DAMAGED
TEXT
IN
ORIGINAL

CHEMICAL POLISHING OF ALUMINIUM

by

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ABSTRACT

The literature concerning the chemical polishing of aluminium has been critically reviewed, with particular reference to the surface morphology of polished aluminium and the addition of heavy metals to polishing solutions. The literature review has included electropolishing, as most of the theoretical work on polishing systems has been confined to this field.

The surface structure of aluminium, formed under various polishing conditions, has been examined using replica, transmission and scanning electron microscopy. Other surface assessment techniques, specular reflectivity and rate of metal dissolution measurements, have also been used.

During the initial stage of chemical polishing the aluminium is etched. The characteristic etched surface structure is produced by the merging of laterally growing, spherical etch pits, nucleated at defects in the original oxide film. As the process continues the etched surface structure is replaced by a finer structure, characteristic of a polished surface. Further polishing results in a deterioration of surface quality. The polishing times at which the characteristic structures are produced, depend on the amount of heavy metal in the solution.

The addition of copper to chemical polishing solutions has been shown to assist brightening. This phenomenon has been

studied by determining the amount of copper deposited on aluminium during polishing, under various conditions. It is apparent that there is a clear relationship between the surface structure of the aluminium and thus its surface finish, and the amount of copper deposited on the surface during polishing.

Electron microscopy examinations have shown that the deposited copper is in the form of discrete particles which increase in size as polishing takes place. The copper is deposited on the submicro asperities of the aluminium surface during polishing. This promotes a localised dissolution at the asperities, which results in a decrease of the scale of the surface features and a smoother, brighter surface is produced.

Electrode potential readings of the aluminium during chemical polishing indicate that a compact solid film exists on the surface whilst polishing takes place. It is suggested that brightening of the surface is maintained by the presence of a compact film which prevents structural etching of the metal.

The effect of surface pretreatments on the chemical polishing of aluminium has been studied. The effect of pretreatments is only pronounced until the original oxide is removed and the etched surface structure produced.

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CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

1.1. Introduction

Metals undergoing anodic dissolution may under particular electrical and chemical conditions develop lustrous, highly reflecting surfaces. Such a process is known as electropolishing.

Chemical polishing techniques have also been introduced, apparently as a result of the accidental observation that polishing of metal occurred, in some electropolishing solutions with no applied voltage.

Although a very large number of electropolishing processes have been developed for some considerable time, their use in industry has never been widespread. This is because a heavy capital outlay is required and the process is costly to operate. The much later, but relatively inexpensive, chemical polishing processes have been used extensively, particularly in the finishing of non-ferrous metals. In the Aluminium Industry chemical polishing is invariably used as a polishing treatment prior to anodising.

A considerable number of processes have been developed to chemically polish aluminium, which have been described in detail by previous workers(1,2,3,4).

Most important of these in practice are the concentrated phosphoric-sulphuric-nitric acid solutions and the more dilute nitric acid-ammonium bifluoride solutions.

The most significant of the phosphoric-sulphuric-nitric acid solutions are those commercially available under the name of Alupol IV and V(5) in Germany and Phosbrite 159(6) in Great Britain. These patented solutions give good results on super-purity and commercial quality aluminium and on several aluminium alloys. Many of the above chemical polishing baths contain soluble salts of heavy metals e.g. copper, which are believed to enhance brightening, although the mechanism by which this takes place is not clear.

The best known nitric acid-ammonium biflouride process is the E.W. (Erftwert) process developed by the Vereinigte Aluminium Werke in Germany(7), which is widely used in that country. This process is characterised by a high dissolution rate of 0.25 to 0.5 mm. per minute and is applicable only to high purity aluminium and the high purity aluminium-magnesium alloys.

The knowledge of the mechanism of electropolishing is not complete, although its main features are now fairly well established. Chemical polishing has been considered as an extension of the same principles but with the current generated internally in the system and not applied externally.

It is usually considered that polishing consists of two distinct processes, levelling, or the removal of asperities greater than about 1 μm. in size, and brightening, the maintenance during dissolution, of a nearly atomically smooth surface by the suppression of crystallographic etching. Edwards(8) has shown that prominences on the anode surface tend to dissolve more readily than depressions on purely geometrical grounds, if all points on the surface dissolve at a uniform rate, but that the speed of levelling is increased during polishing. Levelling thus occurs to some extent in all anodic-solution systems so that brightening is the characteristic feature of polishing. The suppression of etching requires that the differences in energy between atoms of a metal surface should play no part in determining the dissolution of one atom in preference to another, the removal of atoms should occur purely at random. This ensures that the formation of etch figures by the preferential dissolution of high energy sites, is avoided and a surface giving high specular reflection is produced. Hoar and Mowat(9) suggested that random removal of atoms is achieved through the formation of a compact solid film on the anode surface, so that the atoms from the metal lattice are accepted by random cation vacancies in the film.

Edwards(10) however, proposed that the random arrival of acceptors in the polishing solution at the anode surface, results in uniform dissolution and suppression of crystallographic etching.

Surprisingly little work has been conducted on the chemical polishing process other than that of a very empirical nature. It would be valuable to assertain whether the proposals put forward to explain brightening during electropolishing apply in the case of chemical polishing. Also open to question is the brightening effect of heavy metals in the polishing solution.

An extensive study of the surface morphology of the aluminium after chemical polishing is important in its own right and because of the effect this structure could have on the subsequent anodic film. Previous workers(11,12) have shown that the pores in anodic oxide films are nucleated preferentially at the protuberances of the polished structure. Work of the present author and others(13,14,15) has also shown that on anodising, anodic oxide films less than 6 µm. thick replicate the features of the surface structure produced by polishing.

A phosphoric-sulphuric-nitric acid based chemical polishing solution was used during this investigation as it is a solution of considerable commercial significance and also one which has been studied in the past.

In the course of this chapter the relevant literature has been reviewed. This review has included electropolishing, as most of the theoretical work on polishing systems has been confined to this field.

The scope of the present investigation is then discussed in the light of the conclusions of previous workers.

1.2. Electropolishing

Jacquet and other workers(16,17,18) recorded the typical relationship between the current and the anode potential during electropolishing, shown in Fig. 1.1.

This curve can be considered in four sections, 1) between A and B, increase in current is proportional to increase in potential; 2) from B to C the current is unstable and fluctuates, sometimes with an observable definite periodicity; 3) from C to D further rise in potential is accompanied by little or no change in current density; 4) further increase of potential above D leads to a rise in current density associated with gas evolution.

According to Huber(19), three reactions occur at corresponding steps on the diagram. For aluminium these are as follows:-

$$(1)\quad Al \rightarrow Al^{3+} + 3e^-$$

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

$$(3)\quad 4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

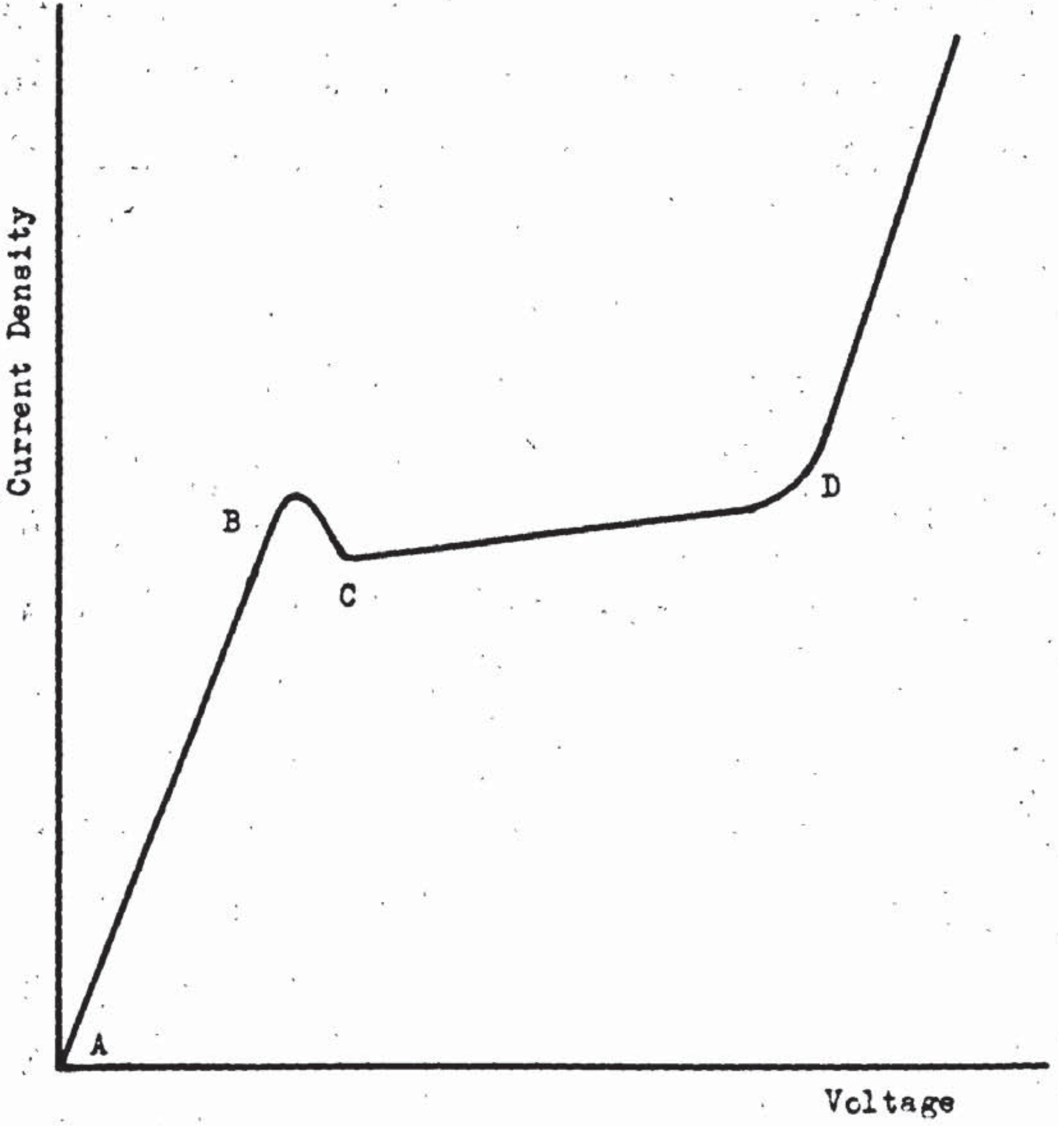


Fig. 1.1 Typical Voltage-Current Density Relationship for Electropolishing.

In the first stage, represented by A - B, metal dissolution is determined by concentration and activation polarisation. The process is that of the normal anodic etch in which atoms are dissolved from the surface according to their free energy. Over the range B - C, the conditions are unstable and some polishing may occur. Reaction 2 takes place between C and D and this is the region where polishing occurs, the limiting current plateau. Reaction 3 takes place after point D where oxygen evolution begins and the current density rises with increasing anode potential.

Jacquet in his early work(20) noted that a layer of solution of higher viscosity than the bulk solution accumulated at the anode. Using a vertical anode this viscous layer can be seen to stream away slowly from the metal surface under the influence of gravity. He observed that the interface between this layer and the bulk of the solution was vertically plane and put forward the hypothesis that the layer had a relatively high electrolytic resistivity. Thus the resistance between peaks on the metal surface was less than that between troughs on the surface and the bulk of the solution. This would lead to a higher current density at the peaks so that a preferential dissolution would occur leading to a polished surface.

This simple early theory can be critisized as, in most circumstances, the potential rise at the onset of polishing would imply an impossibly high electrolytic resistance of the liquid layer.

Elmore(21,22) proposed that diffusion of metal ions through the viscous layer was of primary importance during polishing and developed a quantitative theoretical approach on this basis. He stated that the following assumptions are necessary to account for electrolytic polishing by diffusion. 1) When current passes through the cell, metallic ions are transported from the vicinity of the anode into the bulk solution by diffusion rather than by electrolytic migration. This requires that the concentration gradient at the anode must at all times be proportional to the current density. 2) After the current has flowed for a time t_o, the anode layer becomes saturated with metal ions. 3) After time t_o, the limiting current density is established due to the concentration gradient. From these assumptions it follows that when the limiting current density has been established, metal will be preferentially removed from the peaks, because at these points the concentration gradient will be greater than in the depressions and the diffusion of ions faster. Consequently the surface will become progressively smoother.

Elmore derived from the simple diffusion equation, the following relationship between the applied current i_c, and the transition time t_o, to establish a saturated anode layer and obtain polishing conditions.

$$i_o t_o^{\frac{1}{2}} = \frac{1}{2} C_m F(\pi D)^{\frac{1}{2}} = \text{constant}$$

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

To verify the above relationship, Elmore employed copper electropolished in an ortho-phosphoric acid electrolyte. He found that the values of $i_o t_o^{\frac{1}{2}}$ were a constant for any electrolyte concentration, which he predicted in the theoretical argument.

de Sy and Haemers(23) verified Elmore's equation for different acid concentrations. Walton(24) studied the properties of the anode layer on copper in phosphoric acid and showed that it was highly supersaturated with copper. He concluded that the limiting current density was due to the diffusion of acid cupric phosphate, $CuHPO_4$.

Elmore's hypothesis can be critisized however, because his argument neglected the fact that the diffusion coefficient is effected by changes in viscosity. Edwards(10) extended the work of Elmore and found experimentally that copper concentration has little effect on $i_o t_o^{\frac{1}{2}} 3^{\frac{1}{2}}$ (Elmore's parameter corrected for the variation in diffusion coefficient with concentration, where $_3$ is the dynamic viscosity of the solution).

He postulated that the limiting factor in electropolishing is not the diffusion of metal ions outwards, but the diffusion inwards through the viscous layer of some acceptors necessary for the dissolution of the anode.

In terms of the acceptor theory, first suggested by Halfway(25) and developed by Edwards, it was suggested that suppression of etching is facilitated by the fact that the combination of acceptor and metal ion takes place instantaneously when the acceptor ion reaches the metal surface. Since the acceptors in the electrolyte arrive at the anode surface under the influence of diffusion and possibly convection but not to any great extent by electrolytic migration, their distribution will be random and therefore metal dissolution will be random. If a cation can only dissolve from the metal surface by contact and combination with an acceptor, then a film depleted in acceptors will be established at the anode, which would account for the fall in current after a certain time. However, before the polishing conditions are established, there will be an excess of acceptors on the surface, so that the relative rates of dissolution at different points on the surface will be determined by the energy of the copper atoms at these points. Dissolution will be therefore influenced by crystal structure and etching will result.

Edwards(8) also used a laminated anode to show that on a rough surface of equal potential, the current density on projecting areas was greater than on recessed, but that the ratio did not change significantly on passing from etching to polishing conditions. Thus even anodes undergoing etching become smoothed on a macroscale. Experiments with a copper microgroved record showed that during electropolishing the smoothing efficiency was greater than that calculated for the equal rate case, and was similar to that expected for dissolution under primary current conditions. This work showed that an earlier theory involving the passivation of concavities(26) was invalid.

Wagner(27) carried out a mathematical analysis of the smoothing that occurred during electropolishing, and supported the views of Edwards, concerning the diffusion of acceptors and his smoothing efficiency calculations.

Nicholas and McG.Tegart(28) suggested that the smoothing in polishing solutions could be explained without making any assumptions about the acceptor mechanism of polishing. Their analysis concluded that the rate of metal removal was determined by the local curvature of the surface. Such conditions apparently existed in other anodic dissolution processes i.e. etching and chemical polishing in addition to electropolishing.

Hoar and Mowat(9) emphasised that smoothing or levelling is characteristic of all anodic dissolution processes and that brightening, that is, the suppression of crystallographic etching during dissolution, is the special feature of electropolishing. Hoar and Mowat suggest that etching is suppressed by the formation of a thin compact solid film on the anode surface, rather than the random arrival of acceptors to the surface proposed by Edwards(10). 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(29) demonstrated the existence of this film by droping mercury on the metal surface. Anodes undergoing etching were wetted by the mercury whereas during polishing they were not. Compact solid films have since been shown to exist on the anodes of many metals by cathodic reduction, Allen(30), a - c impedance measurements, Cole(31), Cole and Hoar(32) and electron diffraction, Williams and Barrett(33).

Darmois and Epelboin(34,35,36) considered that a solid oxide film was unnecessary for polishing to occur, but postulated that an anhydrous layer, a monolayer of anions, must be adsorbed on the anode. The high field created by a layer of this nature would lead to random removal of metal ions by the indiscriminate abolition of the energy barrier for all lattice cations. This hypothesis has weaknesses in that a satisfactory explanation is not available to account for the transfer of cations through a close-packed negatively charged layer, should it ever be formed, which is doubtful in view of the fact that it would have lateral coulombic instability. Cations could be pulled into the layer if the anions were not close packed and lateral coulombic stability thus attained. This would in fact produce a two-dimensional compound, which can be regarded as the limiting case of the Hoar and Mowat(9) theory.

1.3. Chemical Polishing

Early workers in this field observed an increase in the brightness of iron and steel samples after immersion in a solution containing oxalic acid, sulphuric acid and hydrogen peroxide(37,38). Cyclic evolution of gas occurred which, according to Hedges(39), was probably due to the formation and destruction of a solid film.

Initially, this phenomenon was explained by assuming that a sparingly soluble film of ferrous oxalate formed on the surface, which was then oxidised by hydrogen peroxide to the more soluble ferric oxalate and redissolved. Other metal-acid systems were explored in an attempt to prove that the fundamental mechanism was based on the oxidation of an insoluble salt to a soluble one, with little reward, and this hypothesis has been discounted(38,40). These authors considered that the film formed was in fact an oxide, the thickness of which was less than 200 Å.

Pinner(41) viewed the mechanism by which aluminium was chemically polished, as basically one of controlled corrosion in an electrolyte. He stated that the reactions are of an electrochemical nature as opposed to the pre-supposed view that only chemical reactions were involved, thus likening the chemical polishing process to that of electropolishing. Pinner suggested that in the absence of an external source of e.m.f., local anodic and cathodic areas exist in different areas on the surface, or, more rarely, alternate in time in the same area. The local anodes or cathodes are due to variations in potential over the surface, which could be caused by impurities, by distinct phases or dispersed constituents in the case of an alloy, by imperfections in the protective film, or by variations in the supply of oxygen or other dissolved constituents in the electrolyte. A surface film could itself be cathodic to the metal.

Brace(42) also concluded that chemical polishing was an extension of electropolishing. He stated that the high cell voltage required to produce polishing can be produced either by raising the temperature, thus increasing the degree of attack, incorporating oxidising agents having a depolarising effect, or incorporating a heavy metal salt, thus forming a local couple on the aluminium surface.

The anodic reaction according to Pinner, is the dissolution of aluminium and is represented by the equation:

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

This reaction was supported by Brace and Kape(43) who further suggested that the aluminium initially formed a complex film containing aluminium phosphate, but continuation of dissolution resulted in further aluminium ions diffusing through the film and dissolving in the polishing bath. Fischer and Koch(44) stated that a further additional anodic reaction may be the evolution of oxygen.

General agreement exists upon the nature of the cathodic reaction, which is partially the evolution of hydrogen, represented by the following equation:

$$3H^{+} + 3e^{-} \rightarrow 3/_{2}H_{2}$$

Fischer and Koch extended this basic reaction to include the reduction of oxidising depolarising agents, for example, the deposition of copper; a view that was supported by Scott(45), and suggested that these reactions constituted the primary reaction whilst the evolution of hydrogen was of secondary importance, although proceeding simultaneously. The suggestions of these authors were supported by their experimental work in which they analysed the gases emitted from polishing baths and found large quantities of nitrous oxide, and smaller quantities of nitric oxide, nitrogen peroxide, nitrogen, hydrogen and oxygen, the proportions of the various gases depending upon the particular bath composition.

Fischer and Koch believed that porous films were formed in chemical polishing solutions of the phosphoric, sulphuric and nitric acid type, due to the high dissolution rates. The authors assumed that the polishing action was due to the high corrosion current densities (50-500 amps./sq.ft.) compared with 0.01 - 1 amp./sq.ft. in other media, at which the local anodes of the surface were partly passivated by a porous surface film.

It has been shown experimentally by several workers(6.46.47) that the addition of nitric acid to phosphoric acid based polishing solutions, reduced the dissolution rate of aluminium.

Brace and Kape(43) stated that high dissolution rates were not required for satisfactory polishing and have shown that an optimum polished surface was obtained with minimum dissolution rate. These authors assumed that in chemical brightening the nitric acid is reduced to release oxygen.

This reaction leads to the formation of a relatively stable oxide film, but one which is in a state of dynamic equilibrium, being continually reformed as dissolution proceeds. Below the optimum nitric acid content etching occurs, probably because insufficient oxygen ions reach the surface to maintain a stable oxide film. Above the optimum content, the film appears to breakdown, which may be caused by local changes in pH or by other reactions at the metal surface.

General agreement exists on the mechanism of smoothing during chemical polishing(1,3,6). It was proposed that this is due to the depletion of anions in the electrolyte adjacent to the metal surface, as suggested by Edwards to explain smoothing during electropolishing. The authors suggested that in phosphoric acid based solutions, a viscous layer is formed at the metal-electrolyte interface, because the dissolution products are more viscous than the bulk of the solution. In a short time this layer is depleted of anions capable of joining with metal ions, so that an anion concentration gradient exists from the outer surface of the viscous layer to the metal surface. Preferential dissolution will therefore take place at the asperities as the concentration gradient is greater at these points than at the depressions.

1.4. Heavy Metal Additions

Most patented chemical polishing reagents contain heavy metal additions(5,6,48,49) e.g. copper, iron, nickel etc. although no theoretical justification has been found as to why these particular metals should prove effective in increasing brightening. In fact it is well known(50,51,52) that the prescence of copper either alloyed with aluminium or in solution in contact with aluminium, generally favours pitting attack.

Fischer and Koch(44) have suggested that the function of the heavy metal in chemical polishing solutions was merely to catalyse the reduction of the oxidising agent.

However, Brace(42) proposed that copper additions produced brightening by assisting micropolishing. He suggested that this could take place by the removal of local discontinuities in the surface, which are of dimensions similar to that of the oxide film. The copper atoms would be deposited in the valleys, which are points of lower potential, and thus act as local cathodes and cause the removal of small imperfections in the neighbourhood, as these are removed by preferential attack.

Brace and Kape(43) suggested that during the chemical polishing process, the heavy metal, in this case copper, was precipitated at defect sites in the oxide film by a simple replacement reaction.

