value was also longer. Therefore, not only is the deposition rate of the copper slower, but its subsequent dissolution from the surface is also slower. Copper is less soluble in these solutions, to the extent that if the solution is allowed to cool, the copper crystalizes out of solution as copper sulphate $CuSO_4IH_2O$(88).

The addition of B.T.A. to the solution prevented a potential cycle from occurringat any of the nitric acid concentrations studied. This can be assumed to be due to the B.T.A. becoming adsorbed onto the surface of the copper reducing its electrochemical influence on the surface to the extent that large amounts of copper deposited on the surface do not produce a potential close to that of copper itself. Alternatively, it may actually prevent the deposition of the large quantities necessary to give the very noble potential of the cycle. A copper electrode immersed in the solutions containing B.T.A. dissolved slowly for approximately 10 seconds after which time all indication of a reaction ceased. The potentials recorded in the other solutions (2,6,8,10,12% nitric acid) did not show any difference from those recorded in the absence of B.T.A.

### 4.6.5 The effect of extended drain time

When aluminium is removed from a solution with a relatively high sulphuric acid content (e.g. solution G), whilst draining the conditions at the aluminium/solution interface will alter considerably. The nitric acid will evaporate from the surface, and will also be consumed by the vigorous reaction which occurs at drain times of 10-45 seconds, from which nitric acid and possibly other oxides of nitrogen(42) are evolved. This leads to the increase, with draining time, in the amount of deposited copper.

However, the loss in specular reflectivity is not due directly to the deposition of copper. No preferential dissolution of the aluminium was found around the large copper deposits. The loss in reflectivity was in fact due to the formation of sulphur rich structures on the surface, of a similar type to those found on 99.99% aluminium after polishing in solution G with approximately 1 second transfer time.

As the aluminium dissolves during draining, the solution remaining on the surface will become saturated with dissolution products. In addition, when the specimen is removed from the solution, water in the solution on the surface will evaporate due to the exothermic nature of the chemical reaction and the relatively large surface area exposed. This will produce ideal conditions for the formation of insoluble reaction products of the surface of the aluminium.

The amount of deposited copper is however, connected with the occurrence of these structures, since areas at the top of the specimens, that drained more rapidly than the majority of the specimen, showed less deposited copper and the incidence of the surface structures was less. The reflectivity in these regions was correspondingly higher, although the average figure obtained for the entire surface did not reveal this.

Culpan(83) found that the addition of 1g/l Cu to chemical polishing solutions (of the composition of solution E) increased the rate of metal dissolution. This would explain the increase in the incidence of the sulphur rich structures on the areas of the specimens that had the larger amounts of deposited copper after extended transfer times, since an increased reaction rate would lead to the formation of a larger proportion of insoluble reaction products.

The addition of B.T.A. to the solution prevented the formation of these insoluble reaction products on the surface, not only during transfer, but also, in the case of the 99.99% aluminium, during polishing in the solution. The mechanism by which the B.T.A. prevents the loss in specular reflectivity during transfer is by the methods put forward in section 4.6.3. The B.T.A. is adsorbed onto the surface of the copper(68, 70) and prevents any increase in the reaction rate caused by the deposited copper. In addition it prevents the solution from becoming saturated in reaction products, and so prevents the formation of the surface structures that are responsible for the loss in specular reflectivity.

# CHAPTER 5

# ASSOCIATED PHENOMENA

## 5.1 Introduction

The chemical polishing of aluminium occurs in solutions capable of producing the special conditions necessary to allow dissolution of the aluminium whilst preventing the occurrence of various forms of defects on the surface. In particular, uneven grain dissolution, and gassing defects associated with the cathodic evolution of hydrogen from the surface.

The object of the work in this chapter was to examine the effect, on the incidence of gassing defects, of applying an external e.m.f., and to determine the anodic polarisation characteristics of phosphoric acid based solutions, with the particular intention of not using rotating anodes, as used by some previous authors(14,74,89), and to use a system that bears a closer resemblence to the conditions encountered in commercial plants.

In the course of the work certain defects were produced, that bore a close resemblence to defects found by some previous authors(3,14,74). At this time, a local metal finishing firm was experiencing a severe pitting problem on electropolished stainless steel. The pits produced in this instance had a very similar structure to the gassing defects produced by the chemical polishing of aluminium in solution A (chapter 3). Consequently it was felt that an investigation into the mechanism of formation of these defects would provide valuable information on the general theory of chemical and electropolishing.

Since the work involves two different metals, the chapter has been divided into a section dealing with aluminium and a section dealing with stainless steel.

## 5.2. Experimental Procedure and Techniques (Aluminium)

### 5.2.1 Materials and Equipment

Spade electrodes (5cm x 1cm x 0,9mm) of 99.99% aluminium (analysis section 2.1) were used. A Wenking 70-HC-3 Potentiostat with a platinum counter electrode was used for the anodic polarisation work. The solution arrangement and the salt bridge system was the same as that used in section 2.5.2, with the addition of the platinum counter electrode.

### 5.2.2 Experimental procedure

The spade electrodes were degreased in acetone and stored in a desiccator until used.

Two procedures were employed:

1) The electrode was immersed in the solution and allowed to dissolve until the potential had reached a steady state (less than 10mV change in one minute), at which point the potential was increased in steps of 100mV per minute.

2) The potential was applied to the electrode before the electrode was immersed in the solution.

### 5.2.3 Solutions

The solutions used were those used in the earlier work described in chapter 3. The compositions of solutions A to F are given below.

## TABLE 5.1

| Solution | Phosphoric acid (S.G.1.75) | Sulphuric acid (S.G.1.84) | Nitric acid (S.G.1.5) | Copper |
|---|---|---|---|---|
| A | 82.5%(by vol) | 17.5%(by vol) | - | - |
| B | 77.5% | 16.5% | 6%(by vol) | - |
| C | 65.9% | 14.1% | 20% | - |
| D | 82.5% | 17.5% | - | 1g/1 |
| E | 77.5% | 16.5% | 6% | 1g/1 |
| F | 65.9% | 14.1% | 20% | 1g/1 |

The solutions were prepared from Analar grade reagents. The solutions contained very little dissolved aluminium due to the size of the electrodes used and the relatively large amount of solution used. 1 litre of solution in a glass beaker was maintained at a temperature of 100°C± 1°C by a thermostatically controlled hotplate, and moderate agitation was provided by a magnetic stirrer.

## 5.3 Anodic Polarisation Results

Fig.5.1 shows the anodic polarisation curves obtained in solutions A to F (table 5.1) using the first method (method 1), where the electrode was allowed to stabilise in the solution before the potential was applied.

The current density, at a given voltage, increased as the nitric acid content of the solutions was increased.

The two solutions containing 20% nitric acid showed oxygen evolution from the surface of the anode at potentials of about+1.8 volts.

At 0% nitric acid the current density, at the same voltage as the solution containing copper, was higher than the solution with no dissolved copper. However, the situation is reversed in the solutions containing 6% nitric acid. Then at 20% nitric acid the current density, at the same

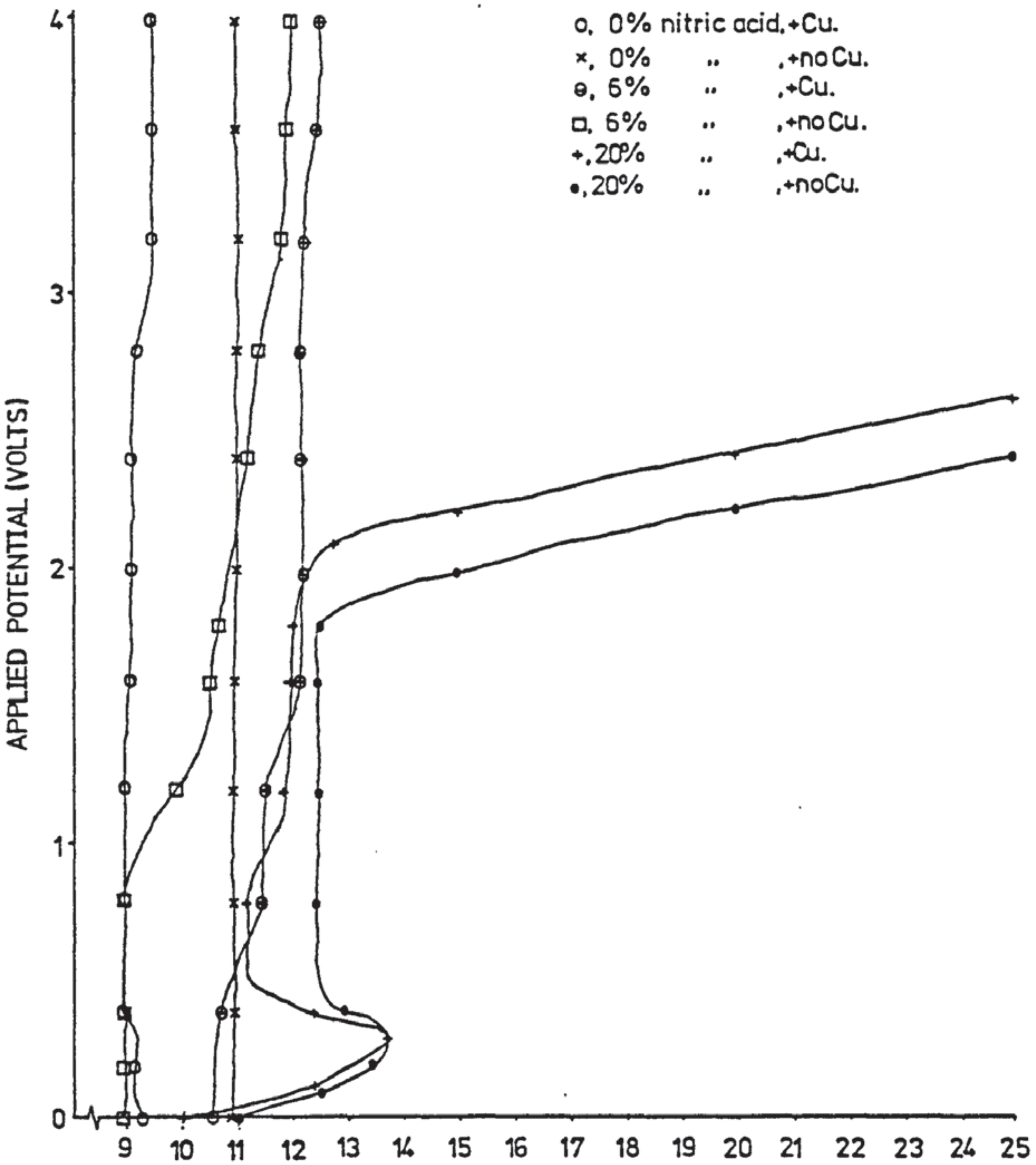


Fig.5.I. Anodic Dissolution curves for Aluminium in solutions A-F, (table 5.I.).

voltage, was higher in the solution with no dissolved copper.

The cathodic evolution of hydrogen on the aluminium anode stopped at different potentials according to the particular solution, as listed in Table 5.2 below:

TABLE 5.2

| Solution | % Nitric acid (by vol) | Copper content (g/1) | Cessation of $H_2$ evolution |
|---|---|---|---|
| A | 0 | 0 | 900mV |
| B | 6% | 0 | 700mV |
| C | 20% | 0 | 1300mV |
| D | 0% | 1g/1 | 1200mV |
| E | 6% | 1g/1 | 1200mV |
| F | 20% | 1g/1 | 1100mV |

All of the electrodes had highly polished defect free surfaces, with the exception of the two electrodes showing oxygen evolution. The surface of these was heavily pitted with evidence of the formation of a thick surface film (Fig.5.2), which on analysis gave a high phosphorus count.

The object of the second method (immersion of the electrode live) was to prevent the initial removal of the air formed oxide film and the subsequent etching of the surface, before steady state conditions were achieved. However, even using a Shandon Electropolishing unit (type 6510) with an applied potential of 80 Volts, it was not possible to suppress the etching stage.

Using the potentiostat at an applied potential of 4 Volts aluminium electrodes were immersed live in the solution. For approximately

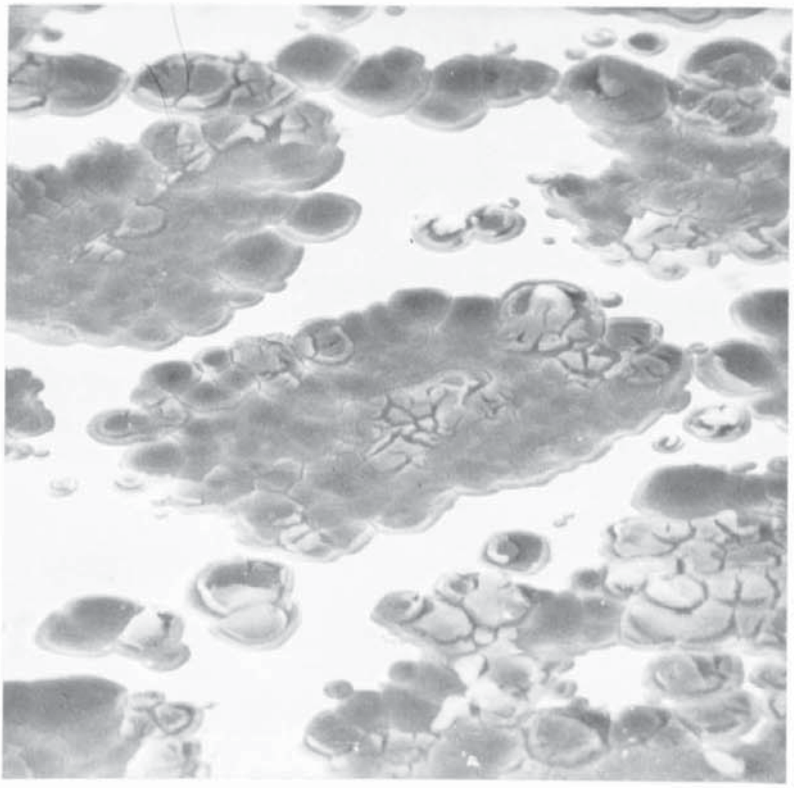


Fig.5.2. Scanning Electron Micrograph of 99.99% aluminium electropolished in the oxygen evolution region of Fig.5.I. for 5 minutes. X 500.

10 seconds gas evolution occurred on the anode, and then ceased. A proportion of the gas produced by this initial gassing, remained attached to the surface, as relatively large gas bubbles, in certain cases as large as 1mm in diameter. These gas bubbles remained on the surface until the anode was removed after 10 minutes of polishing.

Increasing the amount of agitation failed to dislodge the bubbles. The surface was highly polished except for the pitting due to these gas bubbles. The pits produced, under optical examination (Fig.5.3 & 4) bore a close resemblence to those found by previous authors(3,14,74). However, it was felt that the scanning electron microscope would resolve whether or not the central light spot was an optical artifact(74) or in fact a central protrusion.

### 5.3.2 Scanning Electron Microscopy

Samples for electron microscope examination were immersed live at a potential of 4 Volts and allowed to polish for 10 minutes, rinsed in water and acetone, dried in air and mounted in the microscope in the usual way. The defects consisted of a central flat plateau, which was higher than the surrounding aluminium, surrounded by an annular groove that was smooth and non-etched (Fig.5.5). Some of the gas bubbles became detached during polishing, this led to preferential dissolution of this plateau to produce a rounded central mound (Fig 5.6).

Agitation was used in the experiments to provide even solution conditions (e.g. an even temperature distribution throughout the solution). The agitation was increased for subsequent samples in an attempt to prevent the adhesion of these gas bubbles to the surface of the aluminium. The speed of rotation was estimated at two different levels; 60 r.p.m. (approximately) and 250 r.p.m. (approximately). Samples were again immersed live into the solution and polished for ten minutes.

Fig.5.3. Optical Micrograph of 99.99% aluminium immersed live at 4V and electropolished for I0 minutes. X I60.

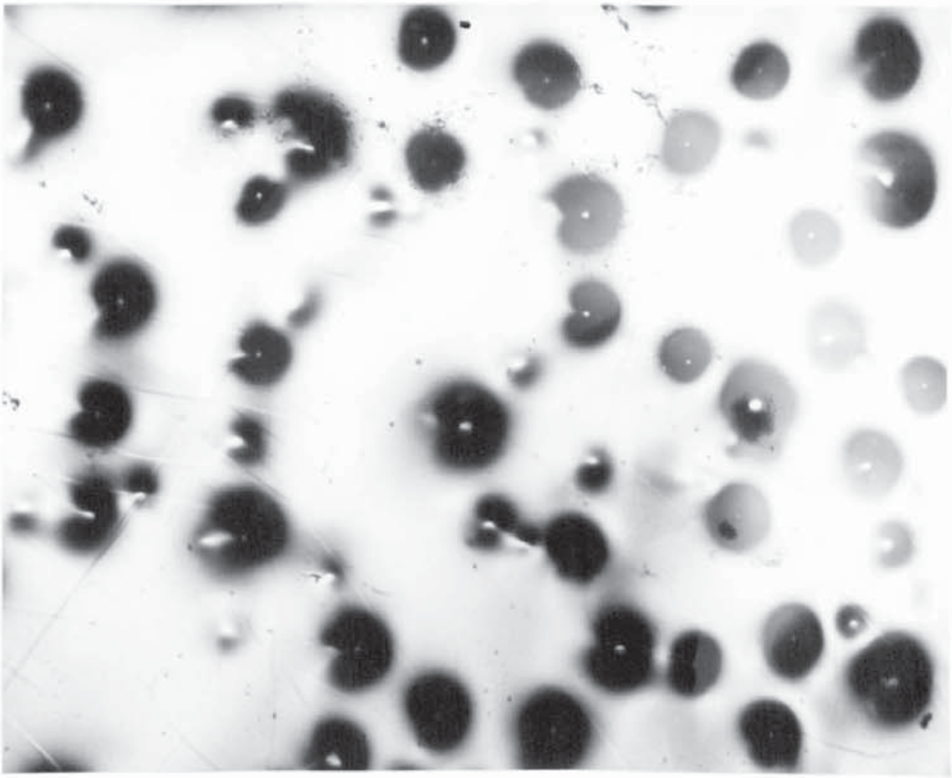


Fig.5.4. Optical Micrograph of 99.99% aluminium immersed live at 4V and electropolished for I0 minutes. X I60.

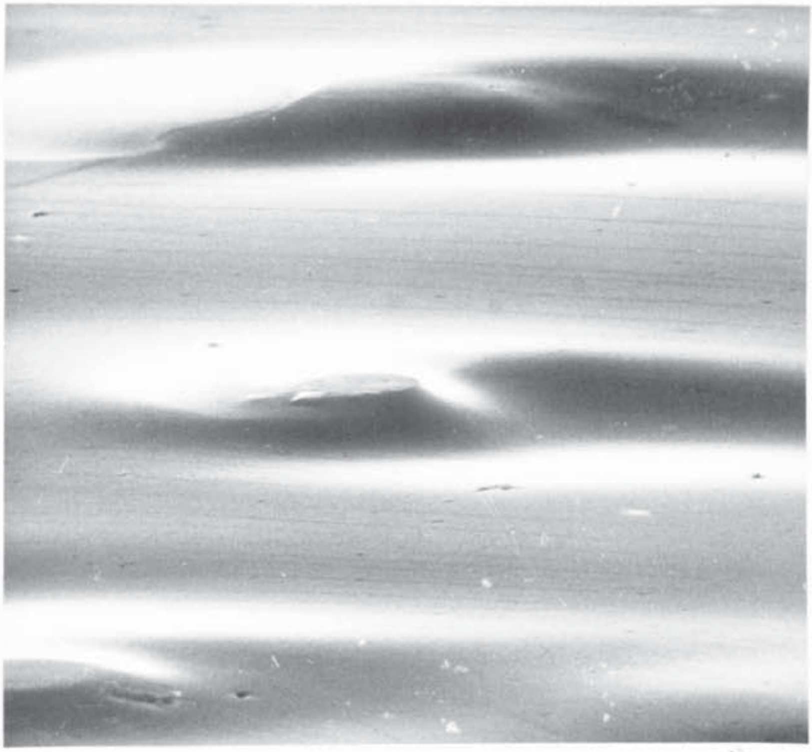


Fig.5.5. Scanning Electron Micrograph of 99.99% aluminium immersed live at 4V and electropolished for IO minutes. X 500.