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

The precipitated copper is presumed to provide local galvanic cells due to the potential difference between itself and the aluminium base. It is considered that deposition of the copper proceeds until the whole surface is covered to a thickness of several atomic layers, this reduces the rate of dissolution of the underlying aluminium and results in microsmoothing. The authors believed that the copper is being continually dissolved and reformed in a similar manner to the oxide film, and they further suggested that when the optimum copper is exceeded the number of atoms arriving at an active zone is increased, and massive loose deposits build up. These cause appreciable local currents and etching of the aluminium in the vicinity, but this soon produces undercutting of the copper deposit which falls off and is redissolved. The process continues as further dissolution creates new sites, but at any instant there are sufficient sites at which etching predominates for the rate of dissolution to be greater and the brightness less than under optimum conditions.

Brace and Kape also proposed that if a redox system operates, the heavy metal itself is also partly oxidised to form cuprous or cupric oxide. They stated that this theory was supported by the fact that considerable difficulty was experienced in removing the copper smudge formed on the surface during polishing which, if pure copper, would have dissolved easily in nitric acid.

Pinner(53) stated that it was most unlikely that copper would be oxidised in a local cell in which it formed the cathode.

1.5. Surface Structures

It is apparent that both chemical and electropolished surfaces show characteristic surface markings. However, in both cases the exact mechanism of formation of these structures is not clear.

1.5.1. Electropolished Structures

Electron microscope studies by Bucknell and Geach(54) and by Brown(55) led to the discovery of fine line markings on replicas taken from electropolished aluminium. The lines, which were interpreted as shallow steps or grooves in the metal surface, were equi-spaced at intervals of about 1,000 Å. They frequently resembled "furrows" in their parallel alignment and changed direction from grain to grain. Brown noted that some grains showed an orange peel pattern, and globular markings 400 - 800 Å in diameter, were observed by Nutting and Cosslett(56). Bucknell, Geach and Welsh(57) using a perchloric acid - alcohol polishing solution, found that the parallel alignment of the "furrows" was preserved only over a limited range of orientation around the (110) pole, the lines invariably following the $\langle 100 \rangle$ direction. Bussy(58) made similar observations using a perchloric acid-acetic anhydride bath. It was suggested by Brown and by Bussy that the surface markings may represent some imperfection in the grain structure of the metal. This suggestion was refuted by Welsh(59) and later by Hollo(60). Welsh investigated the surface markings produced on aluminium by a variety of electropolishing solutions. He found that in all cases the dominant factor controlling the surface morphology was the potential applied to the electrolyte cell. The spacings of the markings increased progressively as the potential increased, the upper limit being set by the breakdown of the anodic barrier layer. Welsh concluded that the changes of pattern and spacing and their dependence on the electric field were incompatible with the concept of a subgrain structure. He suggested that the markings were a surface phenomenon associated with the electrode process, in a somewhat similar manner to the structures produced in porous anodic oxide films.

Hollo investigated the structure of electropolished aluminium using direct oxide replicas, she also noted the similarity between electropolishing and anodising.

1.5.2. Chemical Polished Structures

Investigators using chemical polishing solutions have found that the surface structures produced by these solutions are cellular in appearance, each cell usually being about 0.5 to

1 µm apart. These cellular networks are thought to be unconnected with the finer structures observed in electropolishing. Welsh in his earlier work(59) noted that specimens immersed in an electropolishing solution with no applied potential, gave a coarse cellular pattern characteristic of chemical polishing, whereas when the potential was applied, the fine "furrow" like pattern characteristic of electropolishing was produced.

Hunter and Robinson(61) studied the surface structure of annealed super-purity aluminium, chemically polished in an Alcoa R-5 solution (phosphoric and nitric acids). They considered that the markings developed by chemical polishing represented the boundaries of unusually minute subgrains, and assumed that the subgrain boundaries had been preferentially attacked. This interpretation was questioned by Hirsch(62), Perryman(63) and Welsh(64), who pointed out that if the cells truely represent misorientated crystal blocks, their small spacing would imply a suprisingly high dislocation content for recrystallised aluminium. Phillips and Welsh(65) later demonstrated that the surface markings did not correspond to the subgrain structure of the bulk material. They used electron microscopy to examine metal foils thinned by chemical etching and observed fine cellular surface patterns about 0.2 µm. in spacing, superimposed upon the normal subgrain structure of the metal, of much larger spacing. The authors observed that direct examination showed an absolute lack of correlation between the apparent dislocation distribution and the surface cell peripheries, the dislocations residing almost exclusively in the polygonal subgrain boundaries. The remote possibility that the cell boundaries did contain dislocations of such close stacking that they could not be resolved by transmission electron microscopy was negated by selected area diffraction experiments. These showed that any misorientation across the boundaries was so small that individual dislocations should have been easily resolved at the magnification employed.. Phillips and Welsh also noted that the cell boundaries were actually ridges separating shallow pits and not groves as previously supposed, thus indicating that they were cathodic sites with respect to the rest of the aluminium surface.

Similar observations were made by Bichsel(66) who also examined aluminium surfaces using transmission and replica electron microscopy. Bichsel however, concluded that the ridges represented the anodic areas of local galvanic cells, which appears to be somewhat contradictory to the assumption that polishing occurs predominantly at the cell centres.

More recently, Cuff and Grant(67) carried out an electron microscopy study of the surface structures produced on aluminium by chemical polishing. The authors confirmed by interpretation of shadowed carbon replicas that the cell boundaries were ridges. They also showed that for every polishing solution used, the patterns produced were characteristic of the orientations of the aluminium grains. Their electron micrographs showed that there was an appoximate pattern of square cells on the $\{100\}$ planes, elongated cells on the $\{110\}$ planes, and a dotted structure on the $\{111\}$ planes. Cuff and Grant considered that the substructure was the surface manifestation of a three dimensional network of impurity atom segregation, enclosing volumes of relatively high purity aluminium. They considered that the impurity atoms probably have a Maxwellian distribution about the ridges such that, by influencing the electrostatic forces on the surface and by producing surface corrosive currents, they cause the observed structure to develop.

Keller, Hunter and Robinson(11) have shown that the pores in porous anodic oxide films develop preferentially at the ridges left from the pretreatment process, which may indicate the presence of some impurity segregation at these points. Renshaw(12) however, suggested that the pores develop at the sites of minute cracks in the oxide film covering the ridges. An explanation which seems to be more consistent with the observed facts. Young(68) has also developed the argument, that oxide will form over acute protuberances of metal with internal stresses large enough to cause oxide failure and cracking, which can explain the initial anodic growth at the ridges.

1.6. Oxide Film Formation

Many investigators believe that chemical and electropolishing are, like passivation, connected with the formation of a solid film consisting of products of solution or more frequently of an oxide. Numerous facts show a connection between the oxidation of a readily oxidisable metal, such as aluminium or zinc and its electropolishing. Napier and Westwood(69) have shown that aluminium can be polished by placing it alternately in an anodic oxidation bath and one capable of dissolving the alumina film. In an electrolyte containing phosphoric acid with other additions, it is possible to find conditions of temperature and current density that will give either oxidation or polishing(70). McG.Tegart and Vines(71) succeeded in polishing iron in sulphuric acid at 60° - 70°C under an e.m.f. of 4.5 V; the anodic processes involved were alternately passivation and activation.

Hoar and Farthing(29) have shown indirectly (by the absence of wetting in mercury) that a compact solid oxide film forms on copper during electropolishing in phosphoric acid. Hoar and Mowat(9) also assumed that the periodic oscillations in current and voltage that occurred before the establishment of polishing conditions, were due to alterations of passivity and activation.

If oxidation is a phenomenon associated with electropolishing, a film of oxide should be present on the polished surface. In fact such films have been detected by sensitive techniques such as cathodic reduction, Allen(30), a - c impedence measurements, Cole(31), Cole and Hoar(32) and electron diffraction, Williams and Barrett(33).

At the same time it must be remembered that if the metal is readily oxidised, such a film may well be produced during the operations that follow the removal of the specimen from the solution. Thus results from experiments carried out on aluminium taken from the polishing solution, can be viewed with caution.

The problems involved in experimentally detecting films on metals during chemical polishing, are even greater than during electropolishing, as chemical polishing solutions are usually extremely corrosive and are operated at high temperatures.

McG.Tegart(72) has applied the mercury drop test of Hoar and Farthing(29) to chemical polishing solutions and stated that, in general the results for a large number of metal-solution combinations, indicated that metals were covered with a surface film during chemical polishing. The nature of the films was not revealed by such experiments, but McG.Tegart assumed that they were either oxides or hydroxides because the solutions used were strong oxidising agents.

Hickling, Marshall and Buckle(38) have used the electrometric method developed by Evans and Miley(73) to measure the thickness of film formed on steel when chemically polished in Marshall's solution. They stated that the films formed on steel after chemical polishing and washing were less than 200 Å thick. The authors also noted that when this film was removed by cathodic reduction, a similar film was formed on the steel surface after a short time.

More recent workers have used electrode potential measurements of the polishing metal to indicate the presence of an oxide film.

Hickling and Rostron(40) studied the change in potential of steel samples chemically polished in a hydrogen peroxide-oxalic acid mixture at room temperature. They observed that polishing occurred when the metal was alternating between active and passive states. This was accompanied by a periodic variation in both the rate of dissolution and the potential of the specimen. The authors assumed that these phenomena indicated that the metal was partly covered by oxide under these conditions and that its dissolution was electrochemical in nature. This was caused by local couples on the surface, in which the current flowed from oxide covered hollows to bare metal peaks.

Later work by Britton(74), who used X-ray fluorescence analysis and potential-time measurements to study the properties of the oxide film on chemically polished steel, showed a steady build up of chromium in the oxide film. He assumed that the oxide film persisted throughout polishing and was not removed periodically as suggested by Hickling and his co-workers(38,40).

In a later theoretical paper, Hoar, Mears and Rothwell(75), pointed out that when any film has formed on an anode, the subsequent anodic behaviour depends upon the electrical characteristics of this film. It is evident that the film formed during polishing must have a relatively high conductivity and must also allow easy passage of cations across the metal-film and film-solution interfaces. This is because dissolution has to occur from the metal through the film at a high rate and at quite low anode potentials. The film therefore cannot be simple oxide, because oxide films have a low ion conductivity at ambient temperatures, which will lead to passivity or at high potentials, film growth. Hoar therefore stated that the film formed during polishing should be described as merely the "compact, solid" film.

1.7. Scope of Present Work

Although there seems to be some agreement regarding the general principles of the chemical polishing process, there is a great deal which is not understood.

Little has been reported on the effect of the heavy metal additions to polishing solutions, in particular the exact amount deposited on the surface and its effect on the surface morphology. Also no workers have examined the surface structures produced when aluminium is polished for very short times, and when immersed for longer than the usual treatment time required to obtain a good surface finish. Another technique not previously employed with this polishing system is the electrode potential measurement of the aluminium during polishing.

1.7.1. Heavy Metal Additions

Although most industrial polishing solutions contain these additions, very little is known as to their effect on the surface of the aluminium. Electron microscopy has been used during this investigation to compare the surface structures produced in solutions of different copper contents and after various polishing times. Two stage carbon replicas were normally used, although some thin foils were prepared to observe the deposition of copper and the surface structures produced, in relation to the orientation and defect structure of the basis metal. The amount of copper actually deposited on the aluminium surface under different polishing conditions has been determined and also the electrode potential of the aluminium during the polishing process.

The more usual surface assessment techniques, specular reflectivity and weight loss, have been used to compare the polishing efficiences of the solutions used and to compare the results obtained with other published work.

1.7.2. Effect of Surface Condition.

It is now generally considered that a very thin oxide film is present on a metal surface during chemical polishing. In order that the effect of this oxide film could be determined during the chemical polishing of aluminium, specimens which had been cold worked, etched, electropolished or anodised before chemical polishing were used. The techniques mentioned in the previous section were employed to show the effect on the polishing process of these modifications to the natural oxide film before polishing.

CHAPTER 2

EXPERIMENTAL PROCEDURE AND TECHNIQUES

2.1. Materials

Super-purity (99.99%) aluminium was used exclusively in this investigation, supplied by the British Aluminium Company Ltd., in the form of cold rolled sheet 0.049 in. (0.124 cm.) thick.

2.1.1. Analysis

Spectrographic analysis of the material gave the following results in weight %.

Fe	Cu	Mg	Mn	Ni	Si	Pb
0.003	0.0005	0.001	not detected			

2.1.2. Heat Treatment

The aluminium was annealed prior to most of the chemical polishing investigations. This was carried out by heat treating the material for 1 hour at 350°C in an air circulating furnace controlled to ± 5°C.

Metallographic examination indicated that the aluminium had a grain size of 0.05 mm. after annealing.

2.1.3. Specimen Size

Specimens 10 cm. by 5 cm. were guillotined from the rolled sheet for chemical treatments. No mechanical polishing treatments were carried out as the rolled metal had a very good surface finish.

2.2. Solutions

Analar grade reagents were used, except where otherwise stated, in making up the solutions with distilled water.

2.2.1. Chemical Polishing Solutions

The basic polishing solution used throughout this investigation was a mixture of 77.5% phosphoric acid, 16.5% sulphuric acid, and 6.0% nitric acid, all % being by volume.

Copper additions to the basic solution were made in the form of copper sulphate crystals $CuSO_4.5H_2O$ (~~atomic~~ molecular weight 249.68).

The following polishing mixtures were made up, each comprising of the basic solution and a copper addition.

Solution				
A	Basic Solution	+ 0.25	gms.	Copper per litre
B	"	+ 0.5	gms.	"
C	"	+ 0.75	gms.	"
D	"	+ 1.0	gm.	"
E		Basic Solution only		

2.2.2. Electropolishing Solution

One volume of perchloric acid (S.G = 1.70) to four volumes of absolute alcohol.

2.2.3. Etching Solution

10% (w/v) sodium hydroxide solution

2.2.4. Anodising Solution

3% (w/v) tartaric acid, adjusted with ammonium hydroxide to a pH of 5.5.

2.3. Specimen Preparation

2.3.1. Electropolishing

Certain specimens were electropolished before chemical polishing. This was carried out in a solution of one volume of perchloric acid to four volumes of absolute alcohol, using an aluminium cathode. The bath was operated at 19 volts, supplied by a Shandon Electropolishing Unit (Type 6510), and the polishing time was 10 minutes. The solution was gently adgitated with a magnetic stirrer and its temperature maintained below 10°C with liquid nitrogen.

2.3.2. Etching

Certain specimens were etched to remove the oxide film and to attack the aluminium to produce a matt finish.

The etching solution used was a 10% (w/v) sodium hydroxide solution operated at 50°C(76), and the specimens were etched for 6 minutes. This etching time was found, after a short trial with sample pieces of aluminium, to give a reasonably bright surface commensurate with adequate metal removal, see Table 2.1.

TABLE 2.1.

Time of Etching Minutes	% Specular Reflectivity	Weight Loss gms./sq. dm.
1	22	0.015
2	16	0.032
4	16	0.190
6	19	0.272
7	19	0.340
8	16	0.410
10	14	0.562
15	9	0.884

2.3.3. Anodising

Certain specimens were anodised to form a barrier oxide film prior to chemical polishing. Anodising was carried out for 5 minutes, in a solution of 3% tartaric acid adjusted with ammonium hydroxide to a pH of 5.5. The applied voltage was 100 volts, the cathode was lead in a cathode bag, and the temperature 20°C.

It is known(77,78,79) that anodic films formed in this solution are non-porous and are between 12-14 Å/volt thick. The exact thickness of the barrier film is however, not important in this investigation.

2.3.4. Specimen Treatment

After the chemical pretreatments, all specimens were thoroughly rinsed in distilled water, washed in acetone and dried using an air blower. The specimens were then stored in dessiccators until required.

2.4. Polishing Apparatus

All chemical polishing experiments, except those to determine the electrode potential of the aluminium, (described in section 2.5.9) were carried out in three litre beakers. The beakers were maintained at a temperature of 100°C ± 1°C by a controlled electrical hot plate. This temperature of polishing was used for all the experiments, as it has been shown empirically(6,46,76,80,81) to give satisfactory polishing with the solutions used.

Preliminary experiments showed that the amount of adgitation of the polishing bath was not critical. It was found that only slight adgitation was required to prevent gas streaking, and that greater adgitation made no difference to the quality and structure of the polished surface. During the experiments slight adgitation was supplied by electrically driven paddles, at a fixed distance from the surfaces of the specimen.

The specimen was held in the polishing bath by a polypropylene holder, which was not attacked by the polishing solutions used. The specimen was griped at each end by friction on the polypropylene and totally immersed in the polishing bath. A simple polypropylene jig was fitted to the top of the beaker so that the specimen and the stirrer paddles could be set at a fixed distance apart for each polishing experiment. A photograph of the specimen holder is shown in Fig. 2.1.

2.5. Experimental Techniques

2.5.1. Procedure during Polishing Run

The specimens of aluminium having various surface treatments, i.e. either original surface, electropolished, etched or anodised, were each chemically polished in the solutions mentioned previously. The polishing times employed ranged from 1 second to 4 minutes. The intervals of time used in the investigations ranged from 2 seconds in the early stages of polishing to 30 seconds at the later stages.

After polishing, the specimens for copper analysis were treated separately, as described in 2.5.8. All other specimens were rapidly transferred to a beaker of distilled water to stop the polishing action, rinsed in hot water and dipped in a solution containing 20 gms. chromic acid and 35 mls. of orthophosphoric acid per litre at 90°C, which does not attack the aluminium,(82,83) to remove the

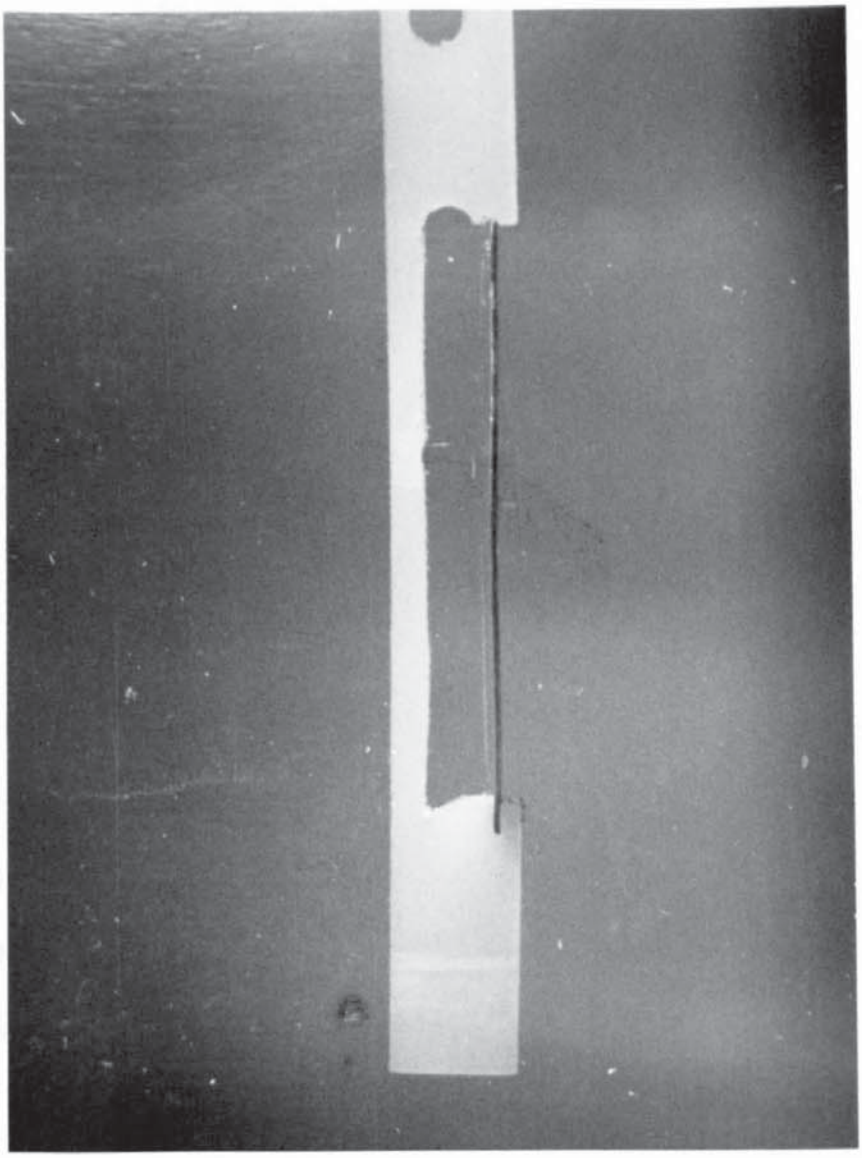


Fig. 2.1. Photograph of Specimen and Holder.

smudge and surface film. The specimens were finally rinsed in distilled water, washed in acetone and dried using an air blower.

It is known(46,76,80) that the presence of dissolved aluminium in the chemical polishing solution can retard the polishing action. This becomes noticeable when the concentration of aluminium reaches 20 gms./litre. To reduce the effect of dissolved aluminium on the results of the present investigation, each chemical polishing solution was replaced with a fresh mixture when the aluminium content reached 1 gm./litre.

2.5.2. Rate of Metal Dissolution

The loss of weight of each specimen was determined by accurately weighing to 0.0001 gm. the specimen before and after polishing. The area of each specimen was calculated and the results expressed as weight loss per sq. decimeter. For each experimental condition triplicate specimens were used and an average taken of the loss in weight per unit area.

2.5.3. Estimation of Surface Quality

The first essential of any instrument for the comparison of surface brightness is that the readings obtained should place the specimens in the same order as would a visual examination, since this is the ultimate test that must be satisfied. A physical test is unlikely to be in exact agreement with a visual test, as personal factors are involved, but the two results should not differ greatly.

Gardam's grid(84) can be used as a simple empirical test to place surfaces in order of their image clarity. The grid consists of an illuminated screen with cross lines in the shape of a grid on the surface of the screen. The test is carried out under arbitary conditions, by noting the distance from the screen at which the image of the grid on the metal becomes indistinct.

It may be thought that total reflectivity (T) would provide a more obvious basis for comparison purposes. This is defined by Scott(85) as the integrated total intensity of the light reflected at all angles, expressed as a percentage of the incident light. It is comprised of two components, a) specular reflectivity (S), defined as the percentage of the incident light reflected at the angle of reflection; b) diffuse reflectivity (D), defined as the percentage of the incident light reflected at angles other than the angle of reflection; thus $T = D + S$.

Scott, however, stated that the total reflectivity of a surface is almost invariant for a given metal or alloy, being practically independent of surface finish, flatness and angle of incidence and hence would not offer a means of comparison for samples of the same material, despite varying degrees of surface polish.