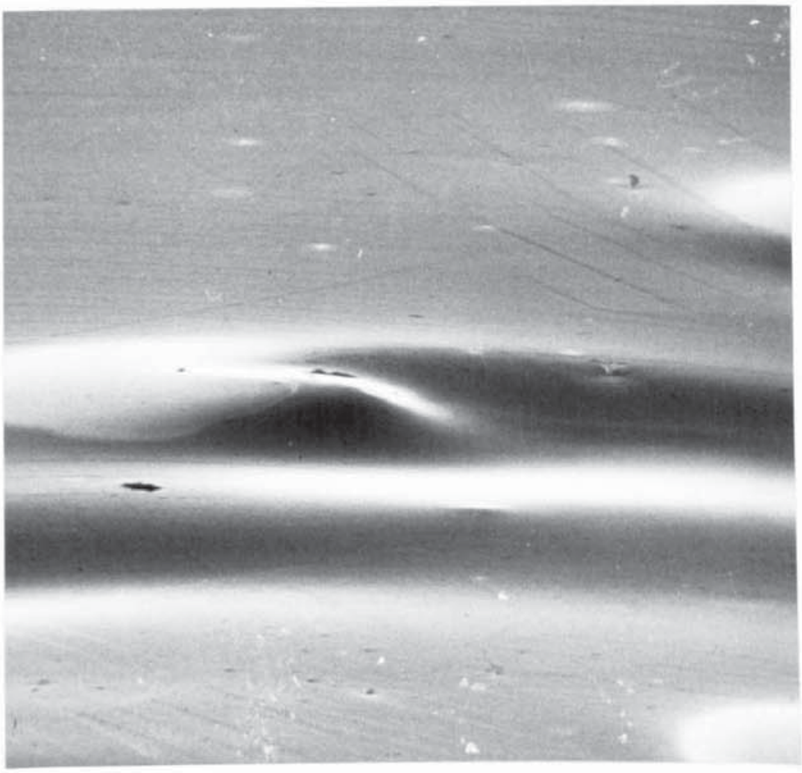


Fig.5.6. Scanning Electron Micrograph of 99.99% aluminium immersed live at 4V and electropolished for IO minutes. X 500.

At a solution speed of 60 r.p.m. (Fig.5.7) the extent of the annular groove had been considerably reduced, a central mound with a flat top was still present and the size of the defects was considerably smaller than on the previous sample. A further increase in agitation to 250 r.p.m. (Fig.5.8) produced a surface with shallow but extensive pitting. However, no protrusions of aluminium were visible so that the point of contact of the gas bubbles was not discernable, although the bubbles were clearly visible during polishing.

## 5.4 Experimental Procedure and Techniques (Stainless Steel)

### 5.4.1 Materials and Equipment

Samples of austenitic 18/8 (EN58) stainless steel with the following composition (in weight per cent) were used:

Fe..... 70.76%
Cr..... 18.29%
Ni..... 8.32%
Mn..... 1.74%
Ti..... 0.1%
C...... 0.08%
Si..... 0.71%

The apparatus used to determine the anodic polarisation characteristics was the same as that used for the aluminium as described in section 2.5.2

### 5.4.2 Experimental Procedure

The specimens were degreased in acetone and stored in a desiccator until used. The specimens were immersed into the solution for 30 seconds and then the potential applied in steps of 100mV per minute.

### 5.4.3 Solutions

In this section two types of solution were used. Fresh solutions prepared from AnalaR grade reagents containing no dissolved metals, and secondly, aged solutions supplied by a commercial user, prepared from commercial grade chemicals and having the following amounts of dissolved

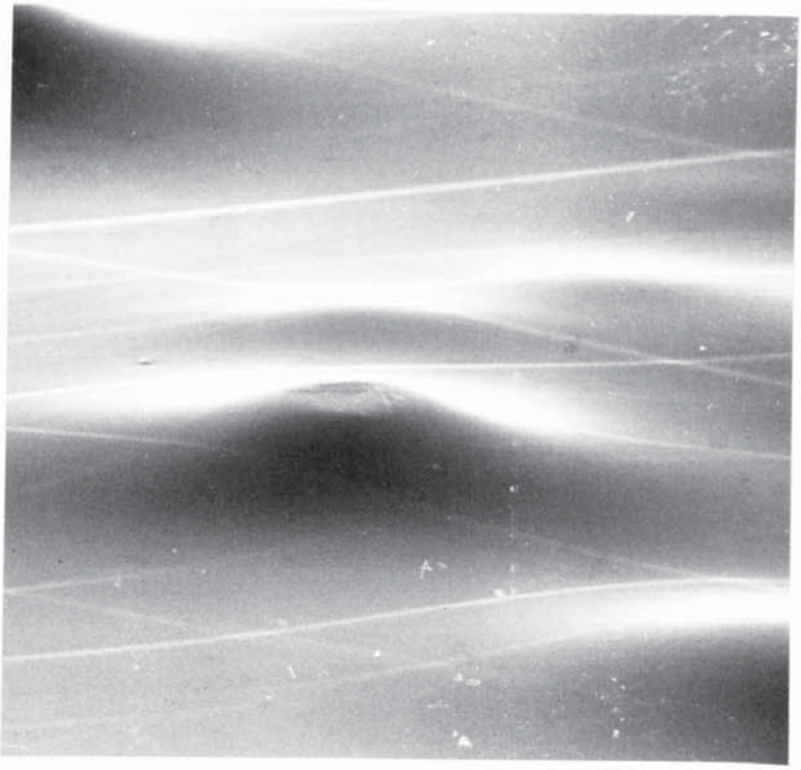


Fig.5.7. Scanning Electron Micrograph of 99.99% Aluminium immersed live at 4V and electropolished for IO minutes with increased agitation (approx.60r.p.m.) X 2000.

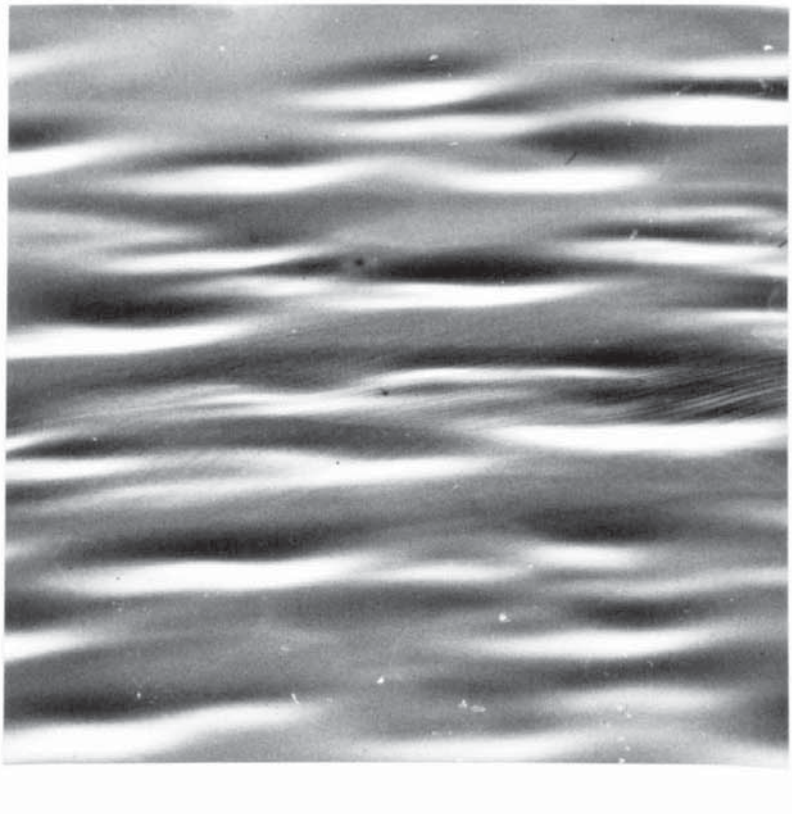


Fig.5.8. Scanning Electron Micrograph of 99.99% Aluminium immersed live at 4V and electropolished for IO minutes at maximum agitation (approx. 250 r.p.m.) X 200.

metals;

Fe..... 43.0g/l

Cr..... 8.1g/l

Ni..... 0.23g/l

Mn..... 0.23g/l

Except where otherwise stated all the solutions were a mixture of phosphoric acid and sulphuric acid in the ratio of 1.3:1 respectively.

### (1) Aged solutions

The following solutions were prepared by making additions to the aged commercial solution.

TABLE 5.3

| Solution | | | | |
|---|---|---|---|---|
| A1 | as received solution, with a S.G. of 160°Tw (measured at 15°C). | | | |
| A2 | " | diluted with water to | 150°Tw | " |
| A3 | " | " | 130°Tw | " |
| A4 | " | (S.G.160°Tw) | with 1g/l dissolved copper | |
| A5 | " | " | with 2g/l dissolved copper | |
| A6 | " | " | with 6g/l dissolved copper | |

Copper additions were made using copper sulphate ($CuSO_4.5\ H_2O$).

A 1% dilution of these solutions reduces the specific gravity by 1.6°Tw at 15°C.

### (2) Unaged solutions

The following solutions were prepared from AnalaR grade reagents and contained no dissolved metals, other than possible impurities in the reagents themselves.

## TABLE 5.4

| Solution | | | | | |
|---|---|---|---|---|---|
| B1 | 1.3:1 ratio | $H_3PO_4$: $H_2SO_4$ | with a S.G. of | 160°Tw | (at 15°C) |
| B2 | " | | diluted to | 150°Tw | " |
| B3 | " | | " | 130°Tw | " |
| B4 | 1.2:1 ratio | $H_3PO_4$: $H_2SO_4$ | with a S.G. of | 160°Tw | " |
| B5 | 1:1 ratio | $H_3PO_4$: $H_2SO_4$ | with a S.G. of | 160°Tw | " |

### 5.4.4 Anodic Polarisation Results

Dilution of the aged solution (A1) increased the current density for a given voltage (Fig.5.9). In addition, the range of voltages of the limiting current density region of the curve was reduced from approximately 1000mV (at 160°Tw) to approximately 200mV (at 130°Tw). However, the onset of oxygen evolution on the anode, although occurring at increasingly lower voltages with increased dilution, remained at approximately the same current density.