Scott further suggested that the ratio of specular reflectivity to total reflectivity gives a basis for the comparison of surface lustre that is in close agreement with visual examination, although it is necessary only to measure specular reflectivity, because of the previously discussed invariability of total reflectivity.

Instruments that measure specular reflectivity directly, as opposed to those that obtain the value by the difference between total and diffuse reflectivities, have to be calibrated against a suitable standard. A common standard is a 45° Chance, hard glass prism, total internal reflection taking place on the hypotenuse face.

Specular reflectivity measurements were taken during this investigation with an Evans Electroselenium Co. "Metspec".* This is a direct reading instrument. The light reflected by the 45° prism is considered to be 100% specular reflectivity and the light reflected by the aluminium specimen is measured as a percentage of this standard.

During measurements, light from a 6 volt, 3 watt frosted lamp is directed through a circular aperture and collimator lens, to hit the surface at an angle of 45° in the form of

* specified in B.S. 1615. 1961.

a parallel beam. The reflected light passes through a corresponding lens to energise a photo cell. The signals from the photo cell are presented on the 0 - 100 scale of an Evans Electroselenium Co. "Unigalvo 20". Fig. 2.2. shows instrument held in position on a sample, together with the "Unigalvo 20" and a standard glass plate and prism.

Before the specular reflectivity reading of a sample was measured, the instrument was first calibrated by adjusting its sensitivity such that the light reflected by the glass prism gave a reading of 100 on the galvanometer scale. The instrument was then held on a sample with the light beam parallel to the rolling direction and three readings taken in different positions on the surface.

The galvanometer reading in each position was noted and the average result expressed as the percentage specular reflectivity of the surface.

2.5.4. Etching to Determine Grain Orientation

The use of etching techniques to determine the orientation of metal grains, has been extensively used in previous work(59,61,66,67). When metals are etched in some solutions, certain crystallographic planes are attacked and the geometric features of the resulting etch pits reveal the grain orientations. Barratt(86) states that the cube planes of face centered cubic aluminium are attacked, and it has

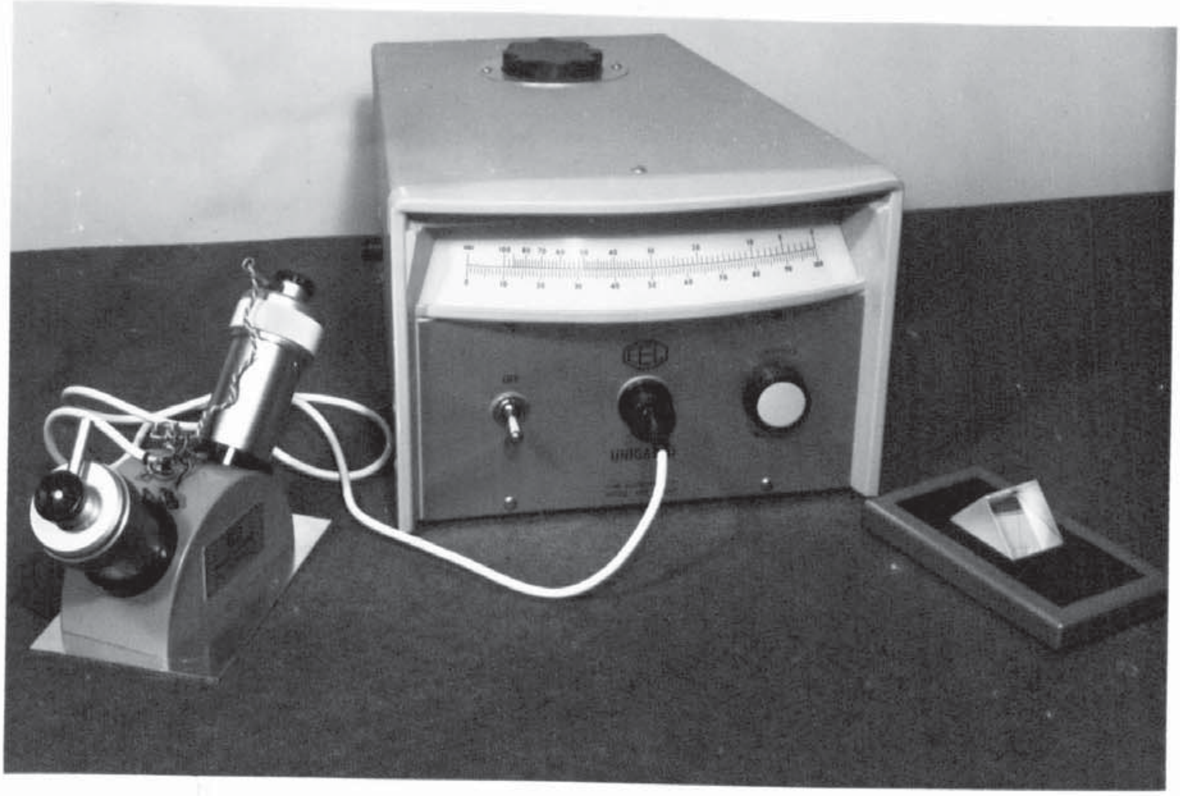


Fig. 2.2. "Metspec" Specular Reflectivity Meter.

been shown(87) that square etch pits are representative of the cube $\{100\}$ planes, triangular etch pits of $\{111\}$ type and rectangular etch pits of $\{110\}$ type and so on. That is, the geometrical feature of the crystallographic plane of a unit lattice of face centered cubic aluminium, parallel to the surface of the sample, determines the geometry of the etch pit.

The etching solution used during this investigation was as follows:

9 parts hydrochloric acid
2 parts hydroflouric acid
3 parts nitric acid
5 parts water

The etching time used was 5 seconds, with the solution maintained at a temperature between 0 and 5°C.

Before the above etching technique was used extensively in the investigation, a short trial was carried out to ensure that the etching solution did not effect the surface morphology of the aluminium. Electron microscopy replicas were taken from etched and unetched specimens, which had been previously chemically polished, and it was found on examination that the dissolution produced by the etching solution was confined to the formation of the microetch pits of geometrical shape.

2.5.5. Replica Electron Microscopy

The replica electron microscopy technique was used to study the surface topography of the chemically polished surfaces. Initially, replicas were prepared using collodion, a 4% solution of cellulose nitrate in ethyl ether and a plastic sheet of cellulose triacetate*. It was soon apparent that the cellulose triacetate sheet replicas were much superior to those taken with collodion, and this method was used for all subsequent replica specimens.

The cellulose triacetate was supplied in the form of thin sheet 0.001 inches thick. A piece of sheet just larger than the area to be examined was taken and placed on the specimen surface which had been sprayed with acetone. The acetone was allowed to evaporate in a dust free atmosphere and the plastic hardened, such that in about 5 minutes it could be stripped from the specimen surface with a pair of tweezers. The plastic replica was then placed on a glass slide with the replicated surface uppermost, and held flat using pieces of sellotape on the corners. The slide was then transferred to an evaporating unit, capable of reducing the pressure to 10^{-4} mm. Hg. In the evaporating unit the replicas were shadowed at an angle of 45° with a gold-palladium alloy deposit and coated with a carbon film about 200 Å thick.

* "Bexfilm" supplied by BX. Plastics Ltd.

The replica was then cut into squares 2 - 3 mm. side and placed on copper grids on a filter paper pad soaked in acetone. The pad was covered to prevent evaporation and the replicas left overnight to ensure that the plastic was completely dissolved. The carbon replica supported by a copper grid was then examined in the electron microscope, and photographs taken of any characteristic regions.

Phillips E.M. 200 and A.E.I. E.M.6.G electron microscopes were used during this investigation.

2.5.6. Transmission Electron Microscopy

A technique for examining the sites of copper deposition and the surface structure formed during polishing, in relation to the internal structure of the metal has been developed. Specimens of super-purity aluminium foil 0.002 inches thick and 1 in. side were chemically polished, carefully rinsed and dried, then one side coated with lacquer. The foil was then electropolished from the other side using the conventional window method described by Tomlinson (88), in a solution of one part perchloric acid and four parts absolute alcohol. Thinning was carried out with an applied voltage of 19 volts and the temperature maintained below 10°C with liquid nitrogen. After perforation of the foil occurred, specimens for insertion in the electron microscope were cut from the perforated window under cover of absolute alcohol. The lacquer was dissolved from the back of the specimen by immersion in acetone. The thin foil was then inserted in a copper grid and examined in the electron microscope. Photographs were taken of characteristic regions.

2.5.7. Scanning Electron Microscopy

A Cambridge Instrument Co. (Stereoscan) scanning electron microscope was used for direct examination of the surface morphology of the aluminium specimens. A specimen of aluminium 1 cm. x 1 cm. was guillotined from each aluminium sample to be investigated, and mounted in the instrument in the conventional manner.

2.5.8. Determination of Weight of Deposited Copper

Aluminium specimens of size 5 cm. by 5 cm. by 0.124 cm. thick, were used in these determinations.

After chemical polishing, each sample was carefully rinsed in distilled water, them immersed in 250 ml. of 25% (v/v) nitric acid solution, maintained at a temperature of 50°C. The specimens were removed from the nitric acid solution after two minutes immersion, as it was found that all the surface copper was removed after this time. This was confirmed by taking aluminium specimens from the nitric acid solution and immersing them in fresh solution for 30 minutes. No increase in the amount of copper present was detected when compared with a blank specimen similarly treated.

The weight of copper in each nitric acid solution was determined by colorimetric analysis, using a 0.01% solution of zinc dibenzyldithiocarbamate in carbon tetrachloride(89). This reagent has a sensitivity of 0.5 μgm., and is also unaffected by other anions in the test solution, e.g. aluminium.

In order to extract the copper for analysis, 50 ml. of the 25% nitric acid solution was taken and diluted to 100 ml. with distilled water. 50 ml. of the diluted solution was mixed with 10 ml. of the 0.01% solution of the reagent in a separating funnel, and shaken vigorously for 30 seconds. The carbon tetrachloride layer containing the copper complex was separated and its optical density measured at a wave length of 435 mμ. with a Hilger and Watts spectrophotometer, using a 1 cm. cell. The zero of the scale of the spectrophotometer was set on the optical density of a blank specimen solution, treated in a similar manner.

A blank specimen was used for each batch of copper determinations. This was an aluminium specimen which had not been chemically polished, but was immersed in 50% nitric acid and the solution obtained given the same treatment as the solutions from the other specimens. The carbon tetrachloride layer obtained from the blank specimen was taken as zero copper deposited on the surface and the other specimens compared with this solution. This arrangement ensured that any copper dissolved from the bulk aluminium or any copper in the analysis solutions used, did not effect the results obtained.

Before each batch of analysis, the spectrophotometer was calibrated by measuring the optical density of solutions containing known amounts of copper, treated in the manner described above. The amount of copper in the test solution was then read off from the calibration curve.

2.5.9. Electrode Potential Determinations

Specimens of size 3 cm. by 9 cm. by 0.124 cm. thick, were used for these experiments. The polishing solution was contained in a 600 ml. beaker and was held at a temperature of 100°C ± 1°C by a combined electrical hot plate and magnetic stirrer. Moderate adgitation was supplied by the magnetic stirrer during the determinations.

As the temperature of operation was higher than the operating temperature of the usual calomel electrode, a pressurised electrode system was used*. This was assembled as shown in Fig. 2.3. It consisted of a polypropylene reservoir (E.I.L. Type RZ68), which contained saturated potassium chloride solution. An electrical connection from the reservoir to the polishing bath was made by a polypropylene liquid junction tube (E.I.L. Type LW68), which contained saturated potassium chloride solution enclosed by a porous

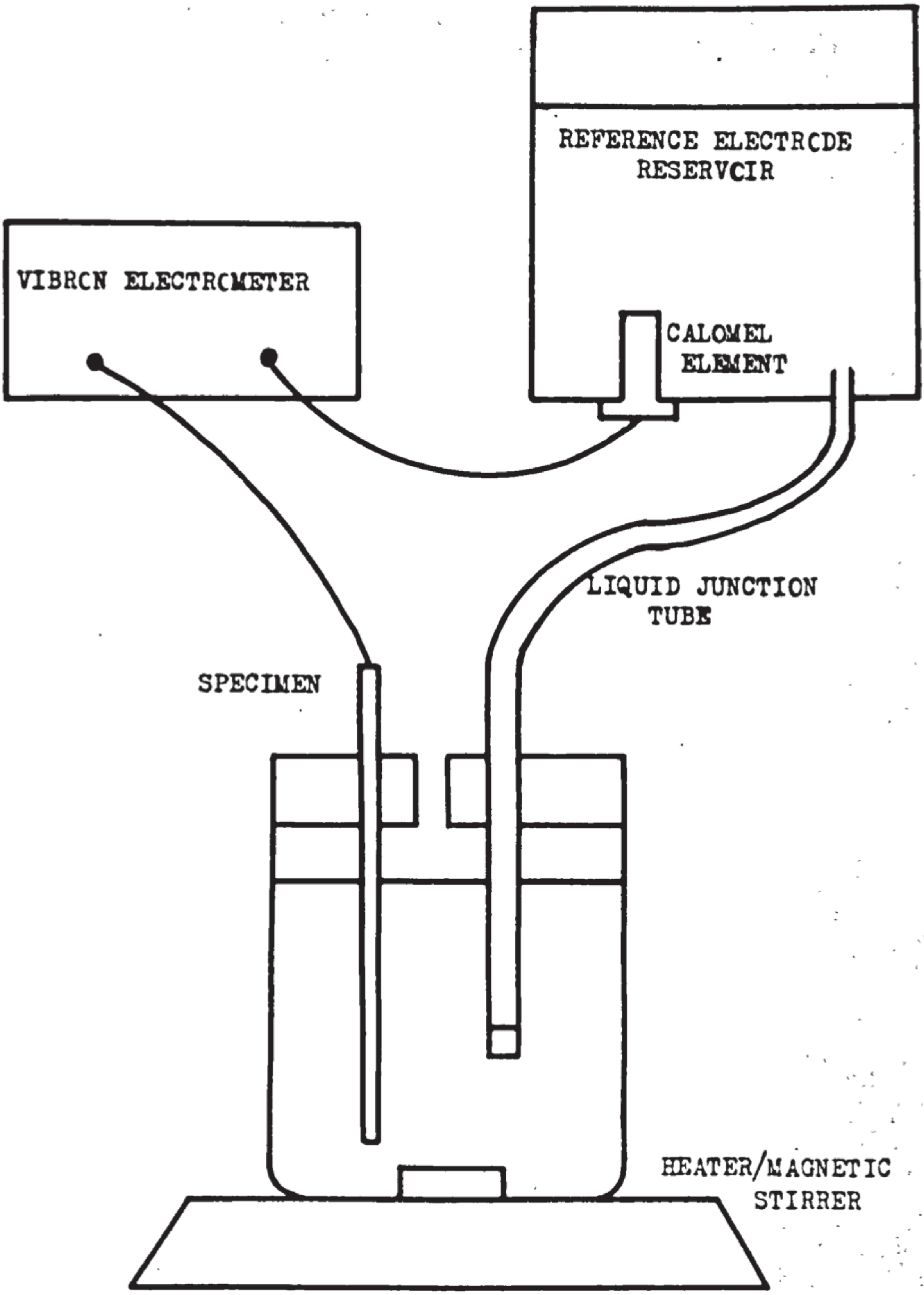


FIG. 2.3. CROSS SECTIONAL VIEW OF APPARATUS USED FOR ELECTRODE POTENTIAL DETERMINATIONS.

ceramic plug at its outer orifice.

Potential readings were obtained from a calomel reference electrode (E.I.L. Type CZ68) inserted into the reservoir next to the connection to the liquid junction. Air was pumped into the reservoir through a valve and the assembly was operated at a pressure of 5 lbs/sq.in. The specimen and liquid junction tube were held in place in the beaker of solution by an araldite jig, which was cast with holes to accommodate the specimen and the tube and to fit on the lip of the beaker.

The potential difference between the aluminium specimen and the calomel reference electrode was measured by a Vibron 33 B2 Electrometer*. The variation of potential with time in each experiment was followed using an S.E. Laboratories S.E. 2005 ultra violet recorder which was fed from the recorder socket of the Vibron Electrometer. The recorder was adjusted to give a full scale reading of 1.8 volts and a chart speed of 1.25 mm./sec.

* supplied by Electronic Instruments Ltd.

CHAPTER 3

EFFECT OF HEAVY METAL ADDITIONS

3.1. Introduction

The object of the work in this chapter was to evaluate quantitatively and structurally, the effect of copper additions to the chemical polishing solution used for aluminium. The secondary aim was to provide a solution with the optimum copper addition for use in chapter 4, where the variables employed are concerned with the surface condition of the aluminium to be polished.

In this chapter the polishing solutions A – E are described, as itemised in section 2.2.1, containing increasing amounts of copper. The aluminium specimens used were annealed and had the as-rolled surface finish.

3.2. Specular Reflectivity Results

The specular reflectivity results obtained from triplicate aluminium specimens, are displayed in Fig. 3.1. and Fig. 3.2. The polishing times used in this investigation were, every two seconds between 0 and 30 seconds, every 10 seconds between 30 seconds and 1 minute and every 30 seconds between 1 minute and 4 minutes. The transfer time required to stop the polishing action was estimated to be about one second. This was a serious error with the very short polishing times, but of little consequence later in the

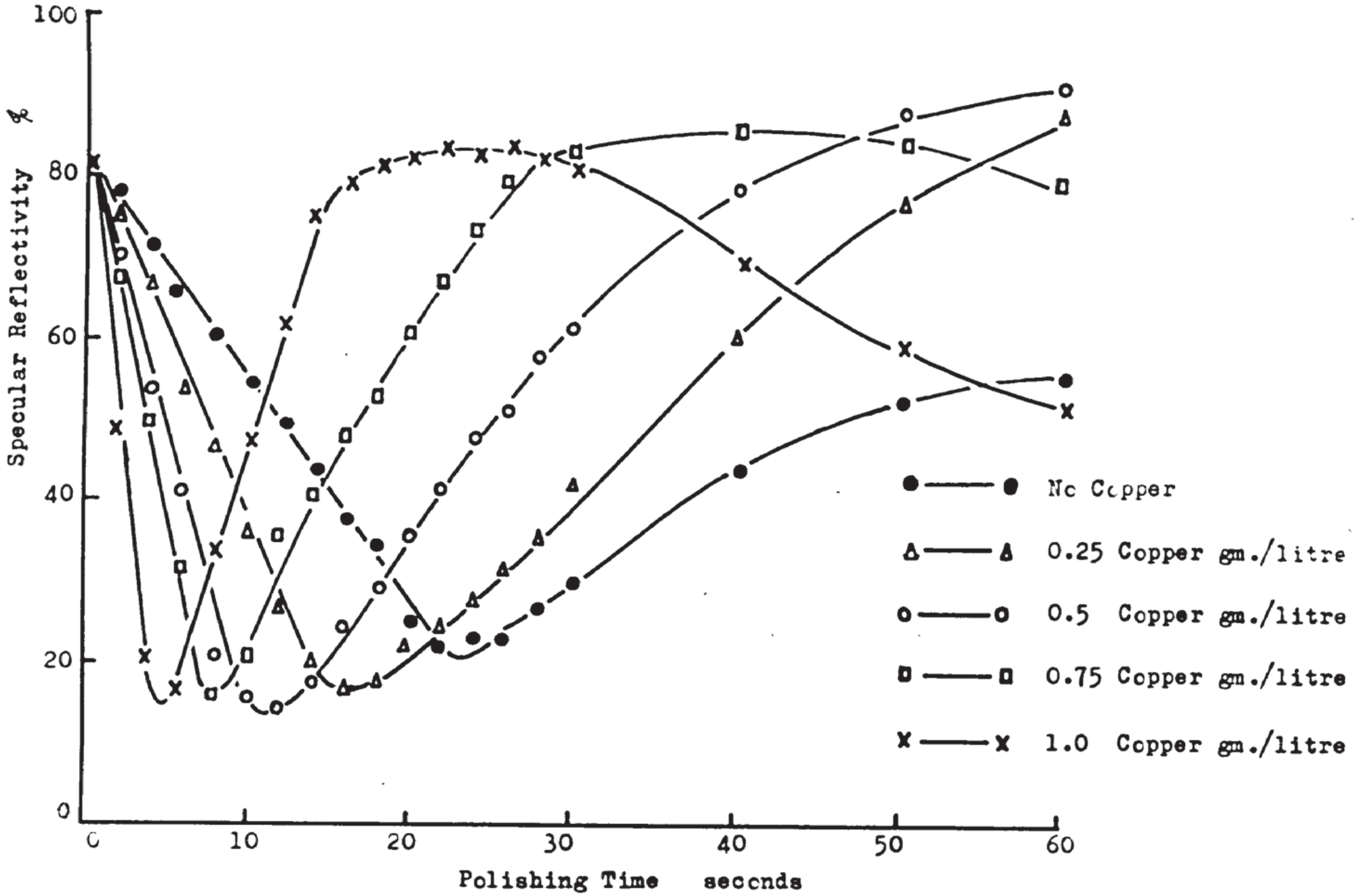


Fig. 3.1. Variation of Specular Reflectivity with Polishing Time in Different Polishing Solutions

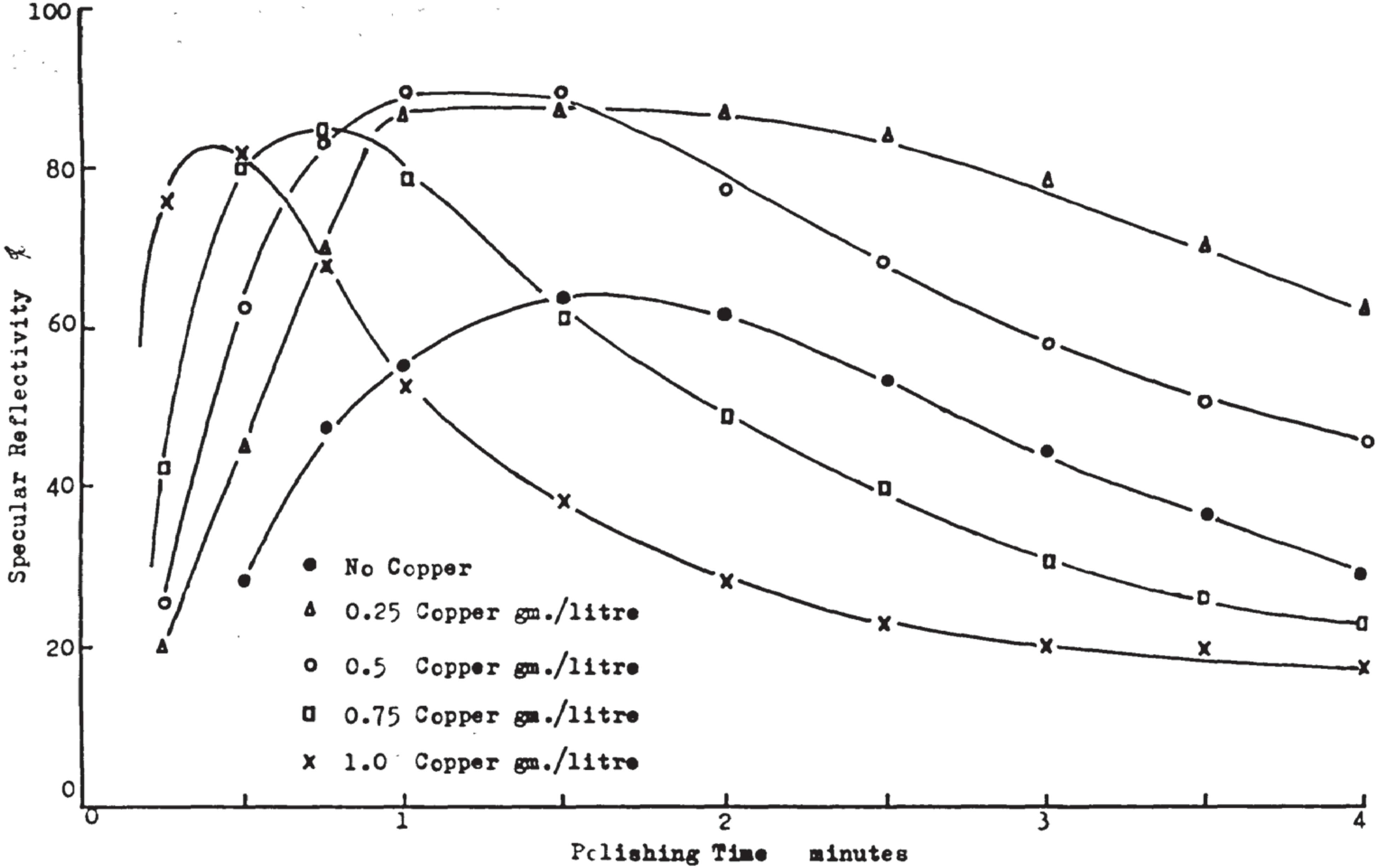


Fig. 3.2. Variation of Specular Reflectivity with Polishing Time in Different Polishing Solutions

polishing cycle. It was found that the reproducibility of results from specimens polished for longer than 30 seconds was within ± 1%. The reproducibility of the results obtained with polishing times shorter than 30 seconds, was variable, but in most cases was within ± 5%.

The results show the marked dependence of specular reflectivity on the time of polishing and on the concentration of copper in the solution.

The specular reflectivity values indicate that the polishing cycle can be divided into three stages. The initial stage perhaps only the first few seconds of polishing, involves a rapid etching of the aluminium and thus a low specular reflectivity is recorded. The second stage involves the removal of the etched structure to give a polished surface and an increased specular reflectivity and thirdly, a marked deterioration of the surface after the optimum polishing time is exceeded.

These changes can be seen qualitatively by the naked eye. Fig. 3.3 shows a photograph of aluminium panels at different polishing times.

The addition of copper to the basic solution, produces a considerable increase in the specular reflectivity readings during polishing. However, increasing the copper content beyond the optimum amount, which in this solution is between

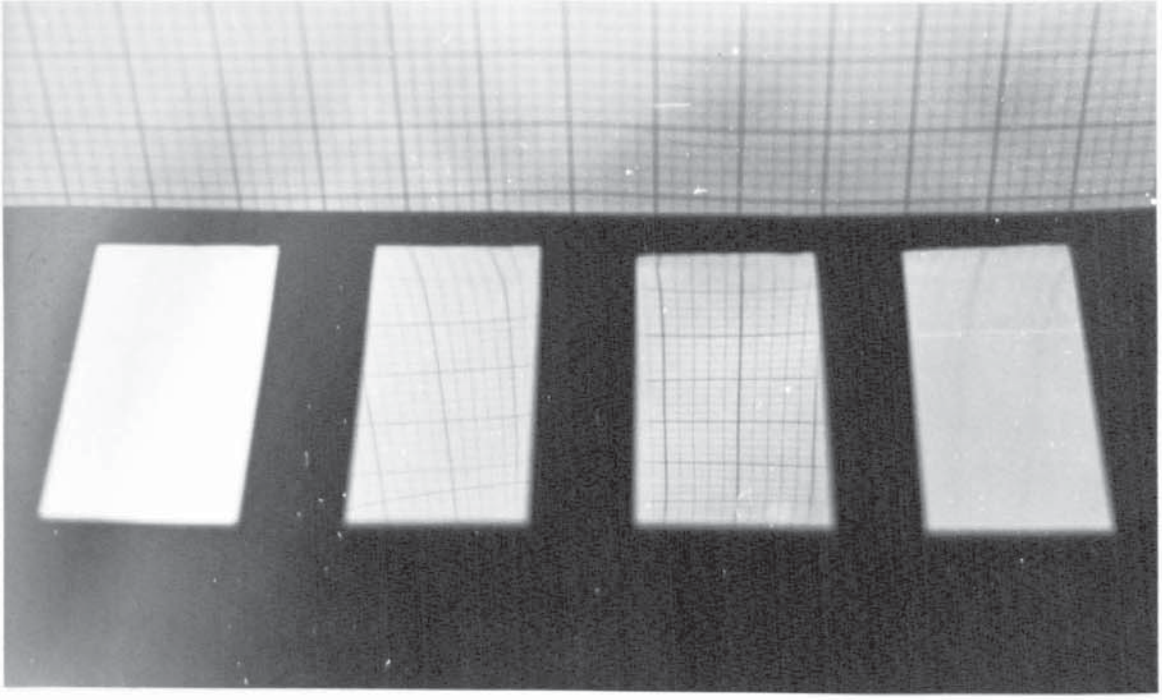


Fig. 3.3. Effect of Chemical Polishing Time on the Image Clarity of Aluminium.

From left to right, polishing times are 10, 30, 50 seconds and 3 minutes respectively.

Polishing Solution B.

0.25 and 0.5 gms. per litre, lowers the maximum specular reflectivity obtained and also shortens the time of the polishing cycle. That is, the maximum specular reflectivity is attained in a shorter time, and soon afterwards a rapid deterioration in surface finish occurs.

3.3. Weight Loss Results

The amount of weight lost by triplicate aluminium specimens polished in the solutions under investigation, are displayed in Fig. 3.4. In each case the reproducibility of the results was within ± 3%.

These curves show the rapid loss in weight of specimens polished in the solutions containing the higher copper contents. This is particularly pronounced towards the end of the polishing cycle. However, the losses in weight of specimens polished in the solution containing no copper, are greater than those polished in the two solutions containing the lower copper contents.

3.4. Replica Electron Microscopy

The electron micrographs obtained from aluminium specimens polished in solutions A - D can be conveniently grouped together, as the features shown are common to all solutions. The only difference is the polishing time required to develop a certain structure, as, with the specular reflectivity results, the more copper in the

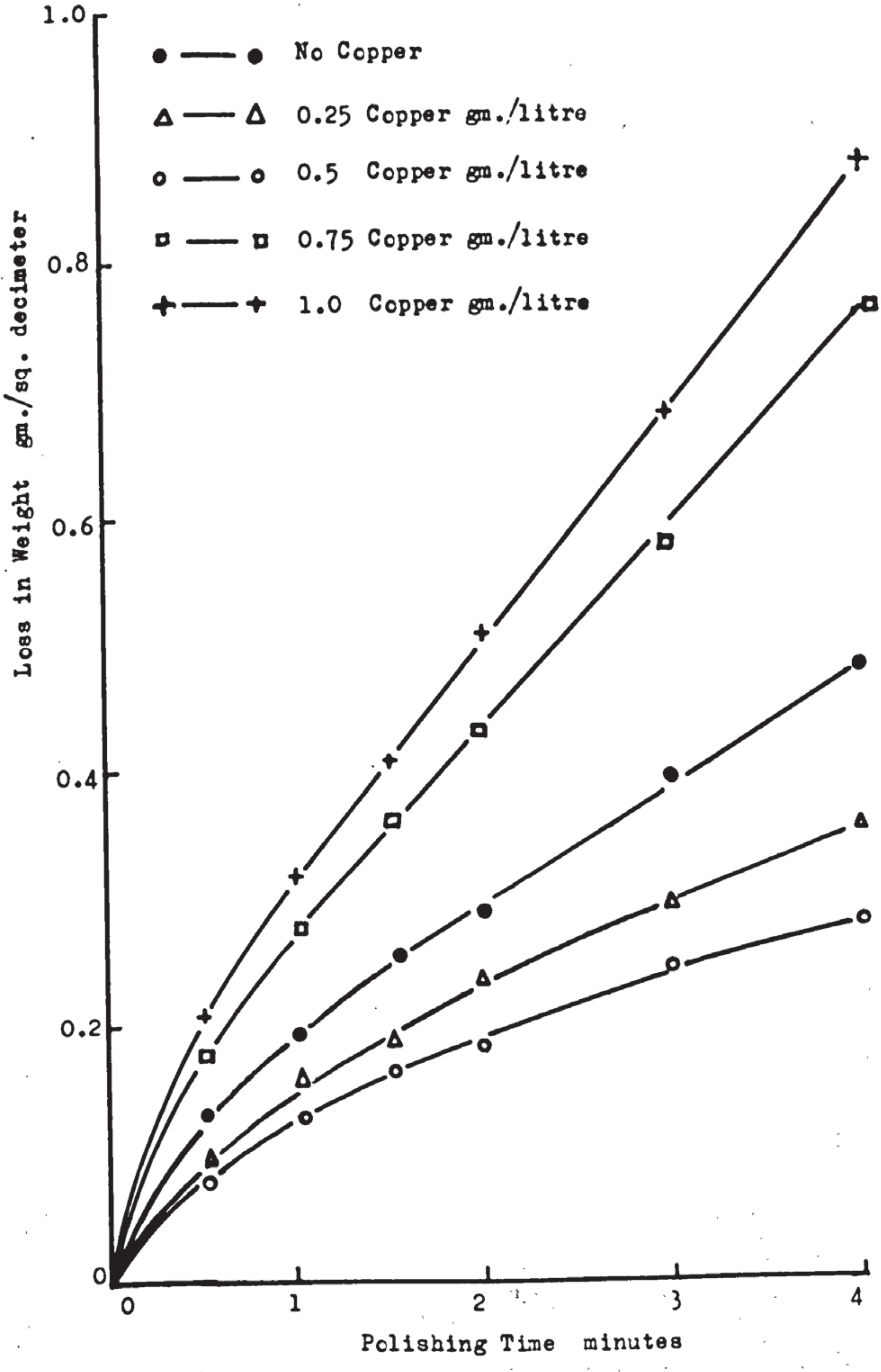


Fig. 3.4. Variation of Loss in Weight with Polishing Time in Different Polishing Solutions.

polishing solution, the shorter the polishing time required to produce the common features. To avoid needless duplication of electron micrographs, the range of structures obtained with solution B, the basic solution containing 0.5 gms./litre of copper, are published, together with a table denoting the polishing times at which the characteristic structures are exhibited in the other solutions. The solution E, containing no copper does not produce some of the characteristic structures found above and will be treated separately.

3.4.1. Solutions A - D

a) Etching Stage

Electron micrographs taken from samples polished for 1,2,4, 6, 8 and 10 seconds are shown in Figs. 3.6 - 3.11 and an electron micrograph of the original surface is shown in Fig. 3.5. The electron micrographs show that the first few seconds of polishing result in the formation of extremely small and apparently randomly nucleated spherical etch pits, around defects such as scratches in the original material. As polishing continues, each etch pit grows laterally until it contacts other similarly growing pits to form a network of cells. The shadowing of the replicas indicates that the cell boundaries are protuberances. Initially, the boundaries between the contacting etch pits are irregular, however, as

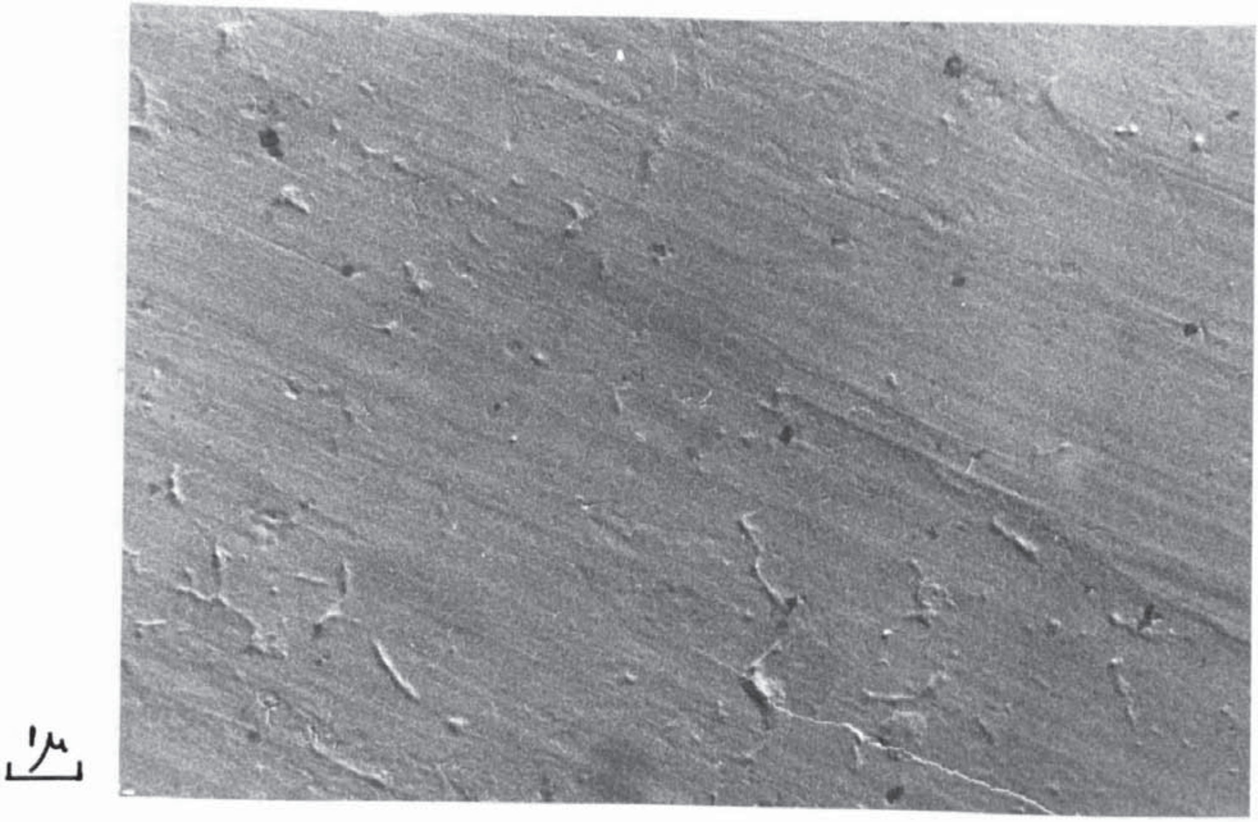


Fig. 3.5. Replica Electron Micrograph of the Untreated Aluminium Surface.

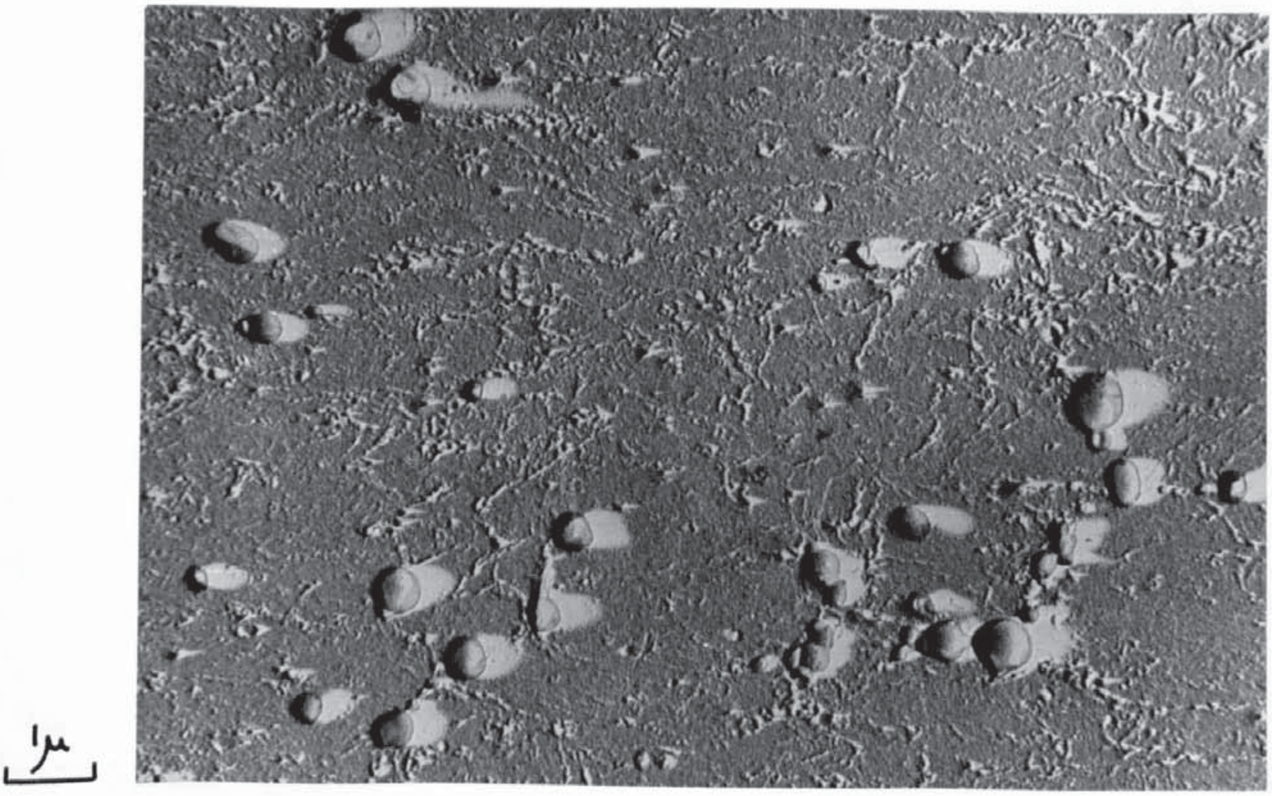


Fig. 3.6. Aluminium Chemically Polished for 1 Second.

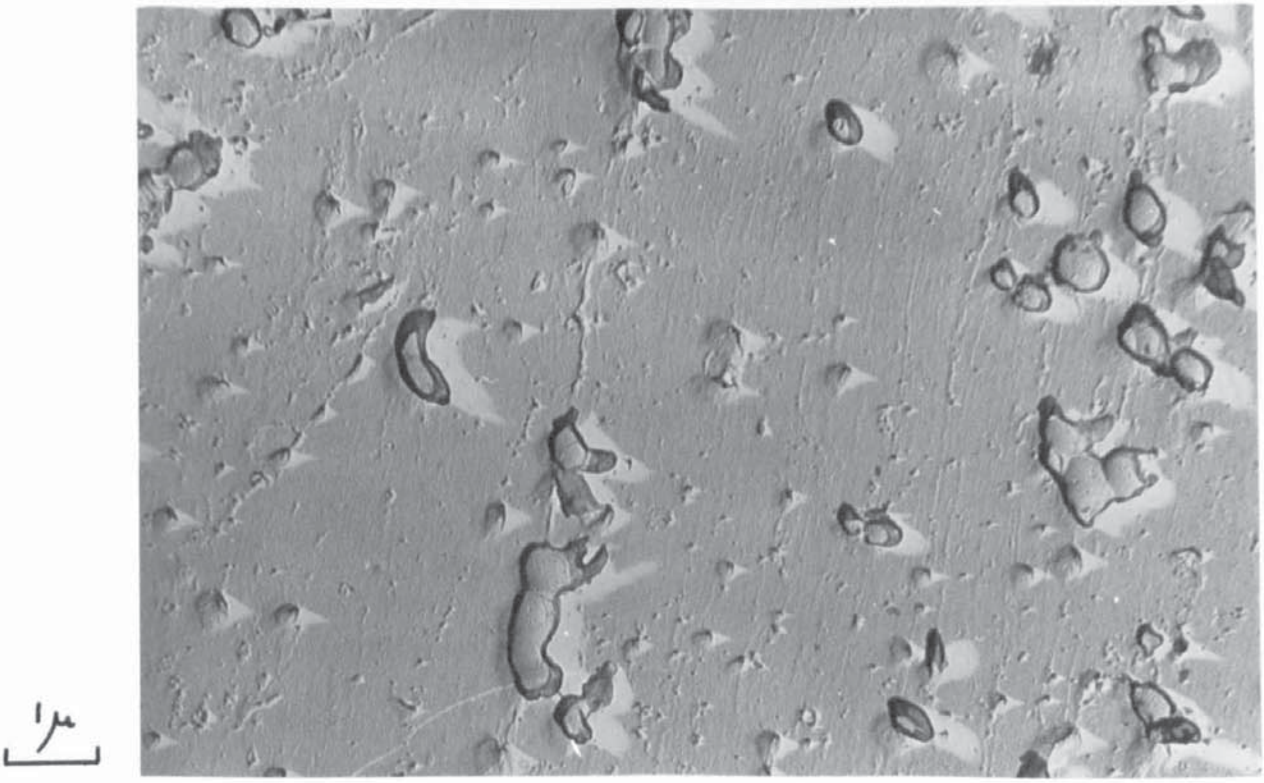


Fig. 3.7. Aluminium Chemically Polished for 2 Seconds.