The same dilution of an unaged AnalaR grade solution produced similar trends but with certain differences (Fig.5.10). In the AnalaR solutions, the onset of oxygen evolution occurred at successively higher current densities as the solution was diluted, although the applied potential was approximately the same. The range of voltages of the limiting current density region was approximately the same (except for the solution at 130°Tw, which had a shorter range). The current densities were, at a given voltage, and at a comparable dilution, generally higher than the aged solution.

The addition of copper to the solutions in the form of copper sulphate modified the polarisation characteristics of the aged, undiluted commercial grade solution (Fig.5.11). The current density at a given

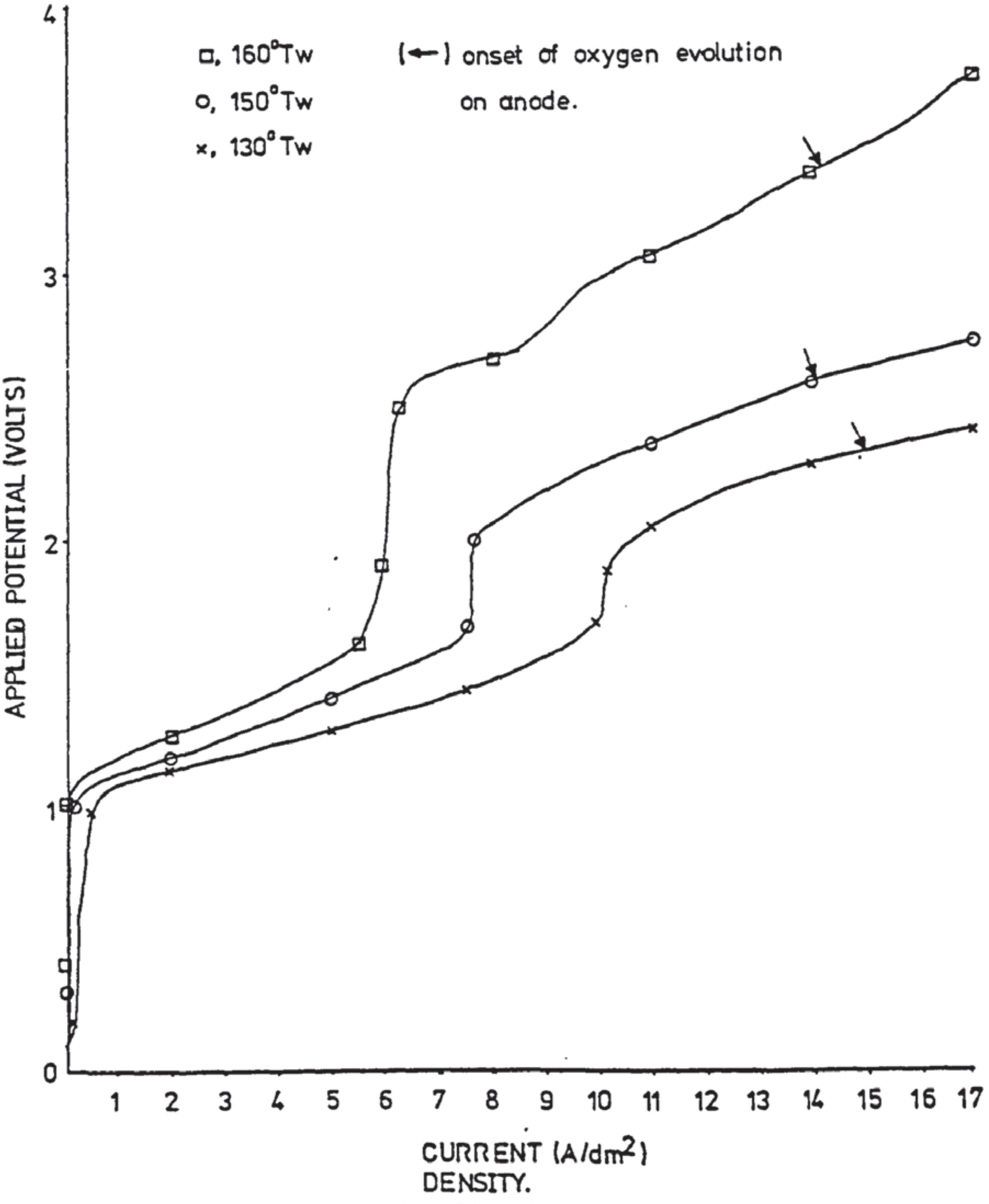


Fig.5.9. Anodic Dissolution curves for stainless steel in solutions AI,A2 & A3, (table 5.3.).

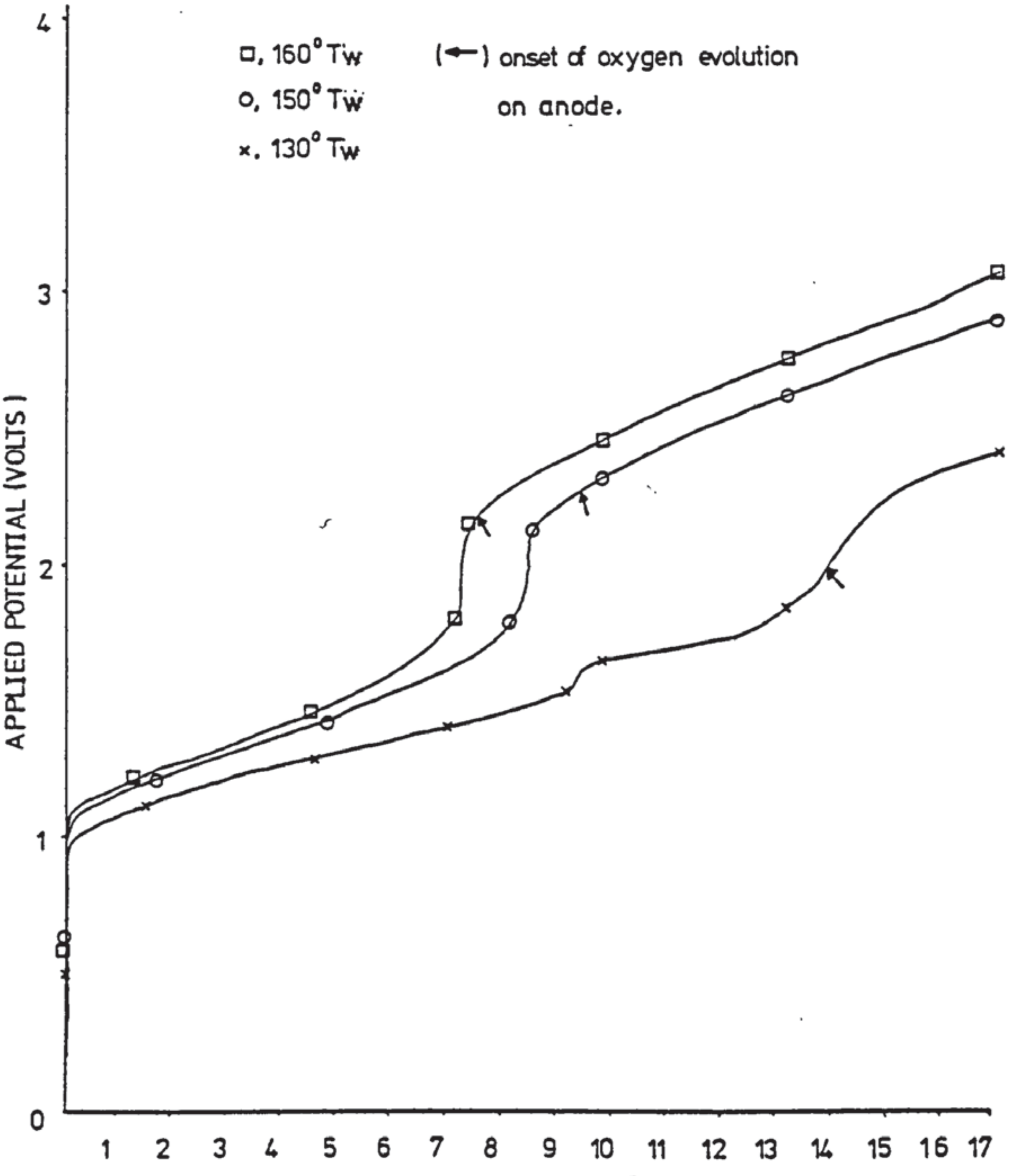


Fig.5.IO. Anodic Dissolution curves for stainless steel in solutions BI,B2 & B3, (table 5.4.).