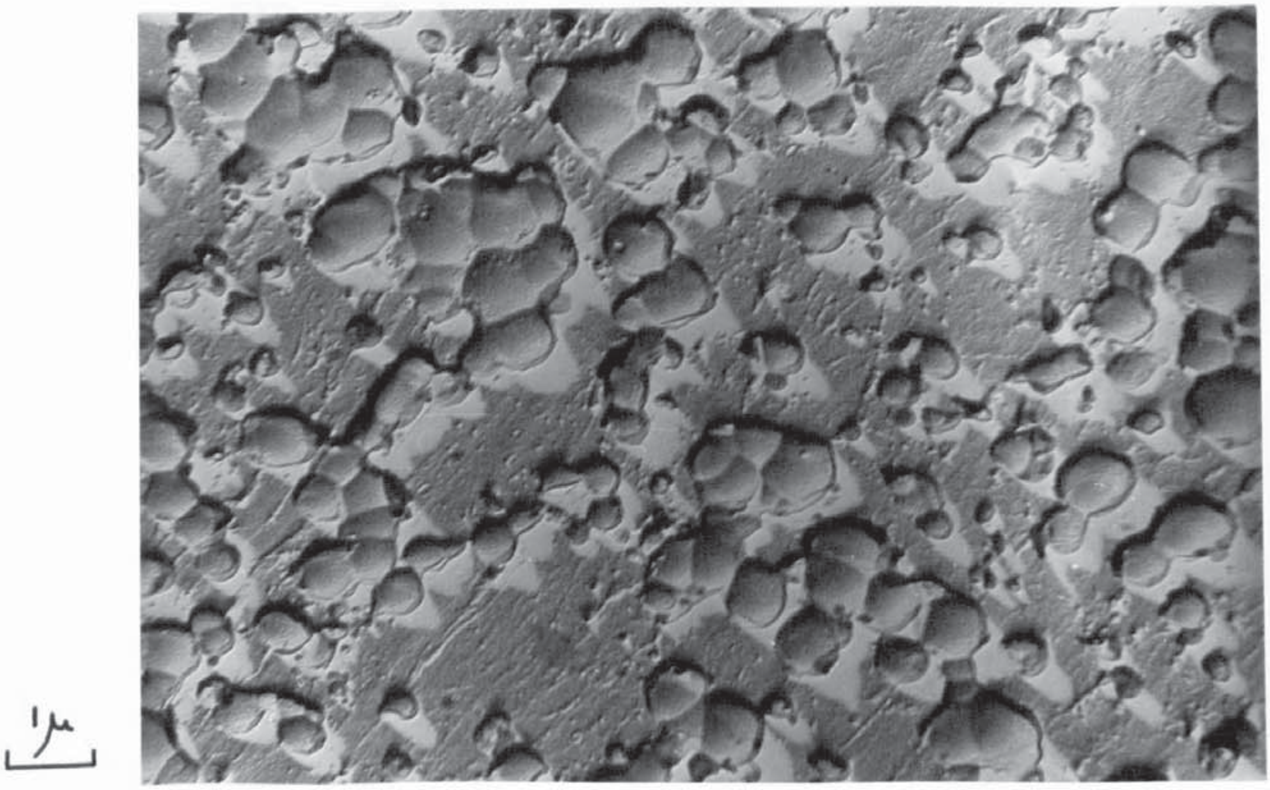


Fig. 3.8. Aluminium Chemically Polished for 4 Seconds.

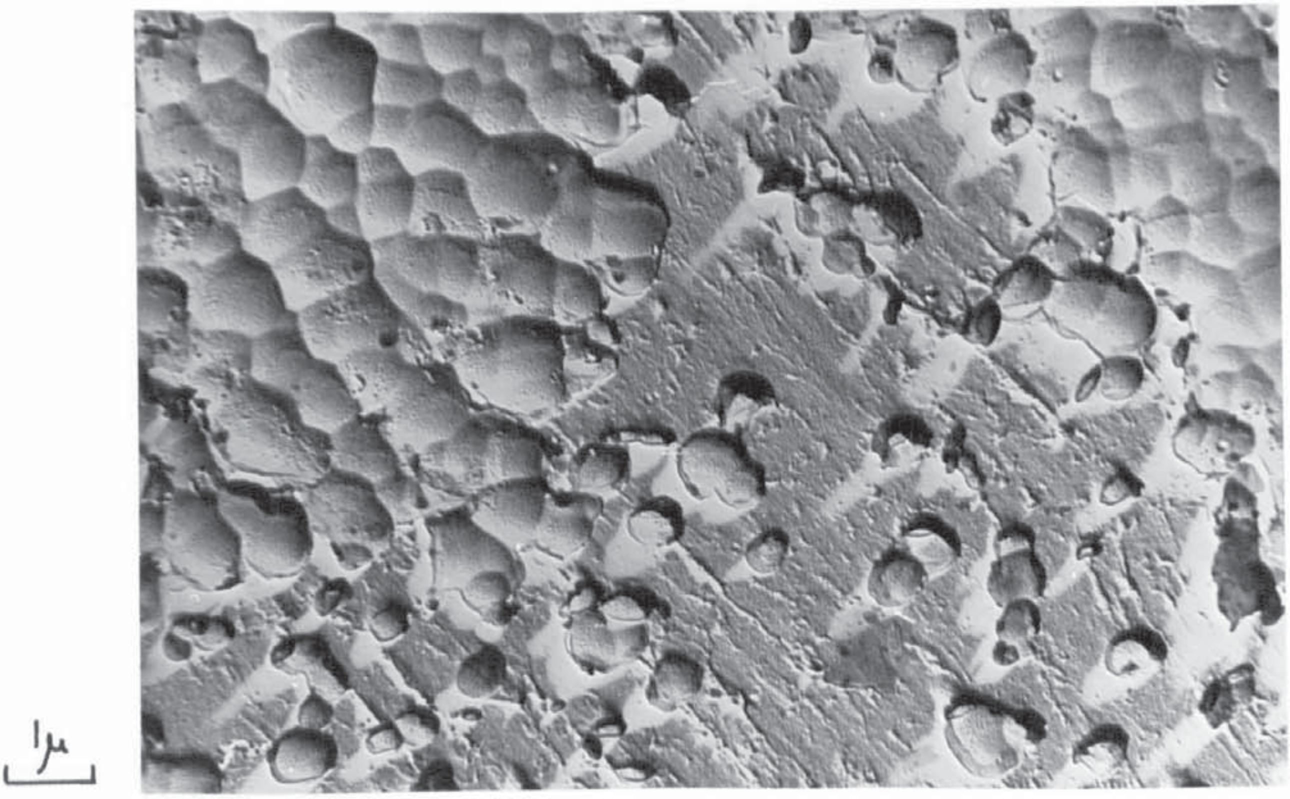


Fig. 3.9. Aluminium Chemically Polished for 6 Seconds.

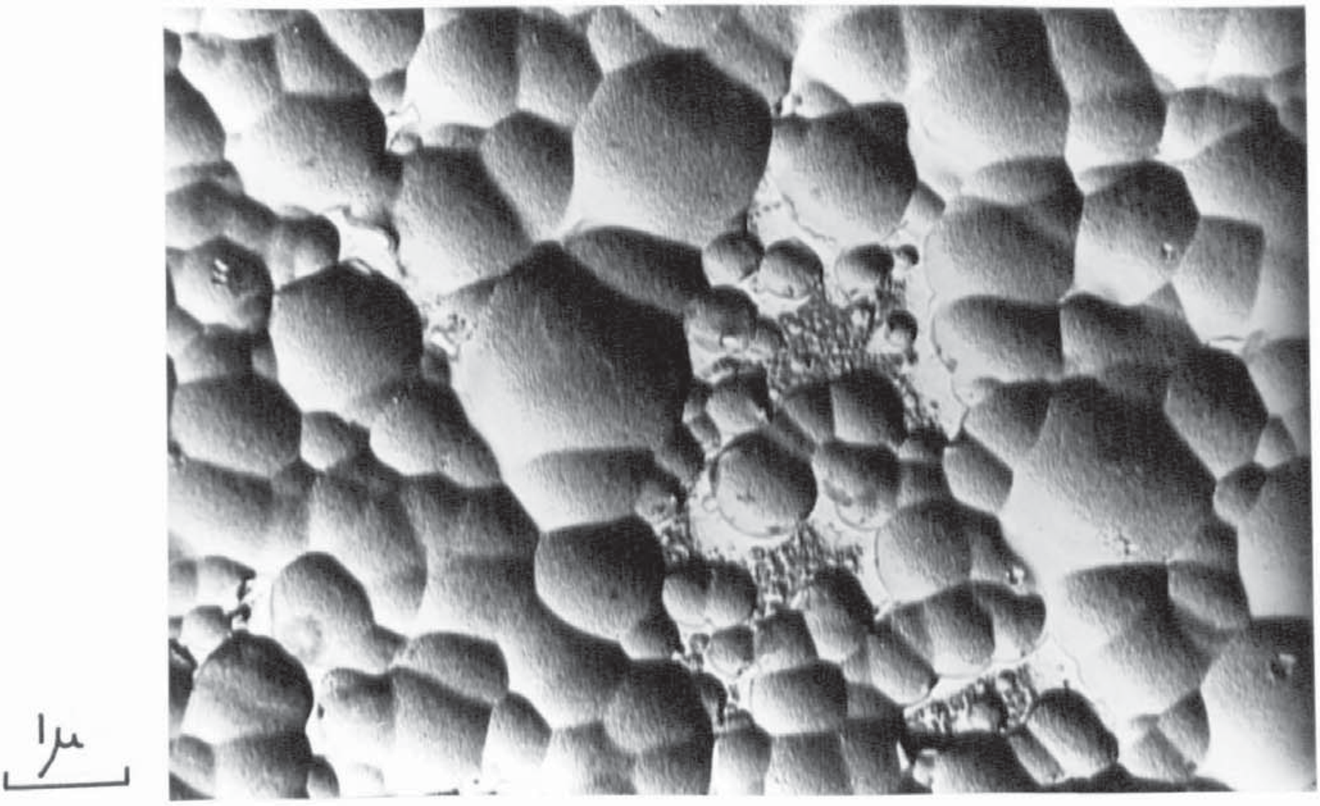


Fig. 3.10. Aluminium Chemically Polished for 8 Seconds.

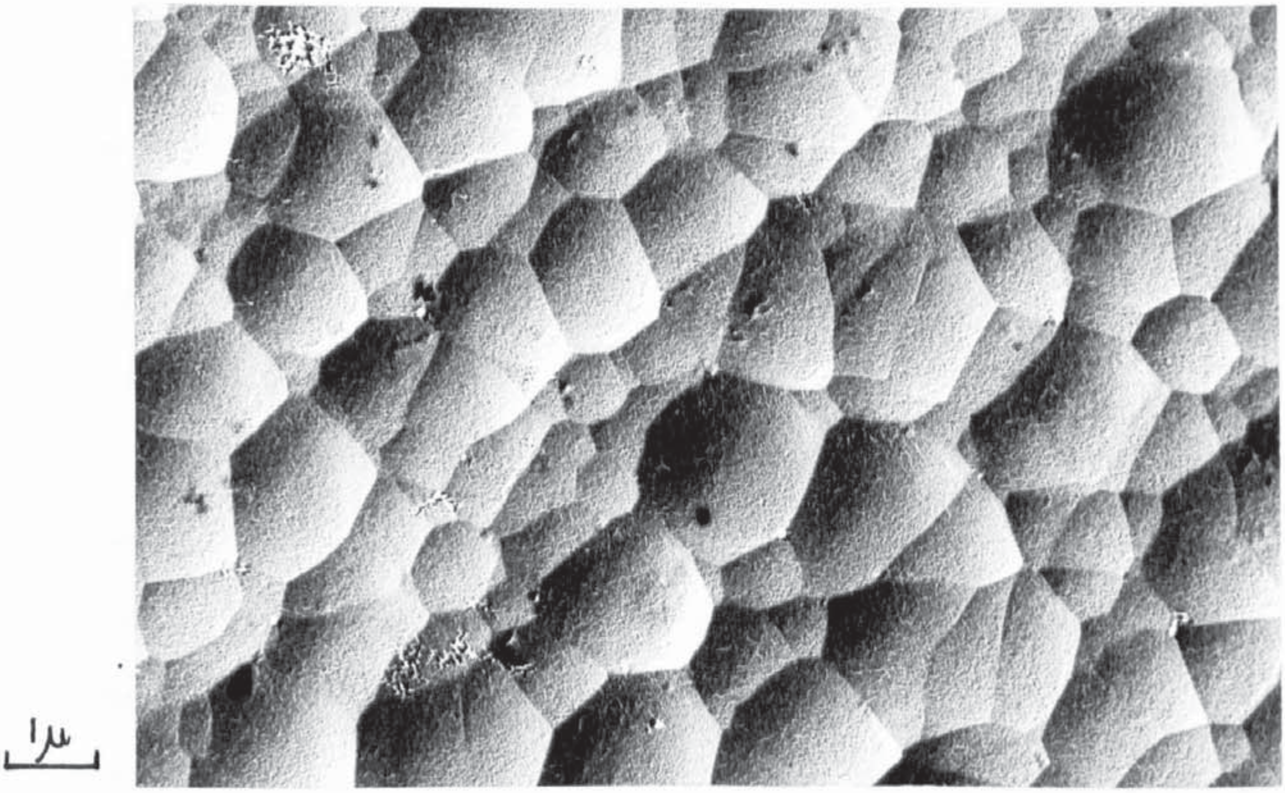


Fig. 3.11. Aluminium Chemically Polished for 10 Seconds.

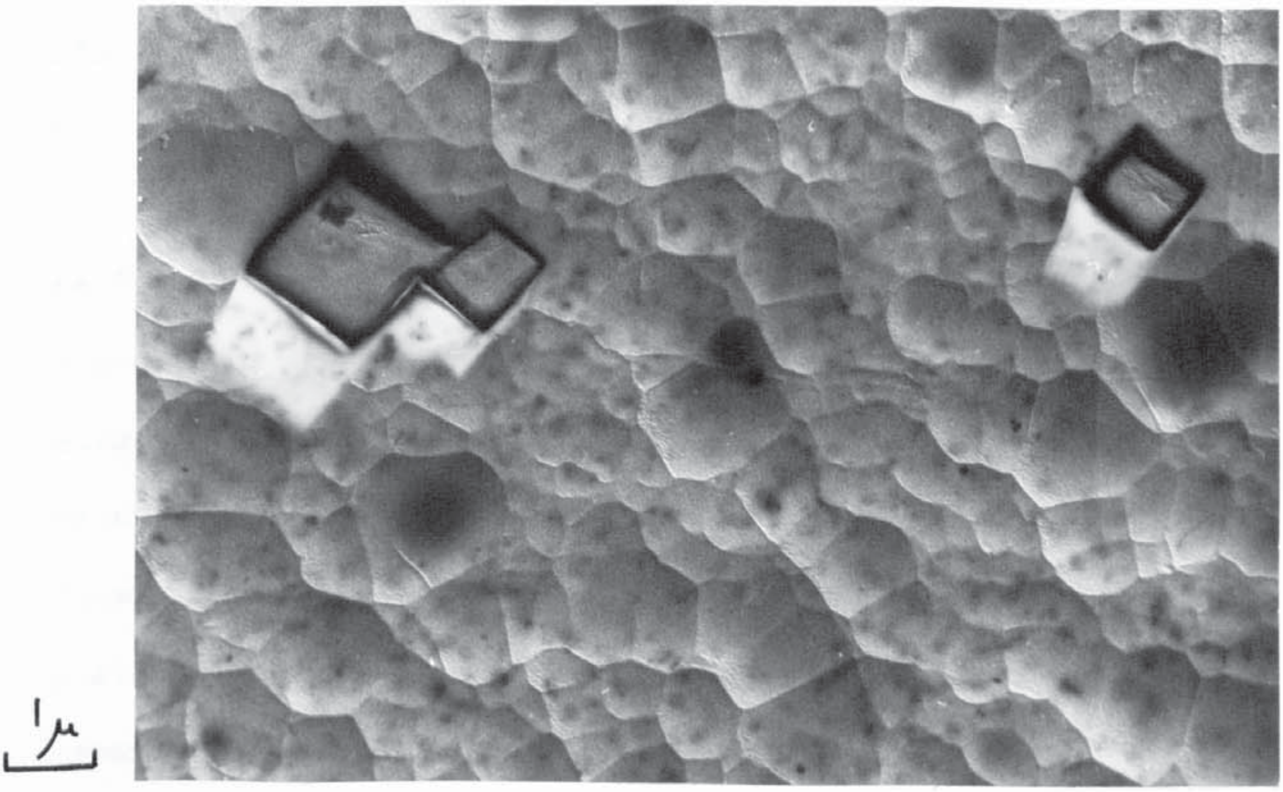


Fig. 3.12. {100} Grain of Aluminium Chemically Polished for 15 Seconds.

further dissolution takes place, each cell is separated from its neighbours by a clearly defined straight boundary. It can be seen that the cells are not regular in appearance, each having either 5,6, 7 or 8 sides or very occasionally 4 or 9 sides.

When the network is complete, which in this solution occurs after 10 seconds immersion, the aluminium surface is covered with fine equiaxed cells, 0.5 - 1 μm. in size. The shape and distribution of the cells are apparently unaffected by the grain orientation of the basis aluminium. This can be seen by comparing the structures produced on different grains, identified by the shape of the etch pits formed in the etching solution, shown in Figs. 3.12, 3.16 and 3.20.

b) Polishing Stage

From the etched surface with the network of equiaxed cells, the surface structure changes with longer polishing times to one characteristic of a polished surface. In this stage it is apparent that the structure produced is dependent on the grain orientation of the basis aluminium. Figs. 3.12 - 3.22 show the development of the structure with polishing time and the clear orientation dependency of the structures produced, Figs. 3.12 - 3.15 show the $\{100\}$ grains, Figs. 3.16 - 3.19 the $\{110\}$ grains and Figs. 3.20 - 3.22

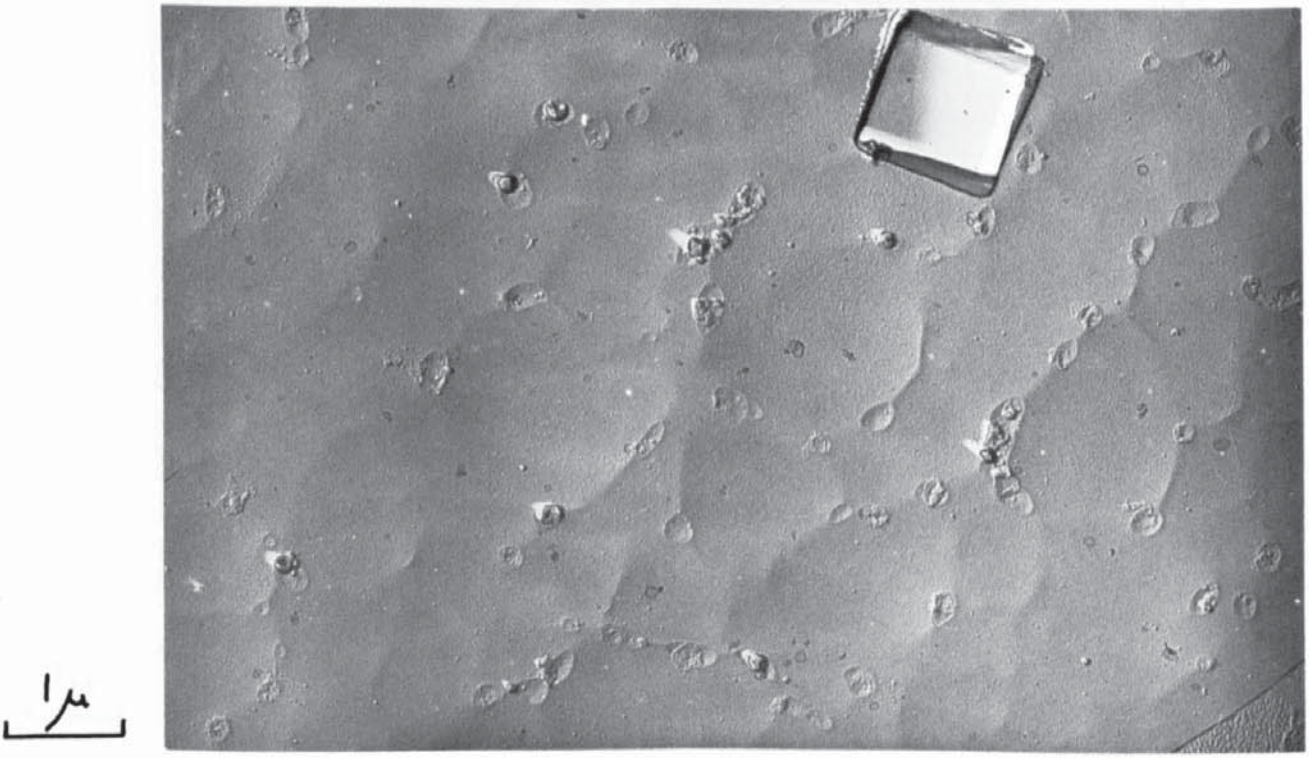


Fig. 3.13. {100} Grain of Aluminium Chemically Polished for 30 Seconds.

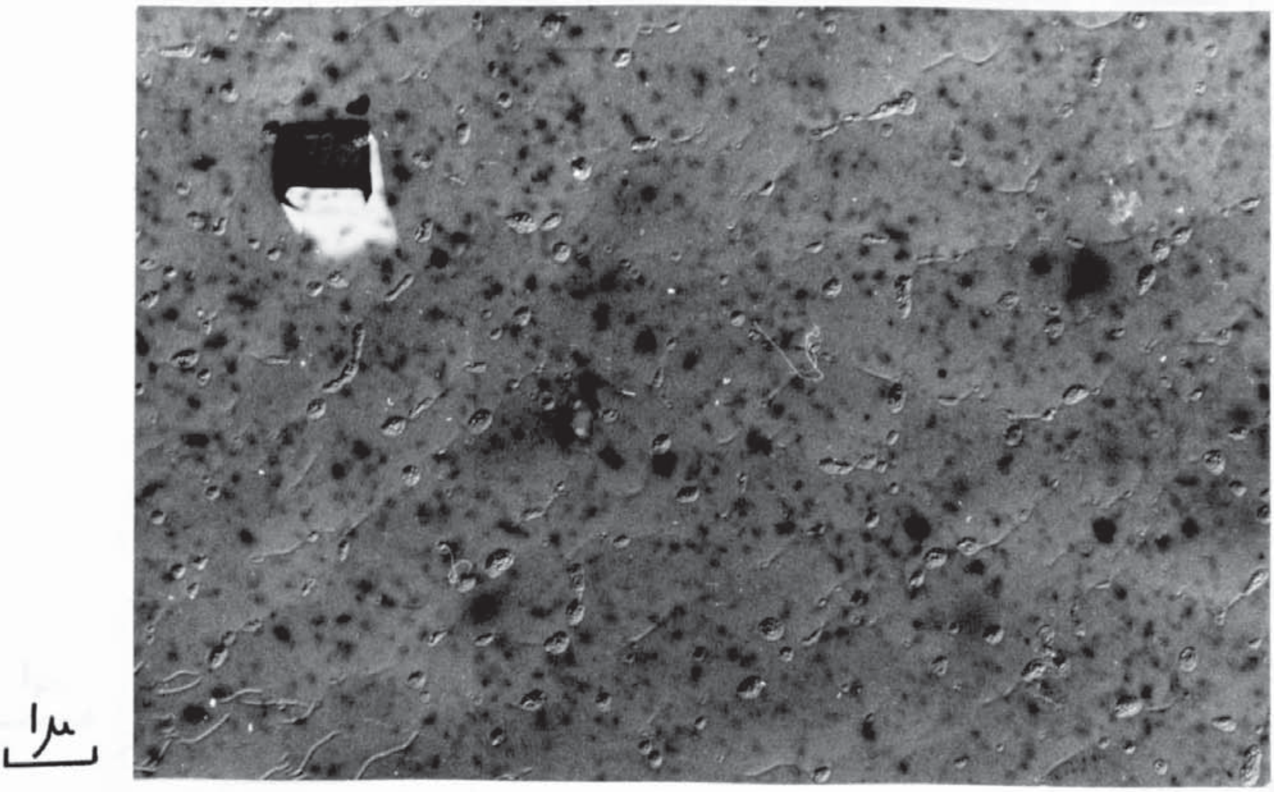


Fig. 3.14. {100} Grain of Aluminium Chemically Polished for 40 Seconds.