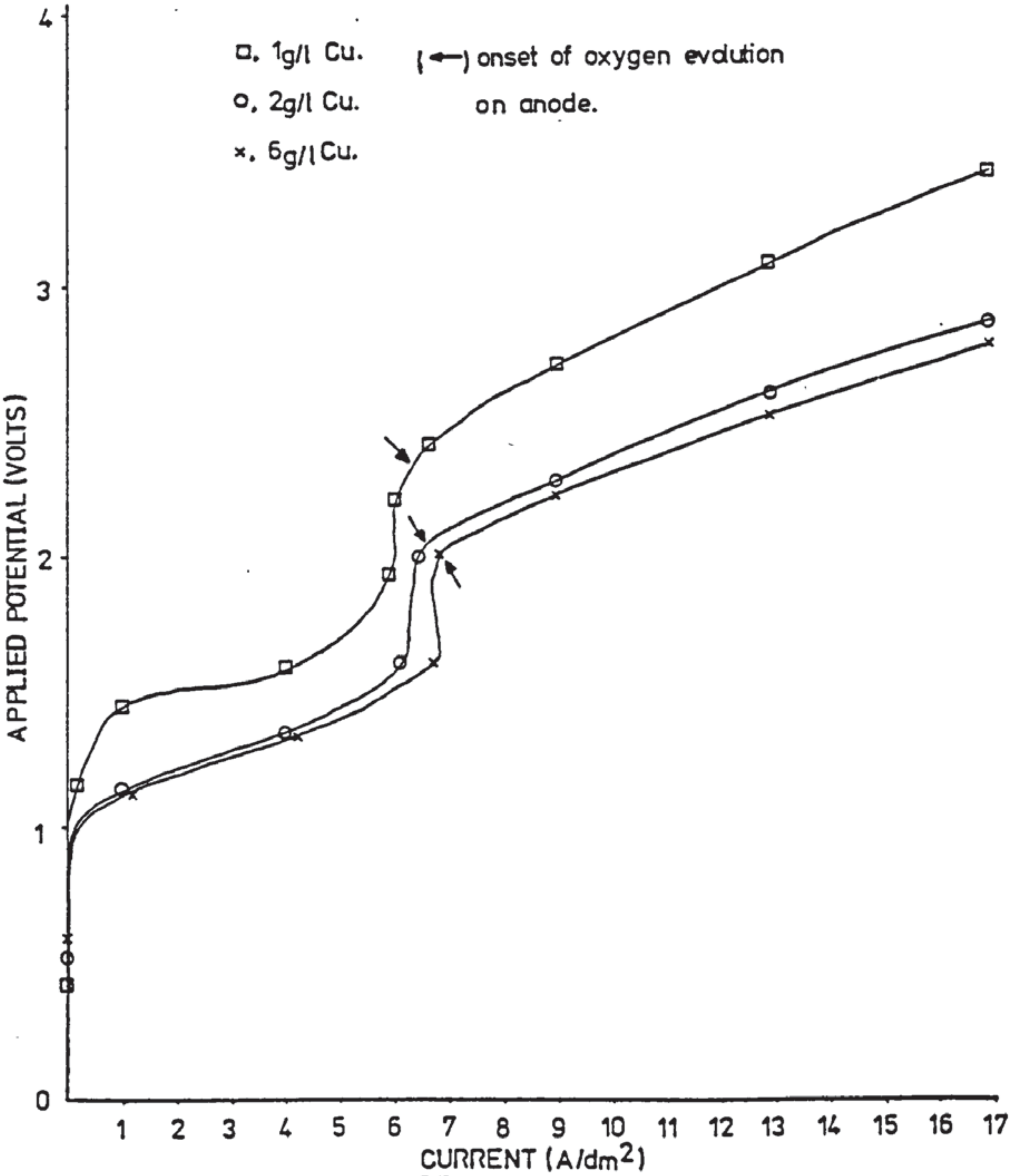


Fig.5.II. Anodic Dissolution curves for stainless steel in solutions A4,A5, & A6, (table 5.3.).

voltage was higher as the concentration of the copper in solution was increased. The range of voltages of the limiting current density region remained approximately the same. The most significant difference was the change in the voltage and current density at which oxygen evolution occurred on the anode. This was reduced from 14A/dm$^2$ in the copper free solution to 6A/dm$^2$ in the solution containing 6g/l dissolved copper.

In order to determine the effect of the addition of sulphate into the solution from the copper sulphate, the acid ratio was altered from 1.3:1 to 1.2:1 and 1:1 and the anodic polarisation curves obtained (Fig. 5.12). As the percentage of sulphuric acid was increased the current density, for a given voltage, decreased, unlike the previous solutions. The other parameters remained more or less the same.

### 5.4.5 Scanning Electron Microscopy (stainless steel)

In each of the 11 solutions a sample was polished for 5 minutes, one each in the three regions of the anodic polarisation curves: The "etching region", "the polishing plateau" and the "gas evolution" region. The voltages were set as near as possible to the mid-point of each of these regions, for a particular solution.

Samples polished in the "etching" region all showed an etched surface (Fig.5.13) with preferential dissolution of certain grains, and of the grain boundaries.

Samples polished at voltages above the etching region but below the gas evolution region, all had gas bubbles clearly visible to the naked eye, clinging to the surface throughout polishing. These defects (Fig. 5.14) had a central prominence surrounded by an annular groove, and had the same appearance as the pitted samples provided by the local firm experiencing the pitting problem (Fig.5.15).

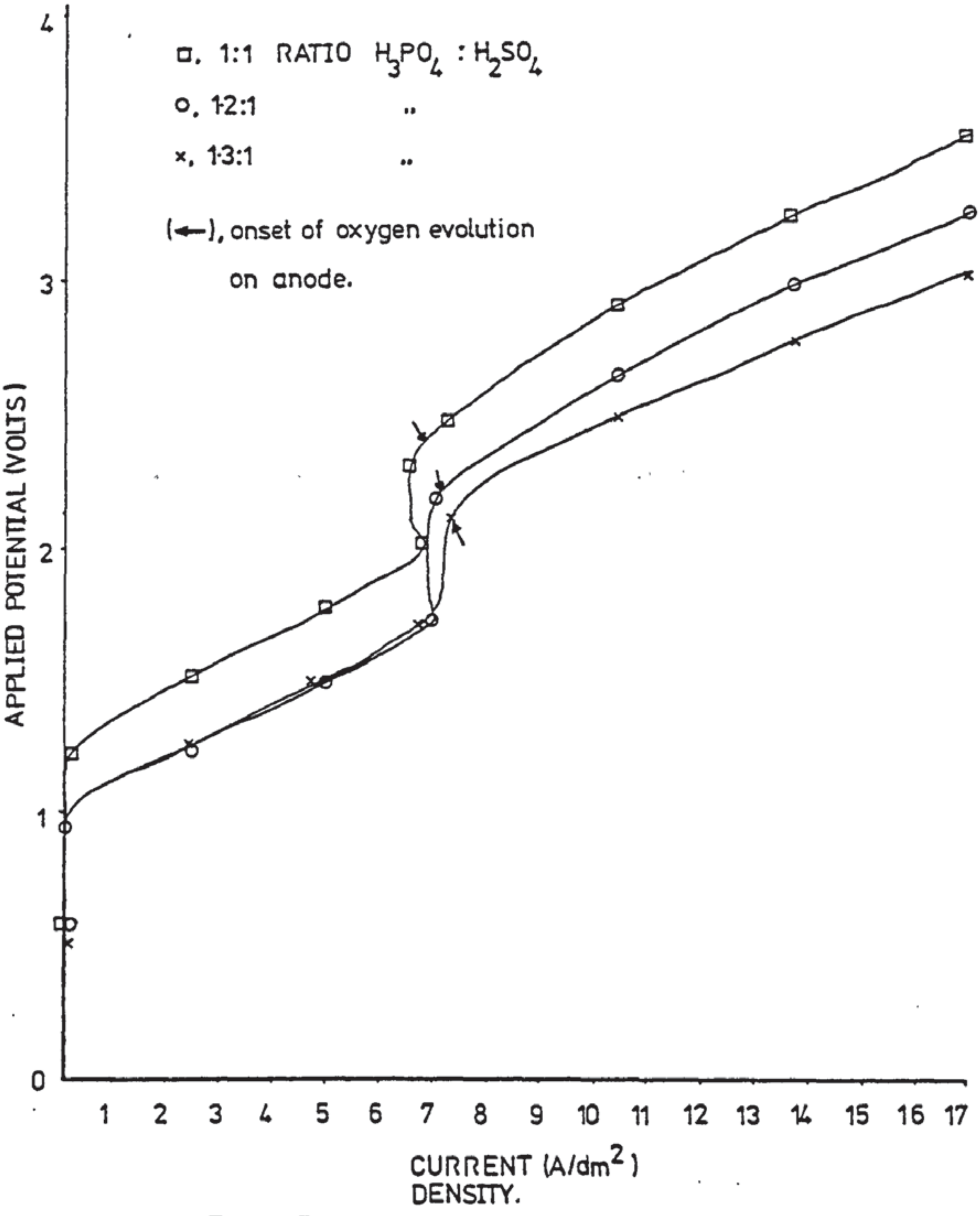


Fig.5.I2. Anodic Dissolution curves for stainless steel in solutions BI,B4,& B5, (table 5.4.).

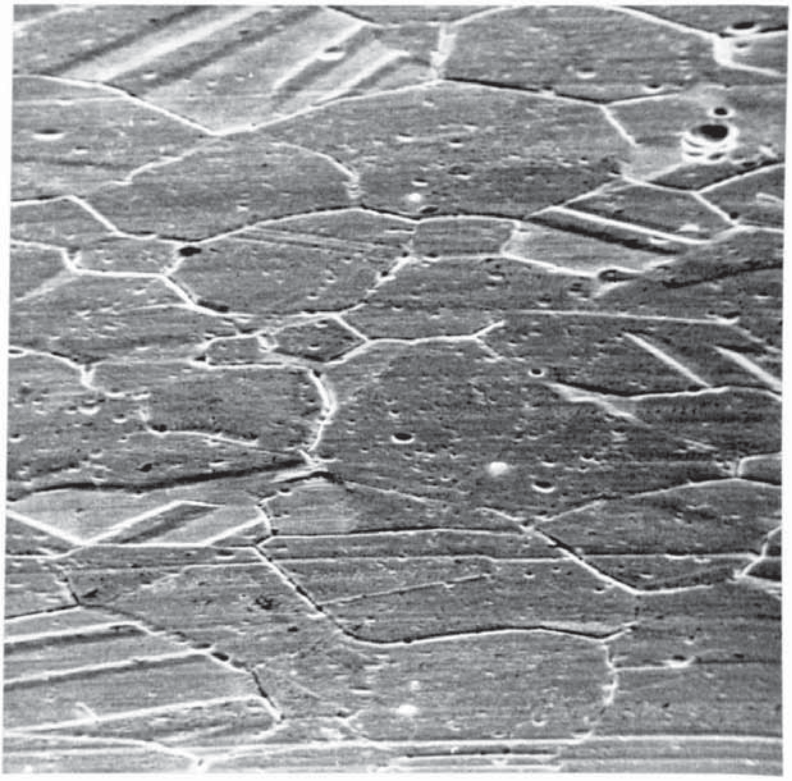


Fig.5.13. A typical Scanning Electron Micrograph of stainless steel electropolished in the "etching region" of the anodic dissolution curves of Fig.5.9-12. X 1000.

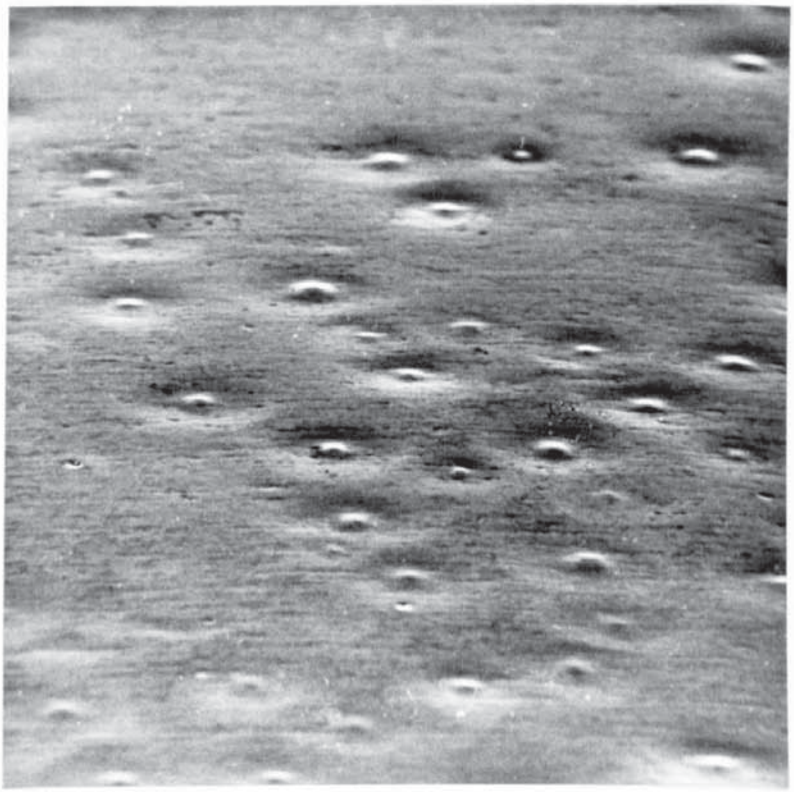


Fig.5.14. A typical Scanning Electron Micrograph of stainless steel electropolished in the "polishing plateau" region of the anodic dissolution curves of Fig.5.9-12. X 100.

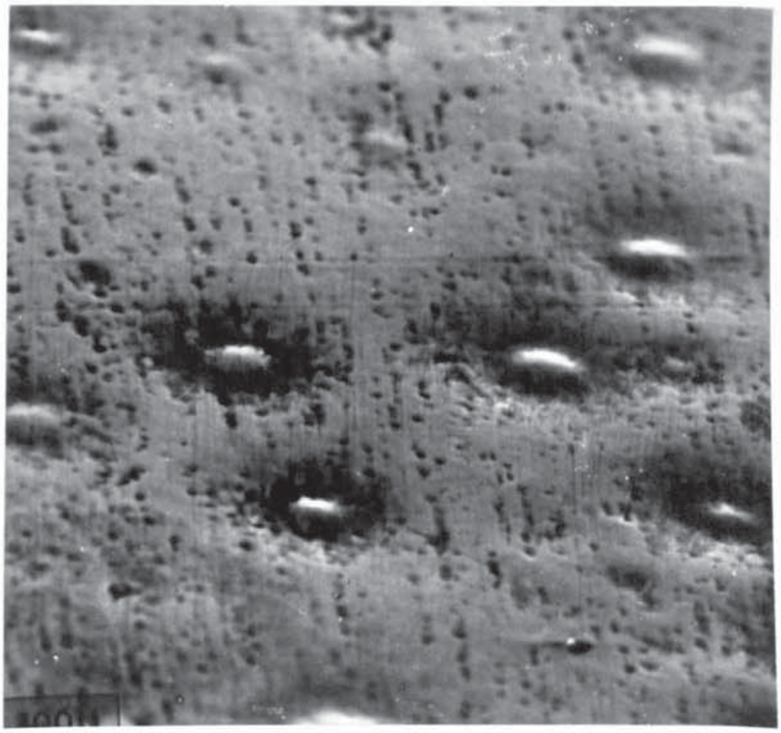


Fig.5.I5. Scanning Electron Micrograph of the pitted sample of stainless steel provided by a commercial user.X 200.

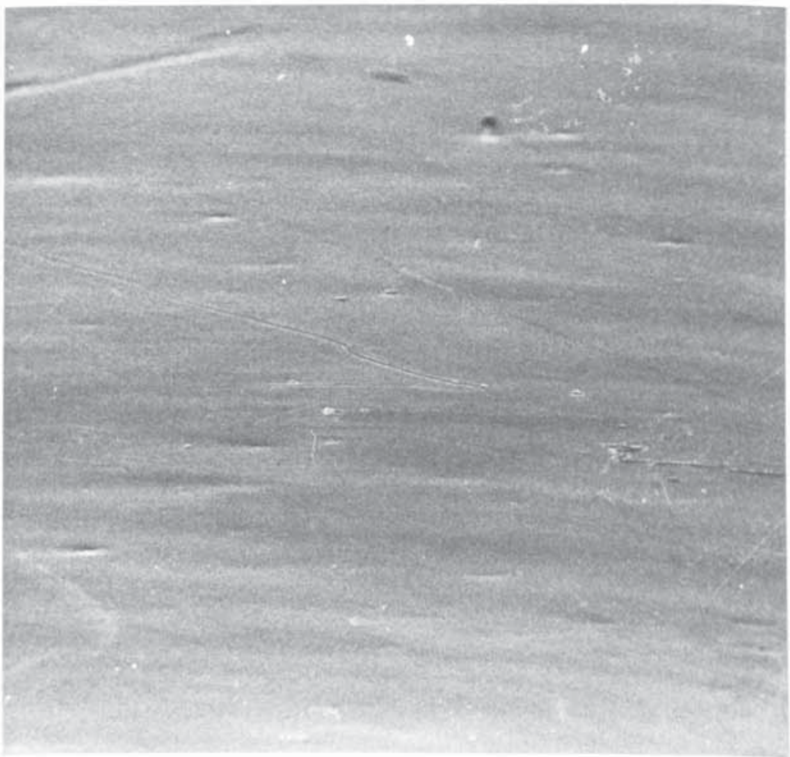


Fig.5.I6. A typical Scanning Electron Micrograph of stainless steel electropolished in the 'gas evolution' region of the anodic dissolution curves of Figs.5.9.-I2. X 550.

However, samples polished in the "gas evolution" region showed highly polished surfaces with no evidence of any defects of any kind (Fig.5.16)

## 5.5 Discussion

### 5.5.1 Aluminium

An increase in the nitric acid content of the solutions produced successively higher current densities for a given voltage. In the solution containing no nitric acid the platinum counter electrode was covered with electrodeposited copper. Since the hydrogen evolution overpotential on copper is higher than on platinum (bright)$^{(85)}$, the cathodic evolution of hydrogen will become more difficult, and this is shown by the lower current densities of the solutions containing copper and the higher current densities of the copper free solutions.

This was not the case in the solution containing 6% nitric acid. Since no copper was visible on the counter electrode surface, one would expect an equal or higher current density and in fact the current density was found to be higher. The presence of nitric acid in the solution catalyses the reduction of the hydrogen evolving off the counter electrode and allows a higher current density.

When a sufficiently high positive potential has been applied to the anode to prevent hydrogen evolution and electropolishing conditions are established, the transport of ions away from the anode will be diffusion dependent, due to concentration polarisation of the solution at the anode interface,producing the viscous layer.

Therefore, as the electron charge of the nitrate and nitrate ions now present in the solution is less than the more abundant phosphate ions, it is likely that the phosphate ions will predominate in the viscous layer.

Oxygen evolution occurs on the anode in the solution with a nitric acid concentration of 20% at potentials over 1700mV. This has the effect of producing a thick film (approximately 2μm thick) on the surface. This film was found to be rich in phosphorus and was not even over the surface but was heavily pitted. The high phosphorus content of the film supports the view that the nitric acid is responsible for increasing the current densities by altering the cathodic reaction and not the anode reaction.

Using an impressed current prior to immersion of the electrode it was not possible to prevent the initial etching of the surface. In the first ten seconds or so, gassing occurred on the anode and then ceased. A proportion of the gas produced towards the end of the ten seconds gassing, clung strongly to the specimen throughout the remaining ten minutes of polishing. These bubbles were clearly visible to the naked eye and ranged in size from 0.1mm to 1.0mm in diameter. The gas bubbles physically obstructed the surface being polished, completely preventing dissolution at the points of contact. Thomas(77) studied similar defects and associated the central prominence with some material masking the surface, but attempts to reproduce these defects in experiments using oils, greases, paints, etc. proved unsuccessful.

Neufeld and Southall(74) observed an apparent central peak on optical micrographs of electropolished stainless steel, but not on electron optical micrographs, and considered that the peaks were not real but optical artifacts due to reflections inside the pit. The authors did realise, however, that this interpretation was open to question. Scanning electron micrographs of the present study, using the high angle of incidence technique of observing the specimen, show clearly the presence of a flat plateau standing proud of an annular groove. The gas bubbles clearly prevent dissolution at the point of contact.

The area surrounding the central peak is dissolved preferentially due to the flow of solution around the bubble causing a localised increase in the agitation and hence increasing the dissolution at these points. The annular groove is not etched, so no breakdown of polishing conditions had occurred in these regions. Increasing the amount of agitation of the solution itself, reduced the extent of the annular groove eventually to the point where the actual point of contact of the gas bubbles was not discernable. This is due to the increased solution agitation preventing any localised variations in the rate of dissolution which produces the annular groove. Neufeld and Southall used a rotating anode, rotating at a speed of 700 r.p.m. which produced a similar effect.

Tegart(3) studied the electropolishing of 70/30 Brass and considered that the defects he found with central light regions were due to the presence of adherent gas bubbles clinging to the surface and thus preventing the underlying metal from dissolving. To determine if brass as used by Tegart(3) had similar gassing defect characteristics as stainless steel and aluminium, the conditions used by Tegart were reproduced (900g/l Phosphoric acid, at 25°C with no agitation) and samples were taken from the 'polishing plateau' and the 'rapid gas evolution region' of the polarisation curve obtained. The samples taken from the 'polishing plateau' region (Fig.5.17) showed a central prominence with a region below (the top of the specimen is to the left of the micrograph) showing preferential dissolution.