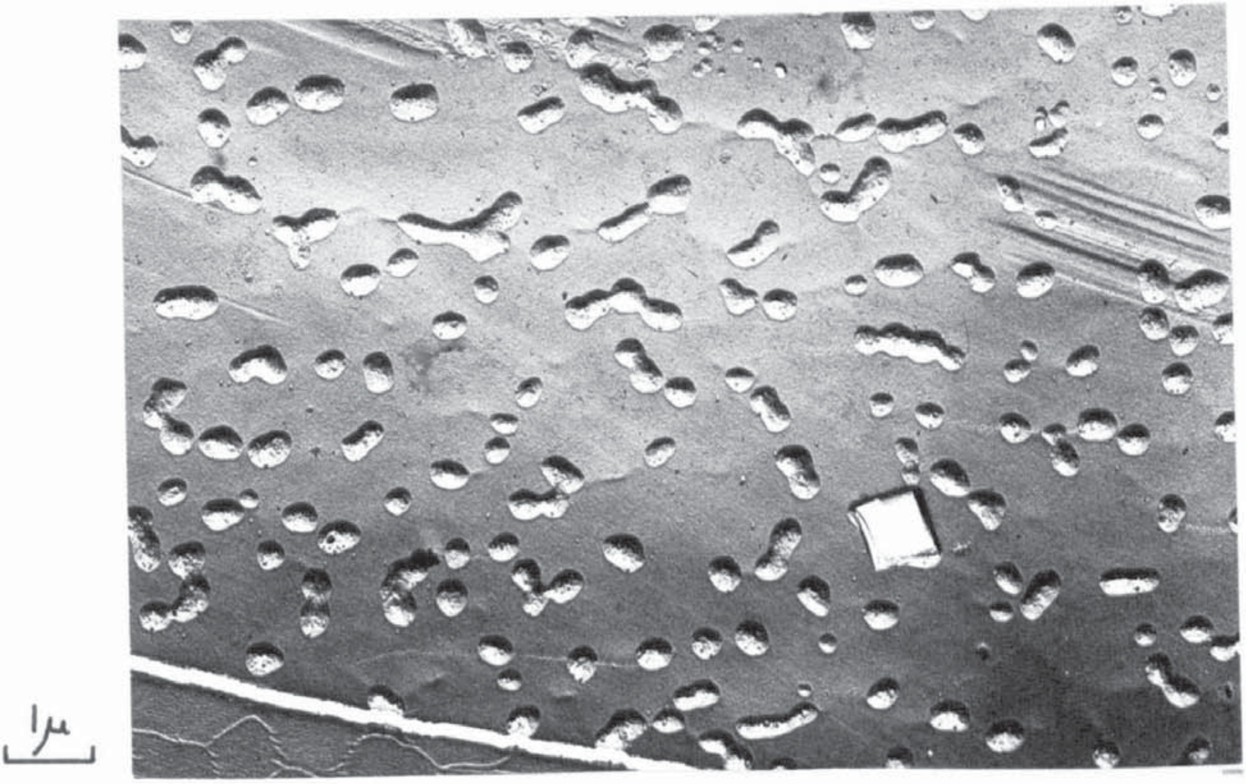


Fig. 3.15. {100} Grain of Aluminium Chemically Polished for 50 Seconds.

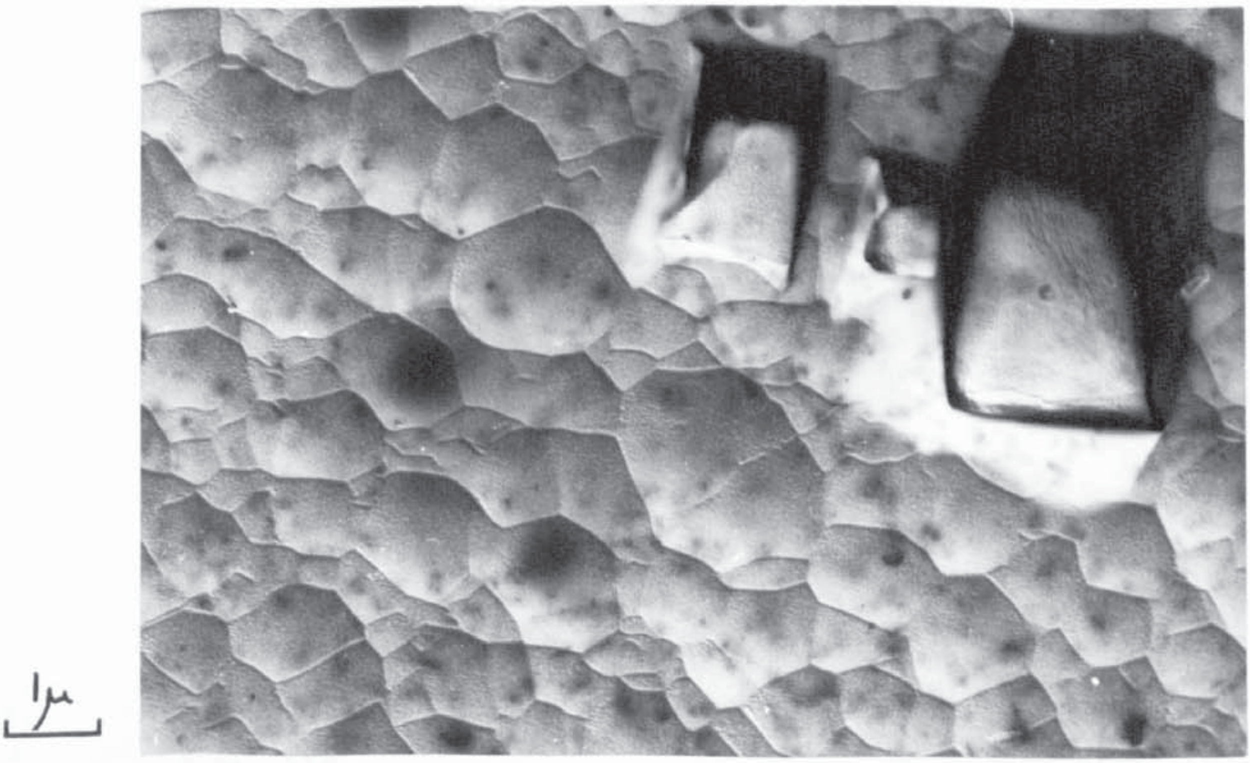


Fig. 3.16. {110} Grain of Aluminium Chemically Polished for 15 Seconds.

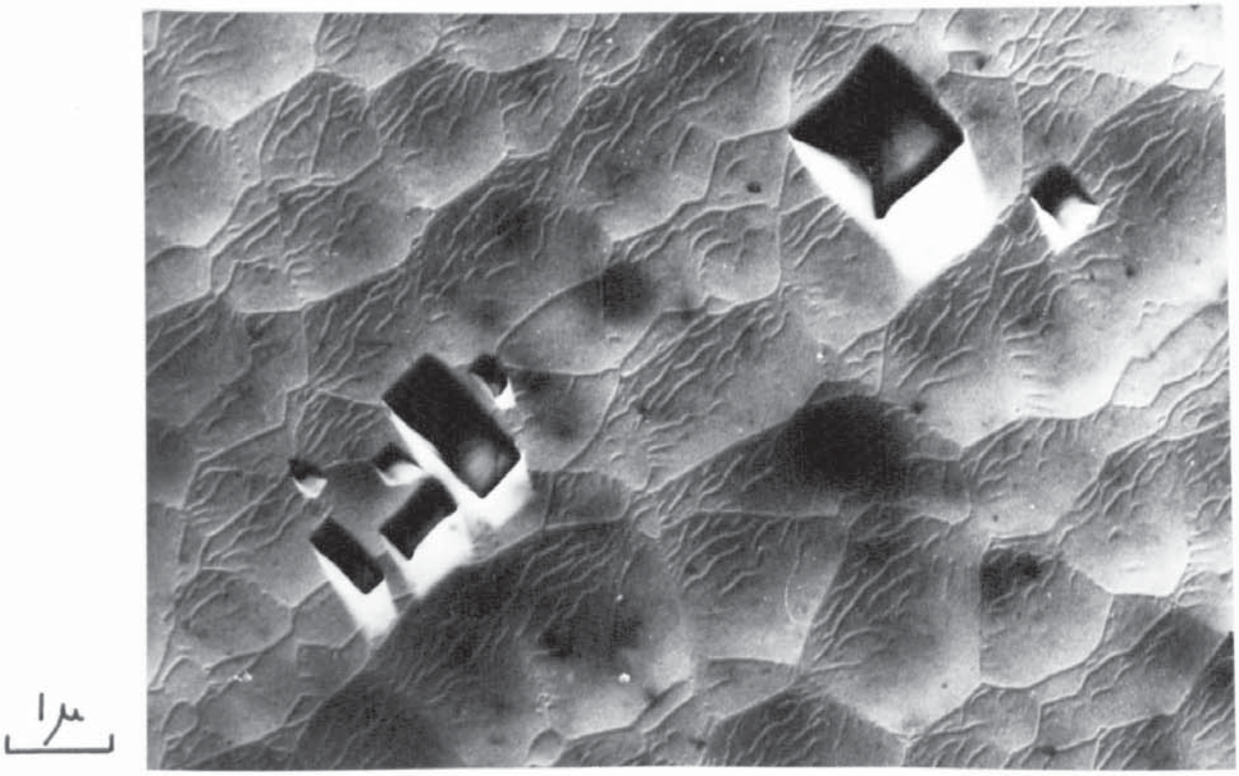


Fig. 3.17 $\{110\}$ Grain of Aluminium Chemically Polished for 30 Seconds.

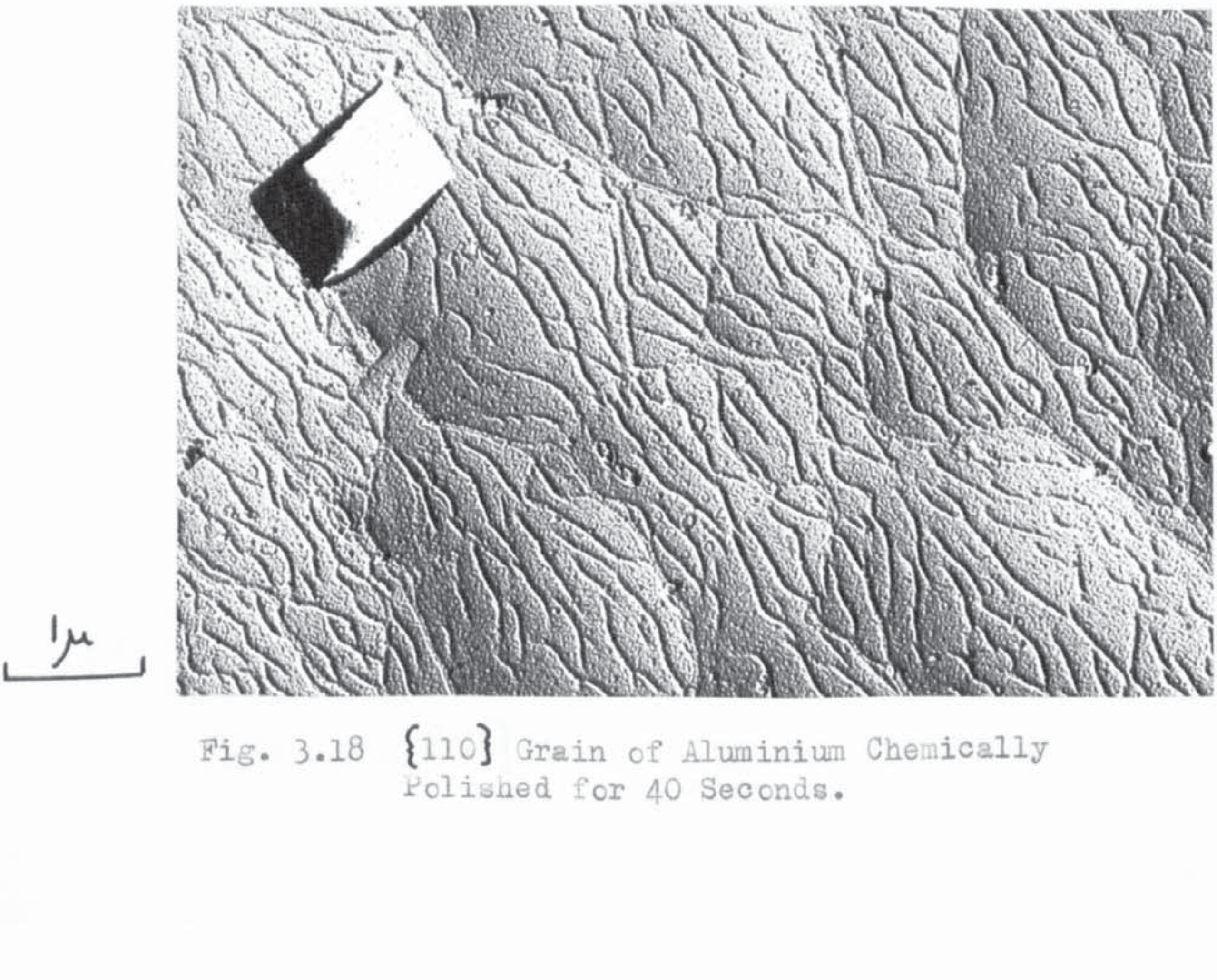


Fig. 3.18 $\{110\}$ Grain of Aluminium Chemically Polished for 40 Seconds.

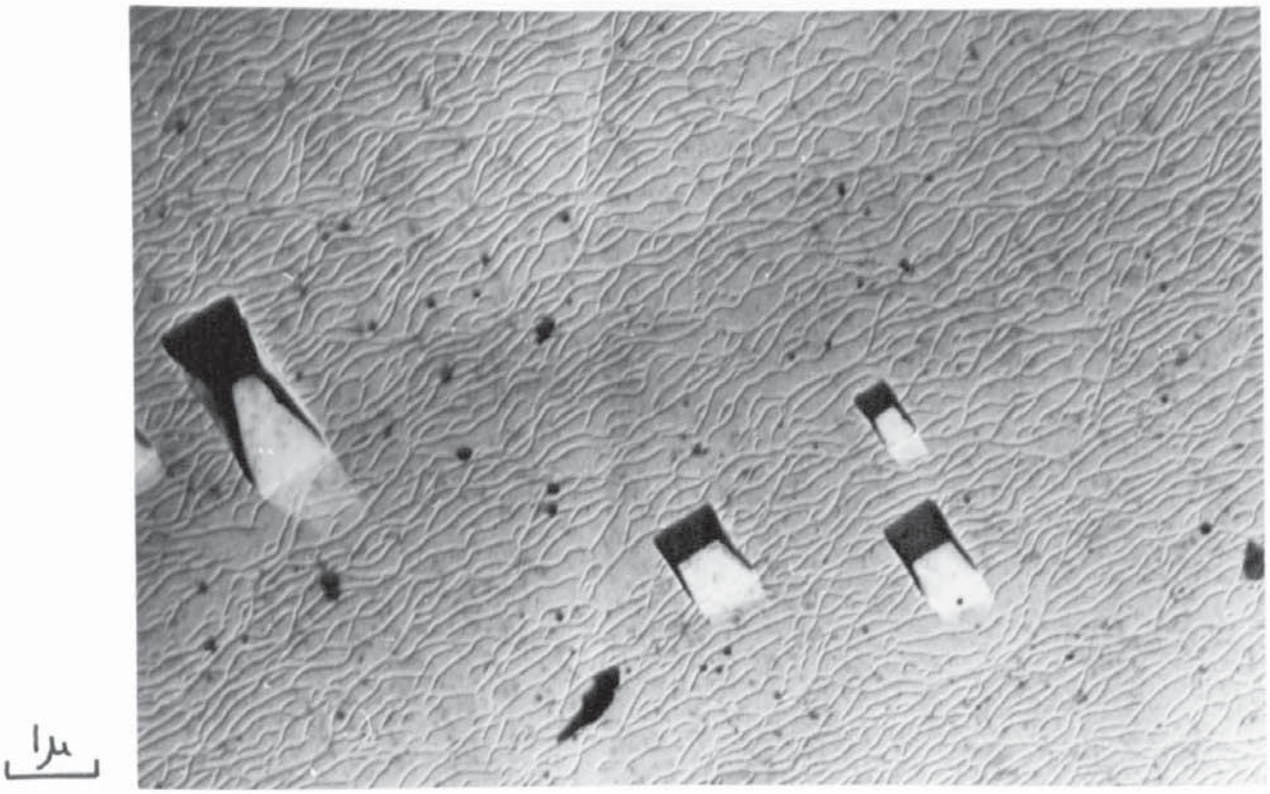


Fig. 3.19. $\{110\}$ Grain of Aluminium Chemically Polished for 50 Seconds.

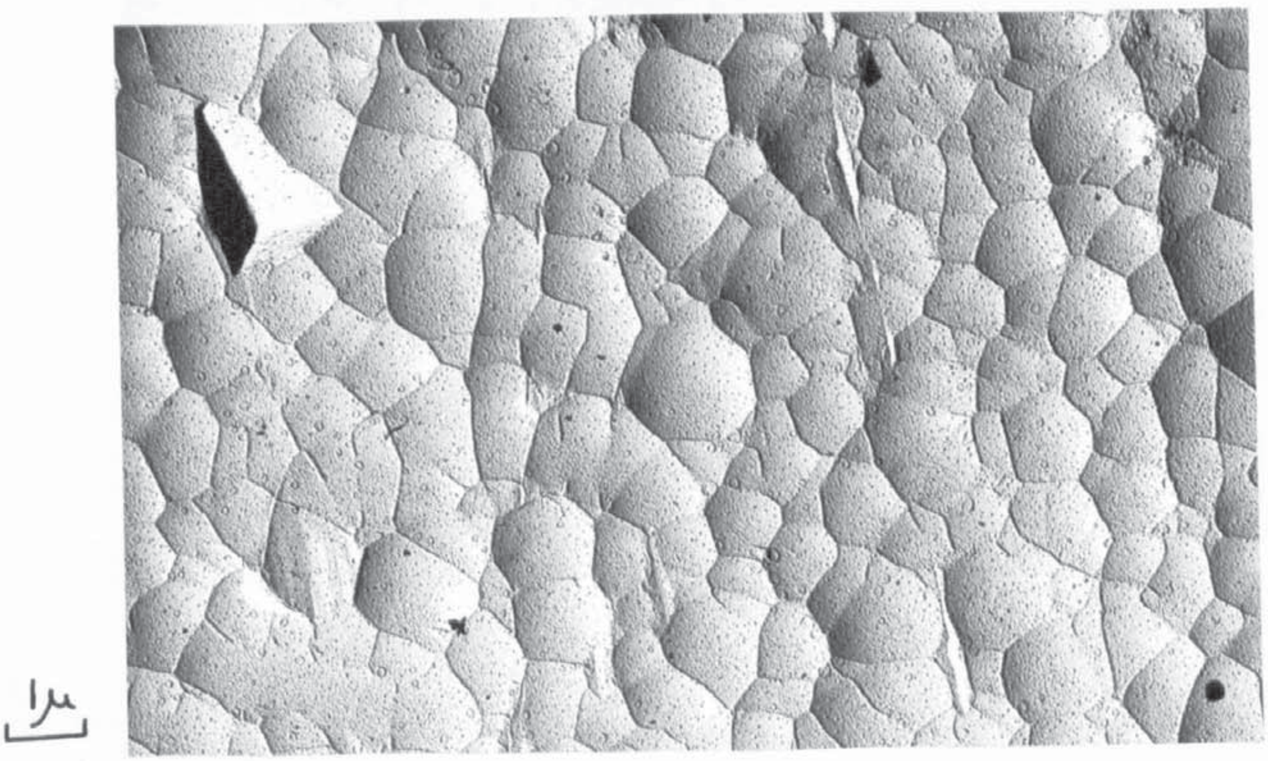


Fig. 3.20. $\{111\}$ Grain of Aluminium Chemically Polished for 15 Seconds.