However, the sample polished in the 'rapid gas evolution region', unlike stainless steel, showed a pitted surface (Fig.5.18). The pits had a central prominence surrounded by an annular groove.

This indicates that stainless steel may represent a special case, and supports the view(3,75) that there are in fact two types of defect

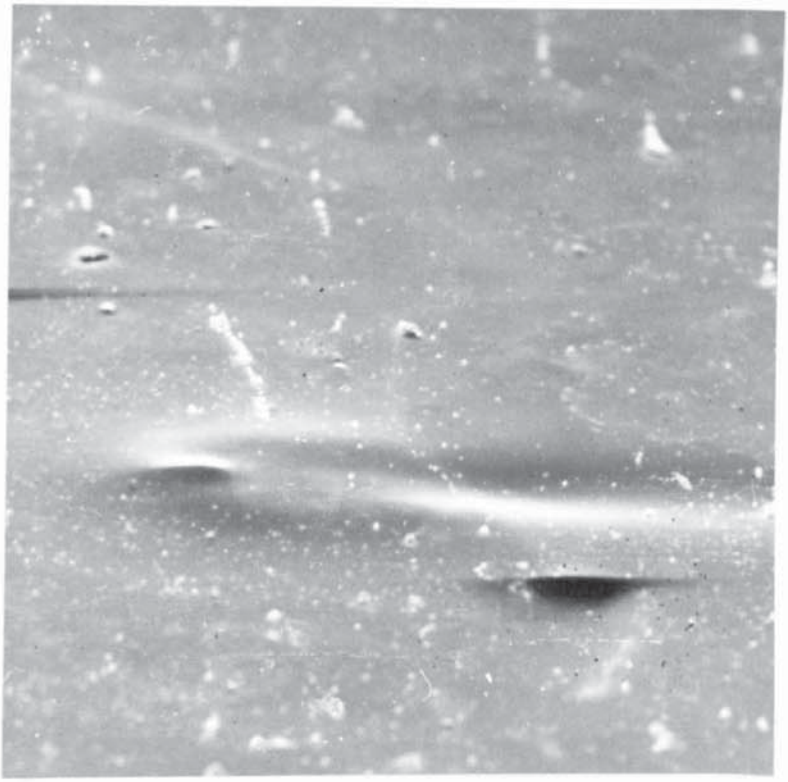


Fig.5.I7. Scanning Electron Micrograph of Brass electropolished in the 'polishing plateau'region. X 200.

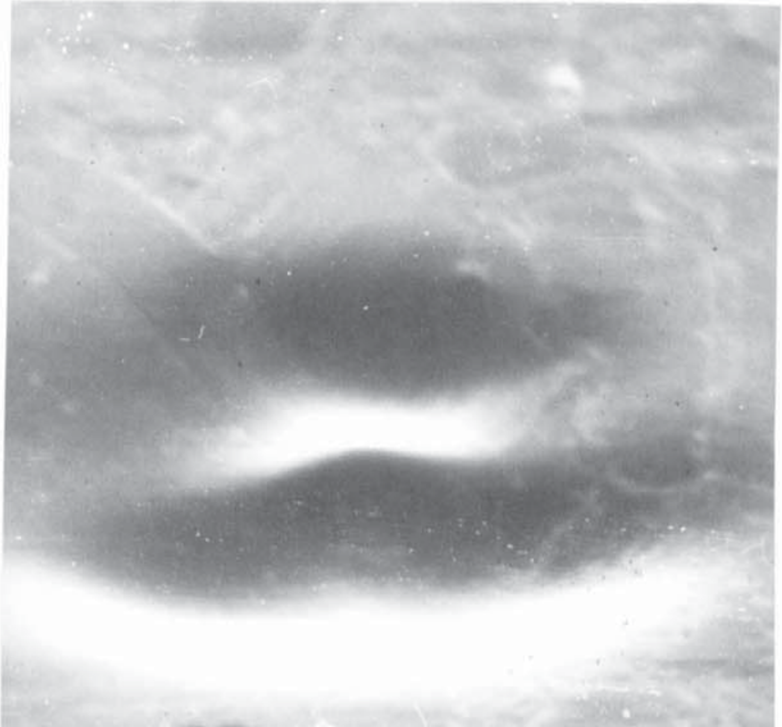


Fig.5.I8. Scanning Electron Micrograph of Brass electropolished in the 'rapid gas evolution'region.X 5000.

characterised by adherent and non-adherent gas bubbles.

### 5.5.2 Stainless Steel

The anodic dissolution curves found in this section (Fig.5.9-12) showed the typical current voltage relationship found by previous researchers.

Dilution of the aged commercial grade solution produced an increase in the current density at a given voltage, which is to be expected since the dilution will increase the ionic mobility and conductivity, and the saturation of the anode layer with dissolution products to form the viscous layer (which was clearly visible to the naked eye) will occur at a higher dissolution rate, and give a higher current density. It is also interesting to note that in these solutions oxygen evolution did not begin at the upper limit of the 'polishing plateau' where the disruption of the viscous layer by the evolution of oxygen is thought to account for the increase in current density as the applied voltage is increased.

In the case of the unaged AnalaR grade solutions dilution again produced an increase in current density for a given voltage, but the onset of oxygen evolution occurred at the voltage where the current density was beginning to rise again after the "polishing plateau". It is evident from this that the dissolved metals in the aged solution retard the onset of oxygen evolution on the anode, possibly by a reduction in the conductivity of the solution, as the aged solutions at a given voltage and comparable dilution gave a lower current density, and more rapid concentration polarisation at the anode. The addition of copper was made because the firm that had produced the pitted sample had moved to a new plant and had made up a fresh solution instead of the decanting and topping up operation normally used, and they had also changed from using copper plated brass jigs to titanium jigs. Preliminary experiments on their solution had shown that the solution would produce a good finish provided that the polishing was done in the oxygen evolution region (for reasons discussed later). The polarisation curves of their solution showed that oxygen evolution was not occurring until relatively high potentials had been applied. Consequently, an addition to the solution was required to lower the potential at which the oxygen evolution occurred In view of the change of solution and the different jigs being used, a copper addition appeared to be the most promising choice. Fig.5.11 shows that this was in fact a correct assumption since copper additions not only increased the current density at a given voltage, but also reduced the voltage required to produce oxygen evolution on the anode from 3400mV to 2300mV.

In solutions not containing copper, there was no visible evidence of the electrodeposition of metal on the cathode. However, additions of copper to the solution produced electro-deposition of iron and copper and relatively small amounts of chromium and manganese on the cathode.

The cathode current carrying capacity is increased by this deposition and will allow the current flowing at the anode to be greater. The copper may also increase the solution conductivity.

The addition of 2g/l of copper can be seen from Fig.5.11 to be the optimum, since a further addition of 4g/l of copper did not produce a substantial increase in the current densities.

The acid ratio was then altered to determine what effect additions of sulphate would have on the polarisation characteristics of the solutions. The sulphate additions were found to decrease the current density for a given voltage, and might have to be compensated for on a commercial scale by the addition of phsophoric acid, to restore the optimum acid ratio.

The morphology of the surfaces was found to be approximately the same for each region of the anodic dissolution curve, regardless of the solution. The etched samples were all etched with preferential dissolution of certain grains and at the grain boundaries. Samples polished in the "polishing plateau" region all showed the presence of adherent gas bubbles, which could not be removed by increasing the agitation to the maximum possible with the apparatus used (a degree to which a commercial plant could not achieve easily).

Neufeld and Southall(74) suggested that the mechanism for the formation of these pits was due to the oxygen evolution producing localised disruptions in the viscous layer, which in turn leads to increased dissolution at the points of evolution. This was not found to be the case in the present study. In the case of aluminium gas bubbles present on the surface produced the same type of smooth rounded pits when the agitation was relatively vigorous, such that the point of contact of the gas bubble was not discernable. The authors also suggested two remedial measures to prevent this pitting. One was to raise the potential at which oxygen evolution occurred in the solution, and the second was to increase the amount of agitation,possibly by ultrasonic agitation. The latter suggestion would be in agreement with the present study since ultrasonic agitation is more likely to dislodge adherent gas bubbles and prevent the subsequent pitting than other forms of agitation feasible on a commercial scale. However, the first suggestion is contrary to the findings of this investigation, where copper additions that lower the potential of oxygen evolutions, have been shown to prevent gassing defects by promoting the rapid evolution of gas bubbles which prevent the adhesion of gas bubbles on the surface whilst at the same time the evolution of oxygen from the surface does not produce any defects.

# CHAPTER 6

## FURTHER DISCUSSION, CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The results of this investigation have shown that the chemical polishing of aluminium proceeds by the etching of the surface, the etch pits initiating at defect sites in the surface oxide film. These etch pits grow laterally until they merge. The edges of the etch pits present ridges of aluminium to the solution which are dissolved preferentially until no evidence of the etched surface remains. Further polishing results in the formation of surface patterns, the dimensions of which are considerably smaller than the etch pit structure, and can in fact be seen to be superimposed on the etch pits (Fig.3.10) and shows the proposal of Bichsel(58), that the patterns arise from the etch network, to be incorrect.

The patterns are influenced by both the crystallographic orientation of the aluminium grains and also the nitric acid content of the solution. The patterns change direction and dimensions according to the grain orientation, and are coarsest in solutions not containing nitric acid or copper. As the nitric acid content is increased the dimensions of the patterns are considerably reduced, until at a nitric acid concentration of 20%, no patterns were resolvable. The cathodic nature of the pattern ridges is clearly demonstrated by the preferential deposition of copper onto the ridges, where present (Fig.3.112). The patterns do not significantly affect the specular reflectivity of the surface. Loss in specular reflectivity has been shown to be primarily due to the presence of peaks of aluminium, associated with gas evolution, and uneven grain dissolution, in solutions not containing copper, and in the case of the 99.5% aluminium, to severe pitting attributable to the presence of predominantly iron rich intermetallics.

The results have also shown that the role of the nitric acid is not the single role of producing and maintaining a surface film. The nitric acid does prevent uneven grain dissolution by the formation of a surface film, but it also modifies the amount and mode of copper deposition, when copper is present in the solution. The optimum nitric acid has been shown to be 6% (by Vol.) in unaged solutions. This corresponds with a total coverage of discrete copper deposits over the surface, that provide sites for the evolution of hydrogen, the cathodic reaction, thus preventing the formation of gassing defects. If the optimum nitric acid concentration is not maintained, then the copper deposition balance is upset and defects arise.

At low nitric acid concentration large isolated copper deposits are found with preferential dissolution in their vicinity. If excess nitric acid is present insufficient copper is deposited and the copper that is deposited is limited to certain grains, which leads to preferential dissolution of those grains.

In addition, as the nitric acid concentration is increased the surface film produced becomes more passive. This is indicated by the increase in the nobility of the potentials recorded, the eventual suppression of the sub-micro pattern (which have been shown to be of an electrochemical nature), the suppression of uneven grain dissolution, and when copper is present in the solution, the lack of deposited copper. The latter proposal is, however, open to question, as it might be argued that the presence of excess nitric acid in the solution merely dissolves the deposited copper at a more rapid rate, so that at any one time, little copper is present on the surface.

The electron spectroscopy results indicate that the surface film is essentially oxide, but the presence of copper incorporated in the film.

suggests that the film is of the 'compact solid' type, as suggested by Hoar, Mears and Rothwell(61).

The idea that a viscous film (estimated to be approx. Iµm.thick(21)) is present as well as a surface film and assists with the polishing process appears inconsistent with the present study, which has shown the presence of discrete copper deposits, of an average size of 2µm, (under optimum conditions) covering the surface, which would necessitate the existance of the viscous layer between these deposits. The continuous deposition and dissolution of the copper deposits and the associated hydrogen evolution would tend to disrupt any such layer.

The presence of intermetallics, in particular those that are rich in iron, are detrimental to the polishing process as they act as sites for hydrogen evolution in preference to the aluminium matrix, in a similar fashion to that proposed by Chatterjee and Thomas(65) for the etching of aluminium in caustic soda. The effect of these intermetallics in chemical polishing solutions is considerably reduced by the presence of copper, deposited, not only on the aluminium surface, but also preferentially in the iron rich intermetallics.

The results of the present study allow further discussions on the mechanism of chemical polishing. The initial etching stage provides for the removal of defects of approximately 1µm and less. Potential measurements have shown that the air formed oxide is removed and replaced by a more noble film that allows metal cation transport through the film. Tegart(3) suggested that polishing involves two distinct processes: the 'smoothing' of irregularities above approx. 1µm and 'brightening' where smaller irregularities (approx 0.01µm) are removed. The present work suggests a modification to this proposal. The smoothing process operates but the brightening is due not so much to the removal of small irregularities but to the prevention of a number of possible defects, whilst even dissolution is maintained. Even dissolution is achieved by the nitric acid providing a compact surface film, to prevent uneven grain dissolution. Other defects like gassing defects, are prevented by the correct nitric acid concentration controlling the copper deposition to prevent such defects.

A lowering of the phosphoric to sulphuric acid ratio from 4.7:1 to 1.6:1 has been shown to be successful in maintaining a polishing rather than a 'bright etch' type of solution(2). However, the 99.99% aluminium showed a poorer finish due to the presence of sulphur rich structures on the surface. These structures also appeared on the surface of the 99.5% aluminium allowed to drain for relatively long periods of time before rinsing, and in a solution deliberately operated at a low water content. Their incidence also rose in the solution with a phosphoric to sulphuric acid ratio of 1:1. These factors indicate the attainment of a solubility limit of aluminium sulphate at the aluminium/solution interface. This can be overcome in the 1.6:1 ratio solution by the addition of B.T.A. into the solution, and to a limited extent in the 1:1 ratio solution. Dilution of the 1:1 ratio solution with water also reduced the incidence of the sulphur rich structures, but other defects (gassing defects due to the absence of deposited copper) arose.

Due to the complex nature, not only of the solutions themselves, but also the possible reactions of the B.T.A. with the solutions, it is difficult to establish a mechanism to account for the behaviour of the B.T.A. However, it is known that B.T.A. acts as a corrosion inhibitor(68-73) and adsorbs onto the surface of copper. As copper is known to increase the rate of dissolution of the aluminium(83), and that the loss in specular reflectivity is due to the formation of insoluble dissolution products on the surface during relatively long drain times, it seems likely that the B.T.A. is adsorbing onto the surface of the copper, reducing the rate of aluminium dissolution and thereby, preventing the attainment of a solubility limit at the aluminium/solution interface and the corresponding production of sulphur rich compounds.

Other possibilities are that the B.T.A. forms a complex with the dissolving aluminium sulphate that is more soluble in the acid solution and prevents the defects in this way. Alternatively, the mechanism may be connected with the proposal of Mayanna and Setty(72) that the B.T.A. affects the kinetics of copper dissolution, by combining with the copper ions in solution thus preventing their deposition which would reduce the rate of aluminium dissolution.

The work on the electropolishing of aluminium and stainless steel in the present study has been concentrated on the production and prevention of surface defects associated with gas clinging or evolving from the surface of the metal. In the case of aluminium it has been shown that adherent gas bubbles are responsible for the defects found and that these defects consist of a central prominence surrounded by an annular groove. This can be prevented by allowing the aluminium to chemically polish before the application of the current. The deposited copper prevents the evolving hydrogen from coming into contact with the aluminium surface and on applying a current no gas bubbles are left on the surface as the copper dissolves. This, however, may only apply to phosphoric/sulphuric/nitric acid mixtures. Alkaline solutions like the Brytal solution have not been studied.

Similar defects were produced on stainless steel when polishing above the etching region and below the oxygen evolution region. These defects were also due to the presence of adherent gas bubbles. An increase in agitation did not dislodge these gas bubbles on the stainless steel or the aluminium. An increase in agitation did, however, modify the shape of the defects on the aluminium, to the extent that the central prominence was no longer present and the point of contact of the gas bubbles was not discernable, although the gas bubbles were clearly visible to the naked eye, on the surface. For stainless steel it was found possible to produce a highly reflective surface by polishing in the oxygen evolution region. Dissolved metals from the stainless steel (at 4% by wt.) increased the oxygen evolution overpotential and effectively extended the range of potentials that produced gassing defects. The addition of 2g/l of copper to the solution was found to reduce the oxygen evolution overpotential and reduce the range of voltages that lead to gassing defects. The copper deposits on the cathode increases the current carrying capacity of the cathode and thus allows more current to flow at the anode. This addition has in fact been found to be successful on a commercial scale(90).

Brass, however, does not show the same properties as stainless steel. Samples polished in the 'polishing plateau' region do show the same kind of defects, but samples polished in the 'rapid gas evolution region' showed gassing defects. This may be due to a subtle difference in the type of surface film produced on the two metals. Hoar and Farthing(27) have demonstrated the presence of a surface film on copper being electropolished, and Williams and Barratt(30) found that the film was rich in copper phosphate. The present study and that of Olefjord(32) have shown that the films on aluminium and stainless steel respectively, are essentially oxide in nature. These facts indicate that a possible distinction may exist between metals that produce a passive 'contaminated' type of film and metals that produce a film of a different nature. Gabe (33,34) has suggested that in the electropolishing of copper at lower temperatures, the process is diffusion layer controlled whilst at higher temperatures it may be surface film controlled. This would explain why on copper, at the temperatures used for polishing, disruption of the diffusion layer by gas evolution leads to the formation of defects. However, on stainless steel, where a passive film is the predominantly controlling factor, gas evolution prevents the adhesion of gas bubbles which lead to defects.

## CONCLUSIONS

1) Chemical polishing proceeds by the sequential etching of the surface, levelling of the etched network and the subsequent prevention of the formation of any surface defects (e.g. gassing defects and uneven grain dissolution).

2) Nitric acid is responsible not only for the formation of a stable passive film on the surface but also controls the size and distribution of copper deposits on the surface.

3) Copper is essential in a phosphoric/sulphuric/nitric acid type of chemical polishing solution to prevent the formation of gassing defects, and to reduce the effect of impurity elements, in particular iron.

4) The surface film present on the surface during chemical polishing is of an oxide type, contaminated with metal cations (e.g. copper). Phosphorus, sulphur and nitrate atoms are only adsorbed onto the outermost layers of the film, and the phosphorus is unevenly distributed over the surface.

5) The ratio of phosphoric to sulphuric acid cannot be reduced to a 1:1 ratio and still provide a highly reflective surface with the only addition being copper.

6) Loss in specular reflectivity with extended drain times can be prevented by the addition of B.T.A. which probably adsorbs onto the surface of the deposited copper and reduces the rate of aluminium dissolution during draining, thus preventing the formation of surface defects.

7) In phosphoric/sulphuric acid solutions gassing defects on stainless steel and aluminium are due to the presence of adherent gas bubbles

and not gas evolution and can be prevented by a prior chemical polish (aluminium) or by polishing in the oxygen evolution region (stainless steel). Copper represents a different situation which may be governed by the reduced effect at relatively low temperatures of the surface film, and the importance of the diffusion layer.

## SUGGESTIONS FOR FUTURE WORK

1) The present investigation has been confined to phosphoric/ sulphuric/ nitric acid type solutions. Alkaline solutions (e.g. the Brytal) may exhibit different properties, particularly with reference to gassing defects. Further work on this and other solutions would provide valuable information on the types of defects produced and on a possible general mechanism of chemical and electro-polishing for all types of solution.

2) The work on the electropolishing of stainless steel was only on 18/8 austenitic steel. This is only one of a wide range of stainless steel alloys which are electropolished commercially. Further work in this area may enable the widening of the range of stainless steels that can be electropolished, and on the best conditions to use to achieve the optimum results.

3) A study of the effect of dilution on the phosphoric/sulphuric/ nitric acid type of chemical and electropolishing solutions may lead to the development of more dilute cheaper solutions.

4) There are at present a wide range of different organic and inorganic additives that are commonly used in both chemical and electropolishing solutions(2) and an extensive study of the polarisation characteristics, and scanning electron microscopy study of the surface under various conditions would provide valuable information on the effectiveness of these additives and the way in which they affect the polishing mechanism.

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