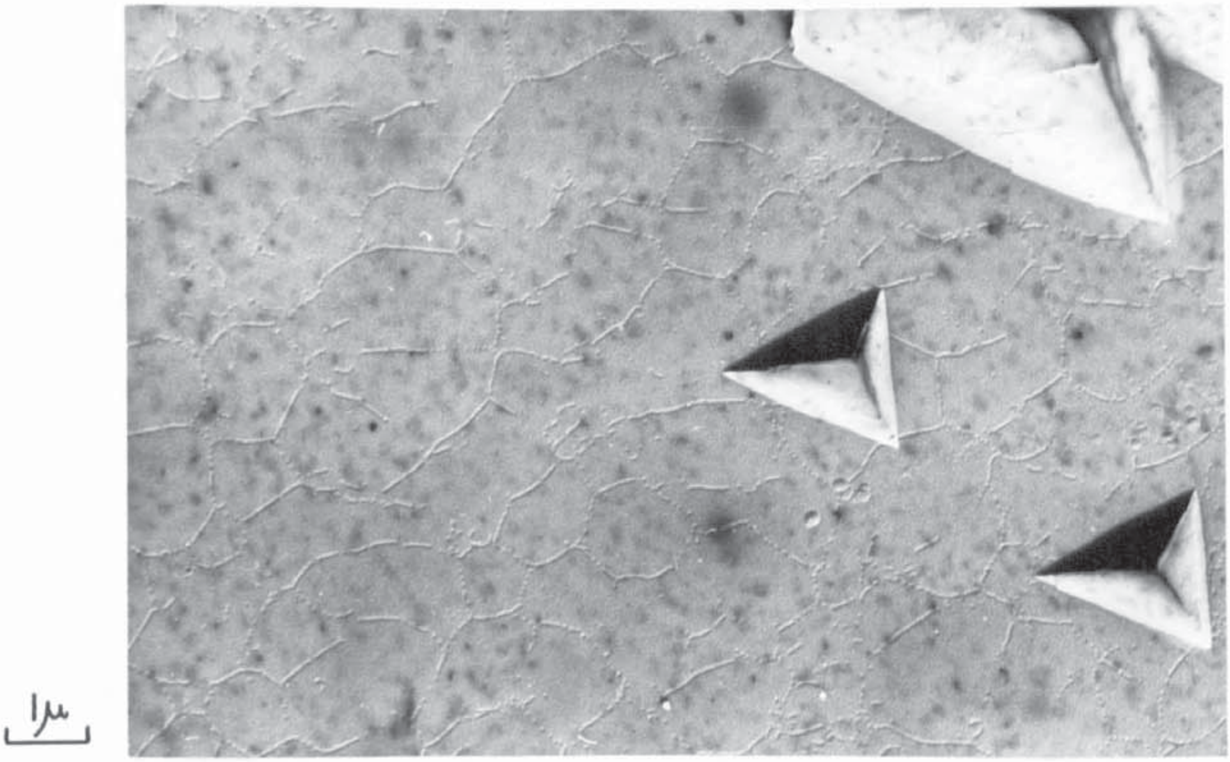


Fig. 3.21. $\{111\}$ Grain of Aluminium Chemically Polished for 30 Seconds.

Fig. 3.22. $\{111\}$ Grain of Aluminium Chemically Polished for 50 Seconds.

the $\{111\}$ grains.

On the $\{100\}$ grains, identified by the cubic etch pits, small approximately spherical pits nucleate on the ridge boundaries of the equiaxed cells, particularly at triple points. As polishing proceeds these depressions grow laterally with the elimination of the original equiaxed cells.

On the $\{110\}$ grains, new ridge boundaries are produced within the equiaxed cells by the local dissolution of aluminium in these areas. As polishing proceeds more dissolution of the aluminium takes place around the new ridges until they are as pronounced as the original cell boundaries. The ridges are formed preferentially in the $\langle 100 \rangle$ direction thus the overall appearance of the polished structure is that of elongated cells, the elongations being in the $\langle 100 \rangle$ direction.

On the $\{111\}$ planes dissolution takes place in certain areas on the ridge boundaries leaving isolated asperities. Eventually complete dissolution of the original cell ridges takes place leaving a network of small asperities.

The higher indeces planes which are occasionally found on the surface, have more complex surface structures as shown in Figs. 3.23 - 3.24.

c) Coarsening Stage

After the polishing pattern is produced, the structure does not change appreciably in form, with increasing

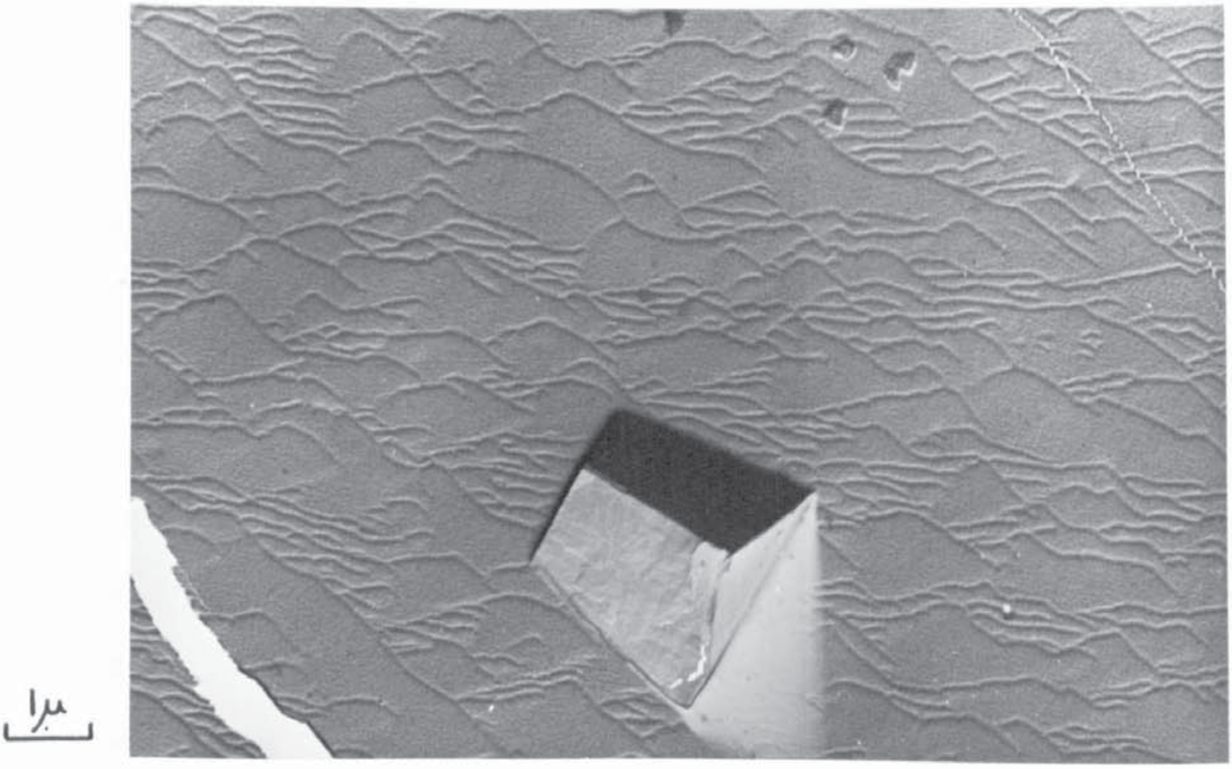


Fig. 3.23. High Index Plane of Aluminium
Chemically Polished for 1 Minute.

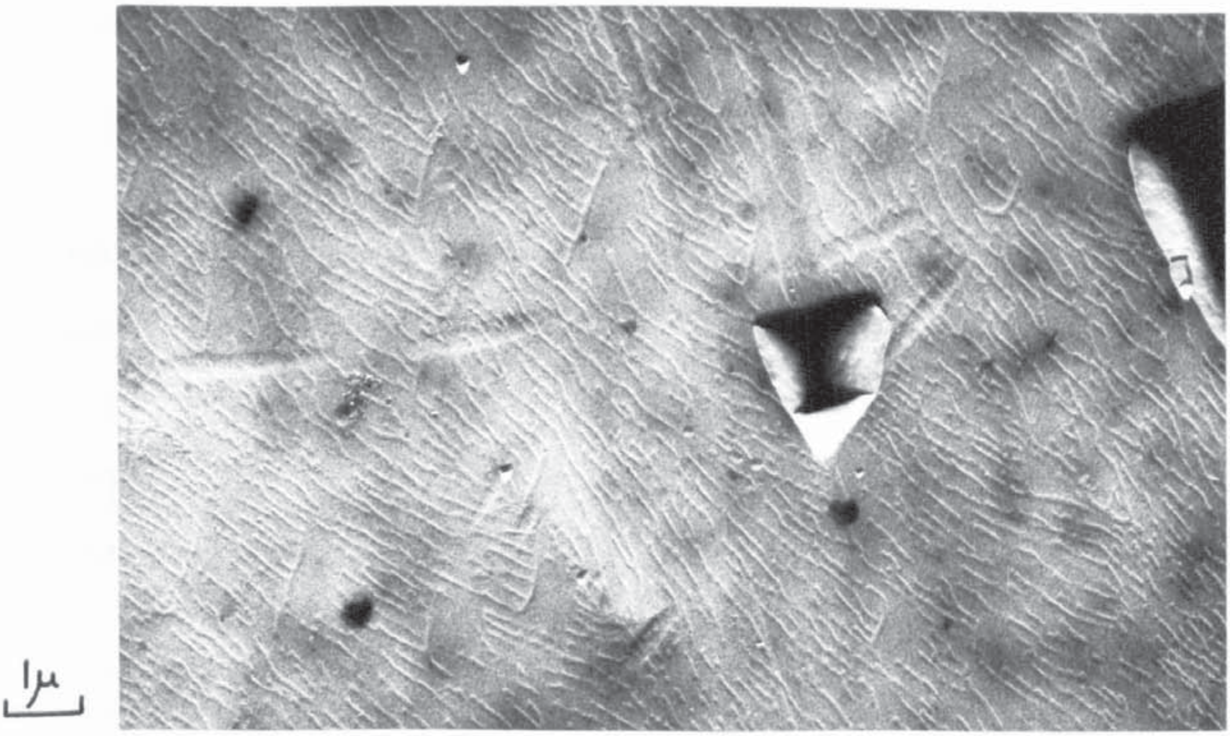


Fig. 3.24. High Index Plane of Aluminium
Chemically Polished for 1 Minute.

polishing time. However, there is a marked coarsening of the structure which occurs very rapidly in solutions with high copper contents and more slowly with solutions of lower copper content.

Electron micrographs taken from specimens chemically polished for 1, $1\frac{1}{2}$, 2, 3 and 4 minutes are shown in Figs. 3.25 - 3.29. These show the effect on the surface structure of increasing the polishing time after the polishing structure has been produced. It can be seen that the depressions on the $\{100\}$ planes enlarge and merge to cover most of the area of the grain, together with pitting of the surface within the depressions. The laminations and asperities on the $\{110\}$ and $\{111\}$ planes also become enlarged and the surrounding surface pitted.

d) Structures Produced with Other Solutions

As mentioned previously, specimens polished in all the solutions investigated which contained copper, exhibited a similar range of surface structures. The only difference being the polishing times at which these structures were obtained. Table 3.1 denotes the relevant polishing times for each solution investigated.

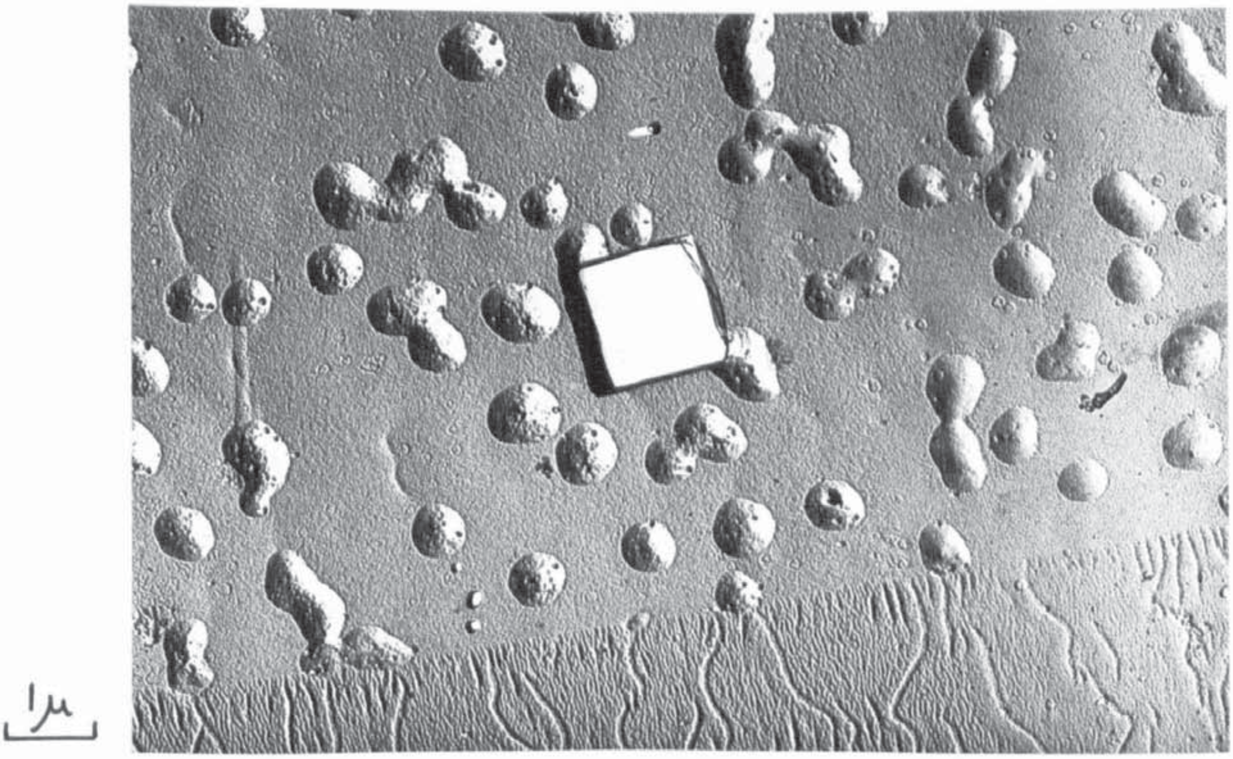


Fig. 3.25. Aluminium Chemically Polished for 1 Minute.

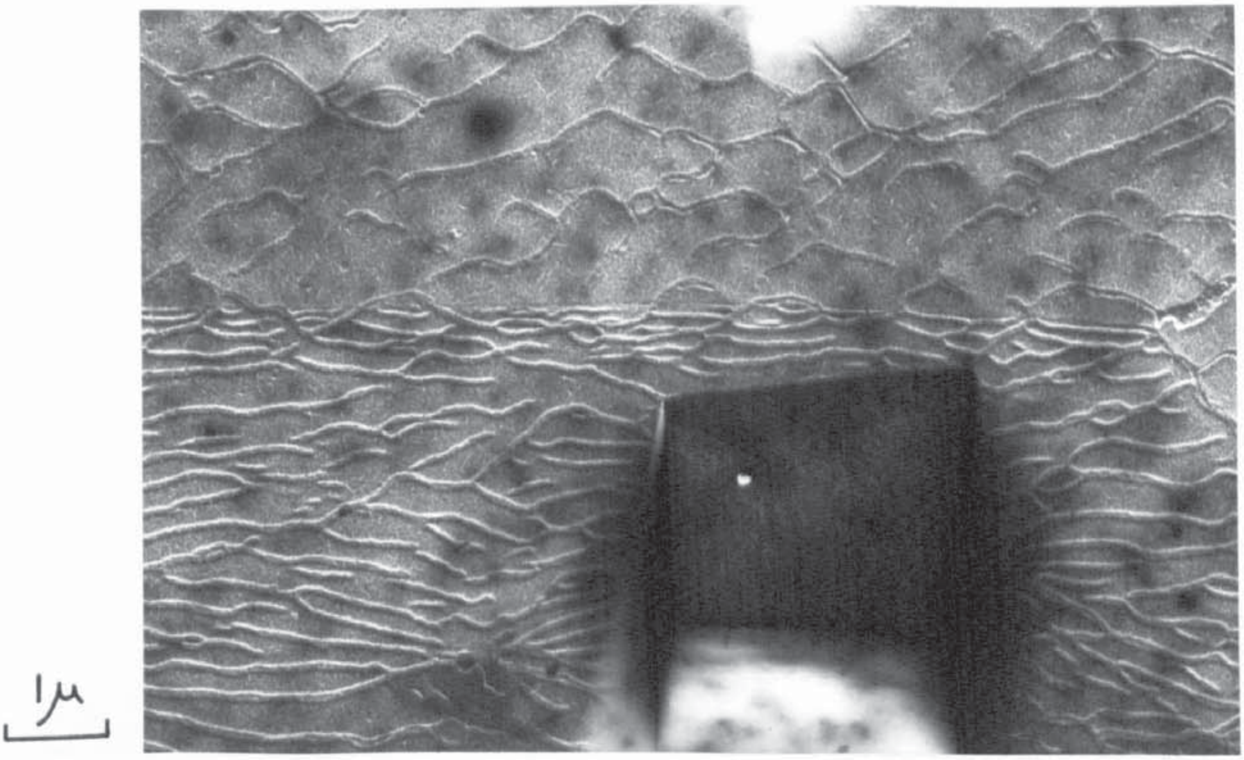


Fig. 3.26. Aluminium Chemically Polished for $1\frac{1}{2}$ Minutes.

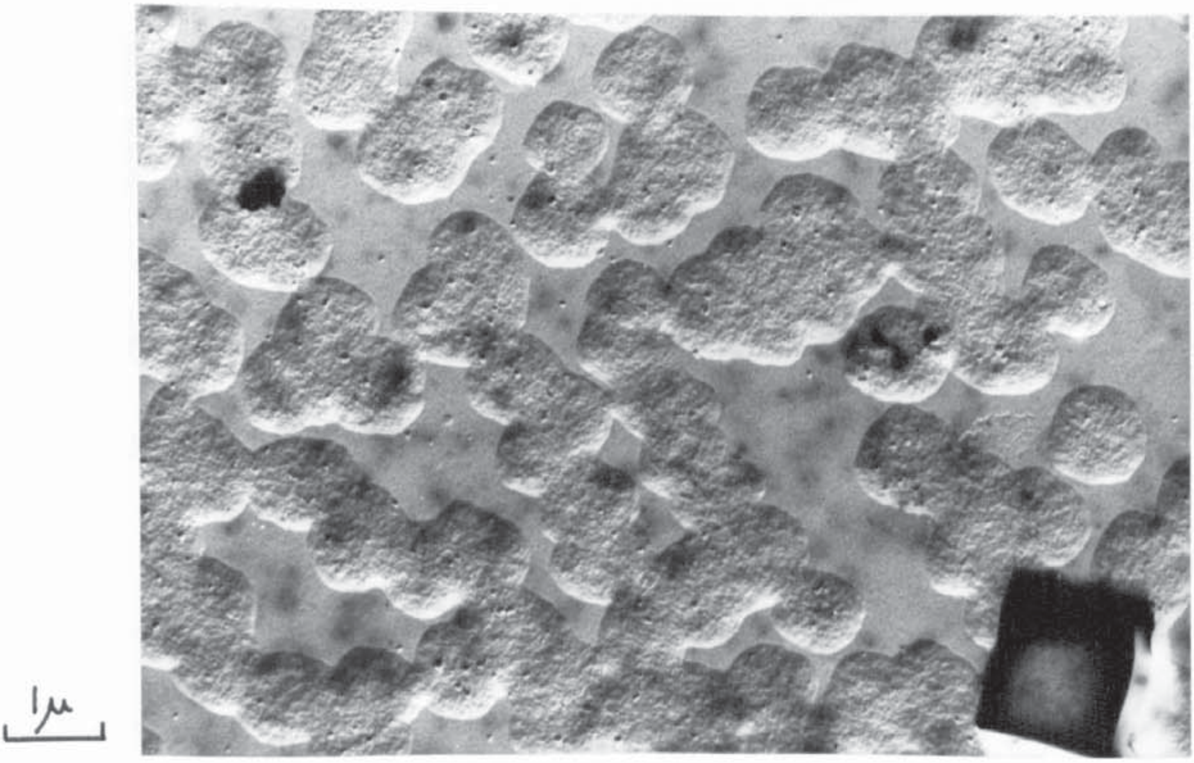


Fig. 3.27. Aluminium Chemically Polished for 2 Minutes.

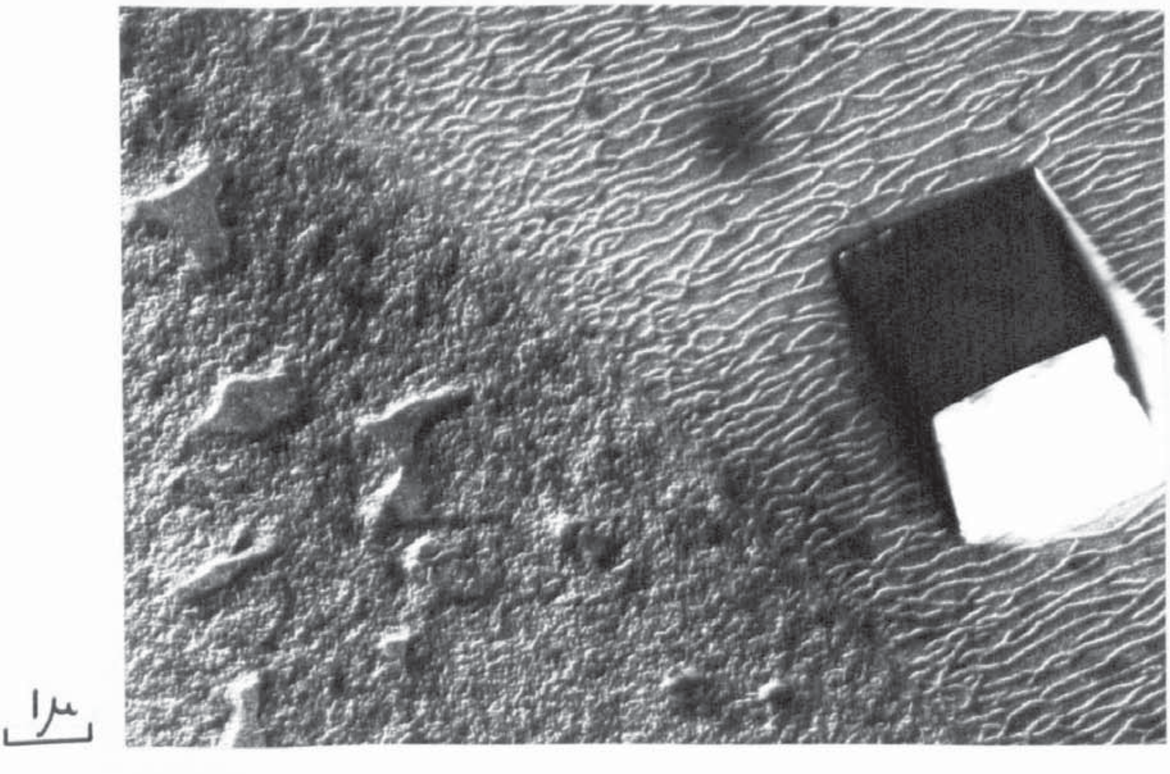


Fig. 3.28. Aluminium Chemically Polished for 3 Minutes.

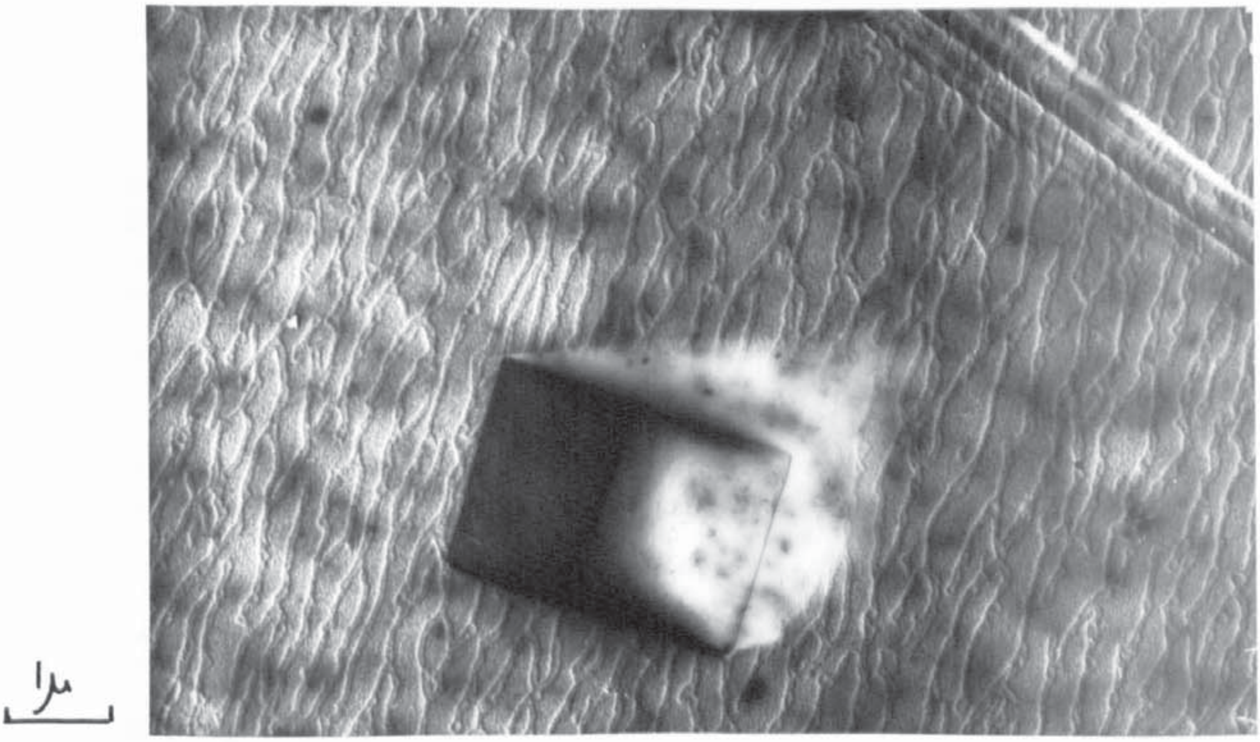


Fig. 3.29. Aluminium Chemically Polished for 4 Minutes.

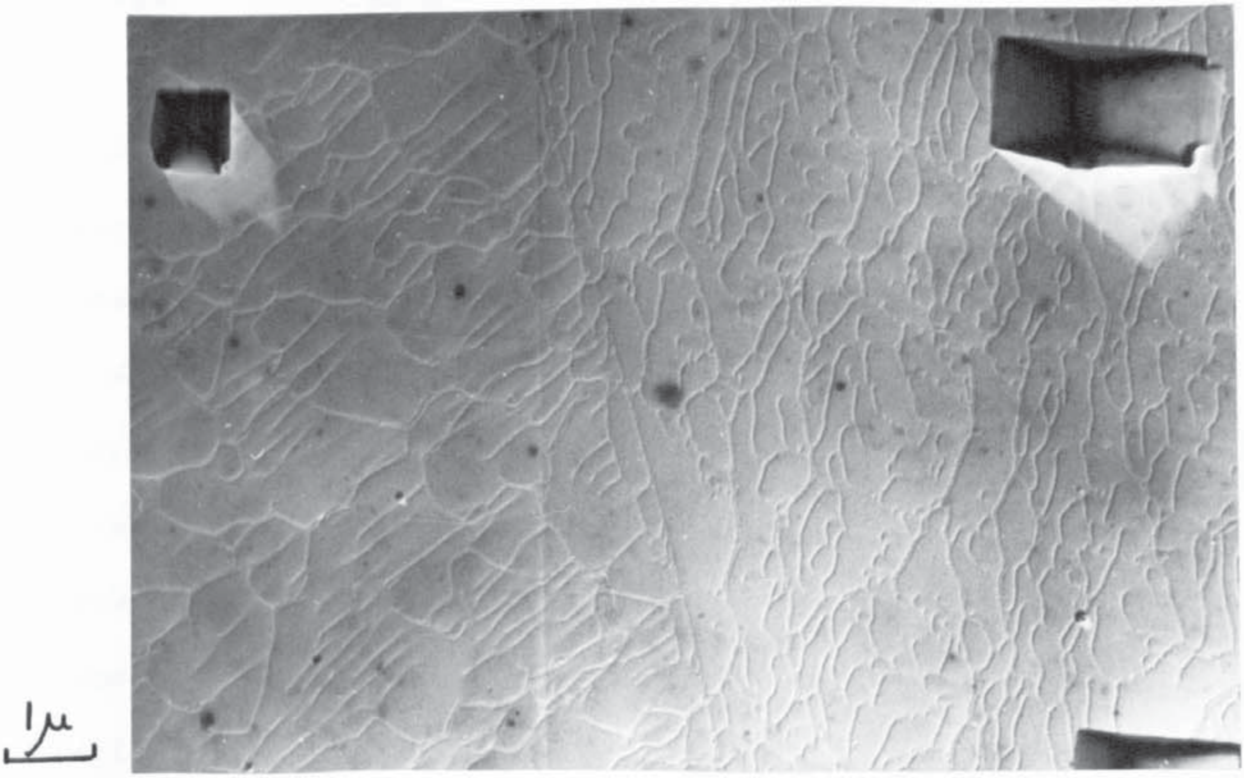


Fig. 3.30. Aluminium Chemically Polished in Solution E (No Copper) for 1 Minute.

TABLE 3.1.

Solution. gms. of copper per litre		Time for Etch Pattern	Time for Polishing Pattern	Time for Onset of Coarsening
A	0.25	15 Secs.	60 Secs.	3 Mins.
B	0.5	10 Secs.	50 Secs.	2 Mins.
C	0.75	8 Secs.	40 Secs.	60 Secs.
D	1.0	5 Secs.	20 Secs.	30 Secs.

Figs. 3.30 - 3.34 show the above effect pictorially, as the electron micrographs are taken from specimens polished for 1 minute, in each of the solutions investigated.

3.4.2. Solution E

The electron micrographs taken of surface structures produced in the polishing solution containing no copper, are displayed in Figs. 3.35 - 3.43. These structures are somewhat different to those produced in the solutions containing copper, in that the etched structure is not completely removed. Figs. 3.35 - 3.37, which illustrate samples polished for 5, 10 and 20 seconds, show the initial etching of the aluminium surface which occurs in a similar manner to the other polishing solutions. However, continued polishing for 40 seconds, 1, 1½ and 2 minutes, shown in Figs. 3.38 - 3.41, does not produce the normal polished

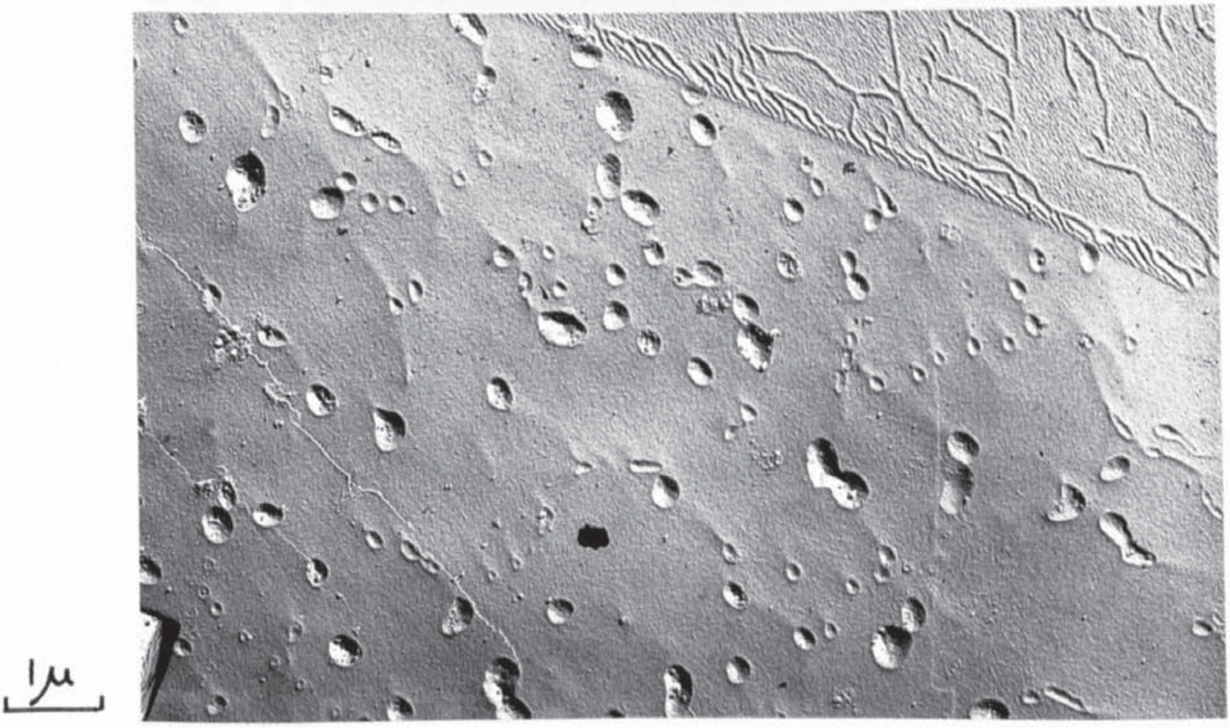


Fig. 3.31. Aluminium Chemically Polished in Solution A (0.25 gms. of Copper per Litre) for 1 Minute.

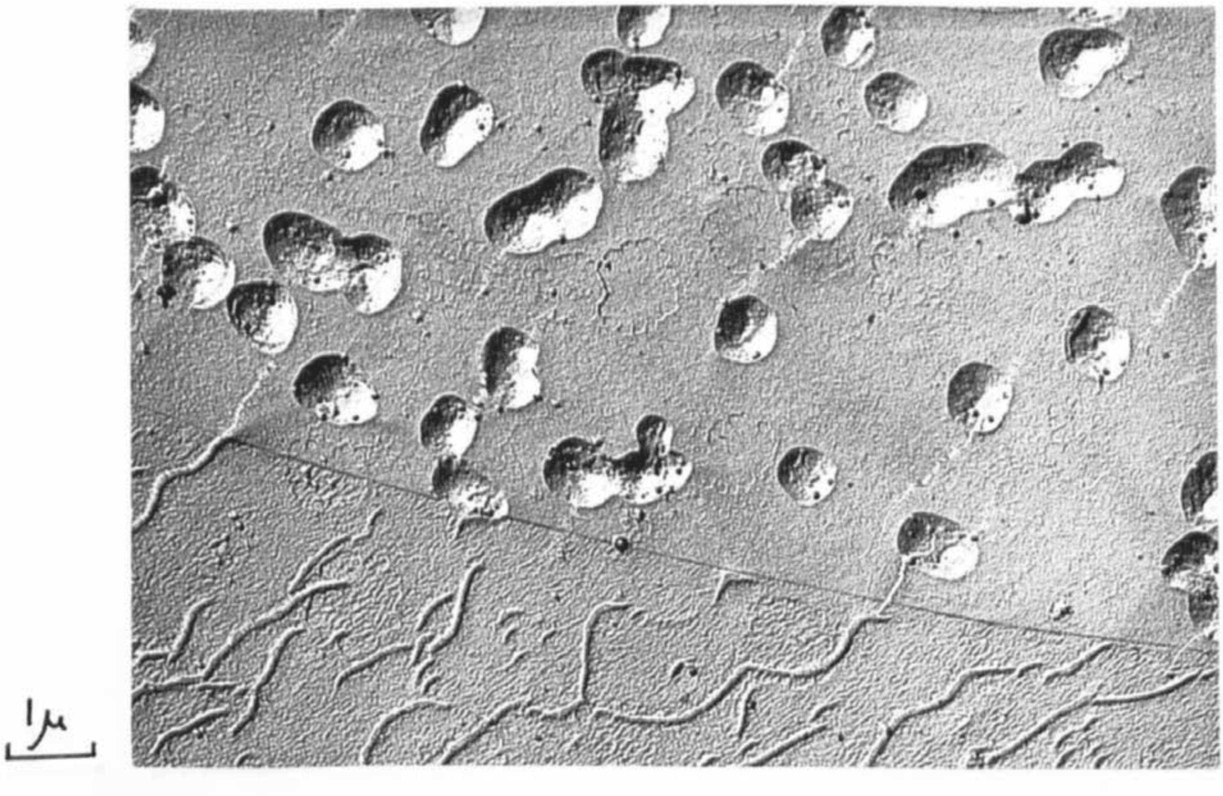


Fig. 3.32. Aluminium Chemically Polished in Solution B (0.5 gms. of Copper per Litre) for 1 Minute.

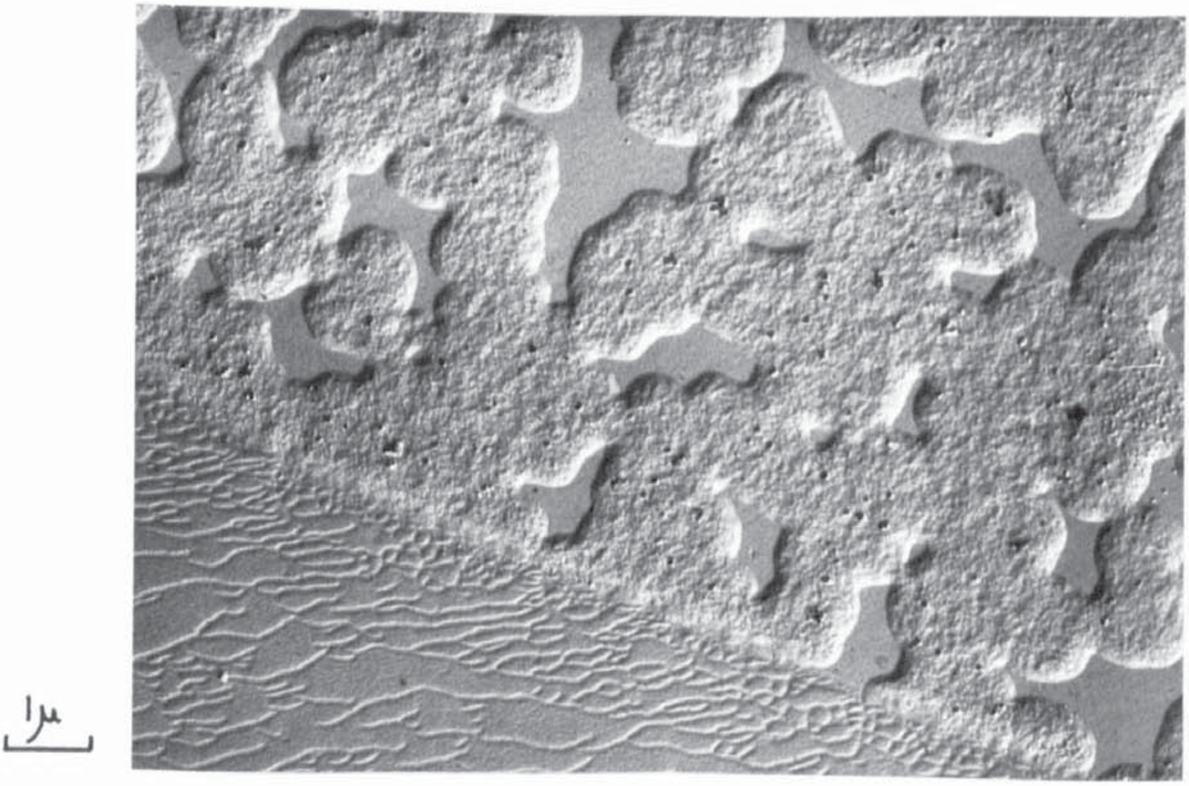


Fig. 3.33. Aluminium Chemically Polished in Solution C (0.75 gms. of Copper per Litre) for 1 Minute.

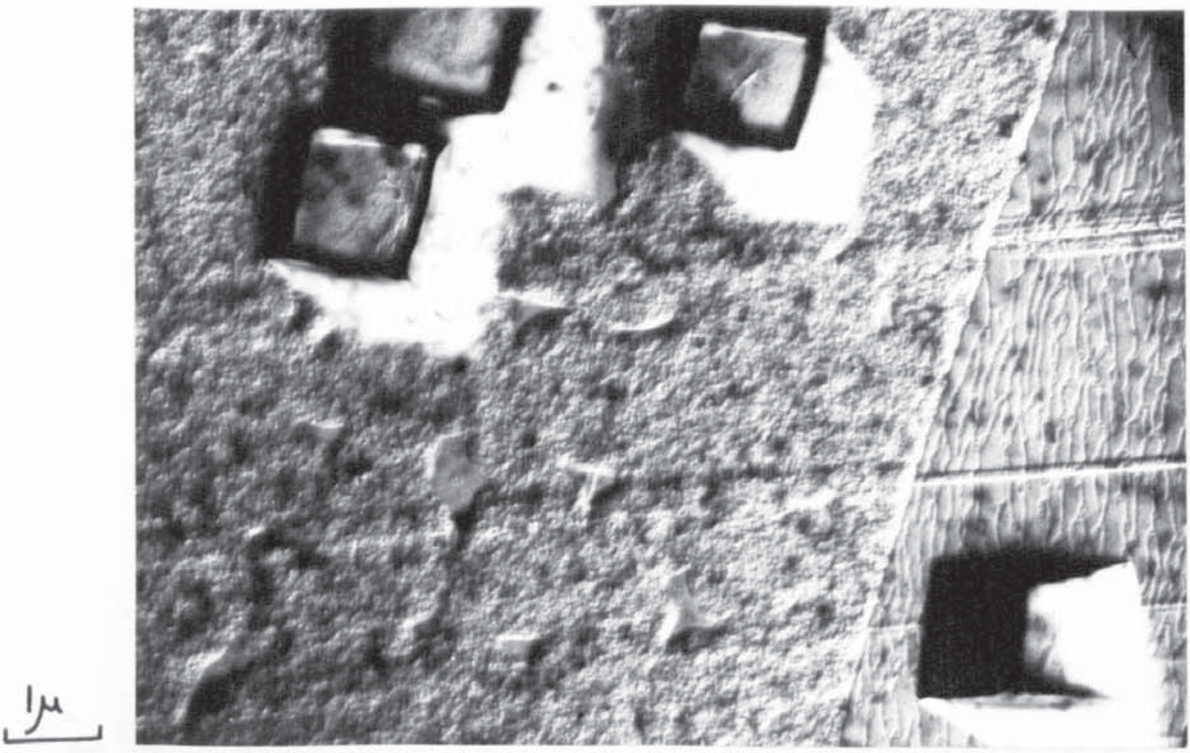


Fig. 3.34. Aluminium Chemically Polished in Solution D (1.0 gms. of Copper per Litre) for 1 Minute.

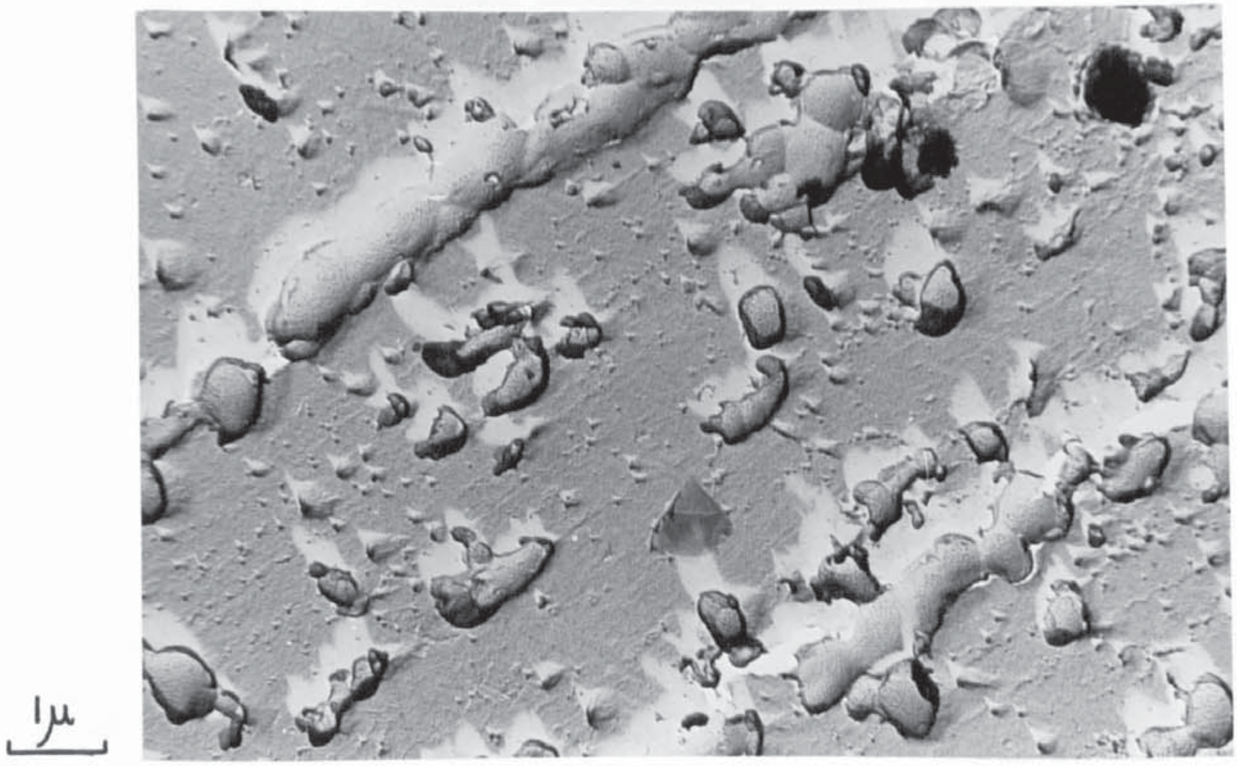


Fig. 3.35. Aluminium Chemically Polished in Solution E (No Copper) for 5 Seconds.

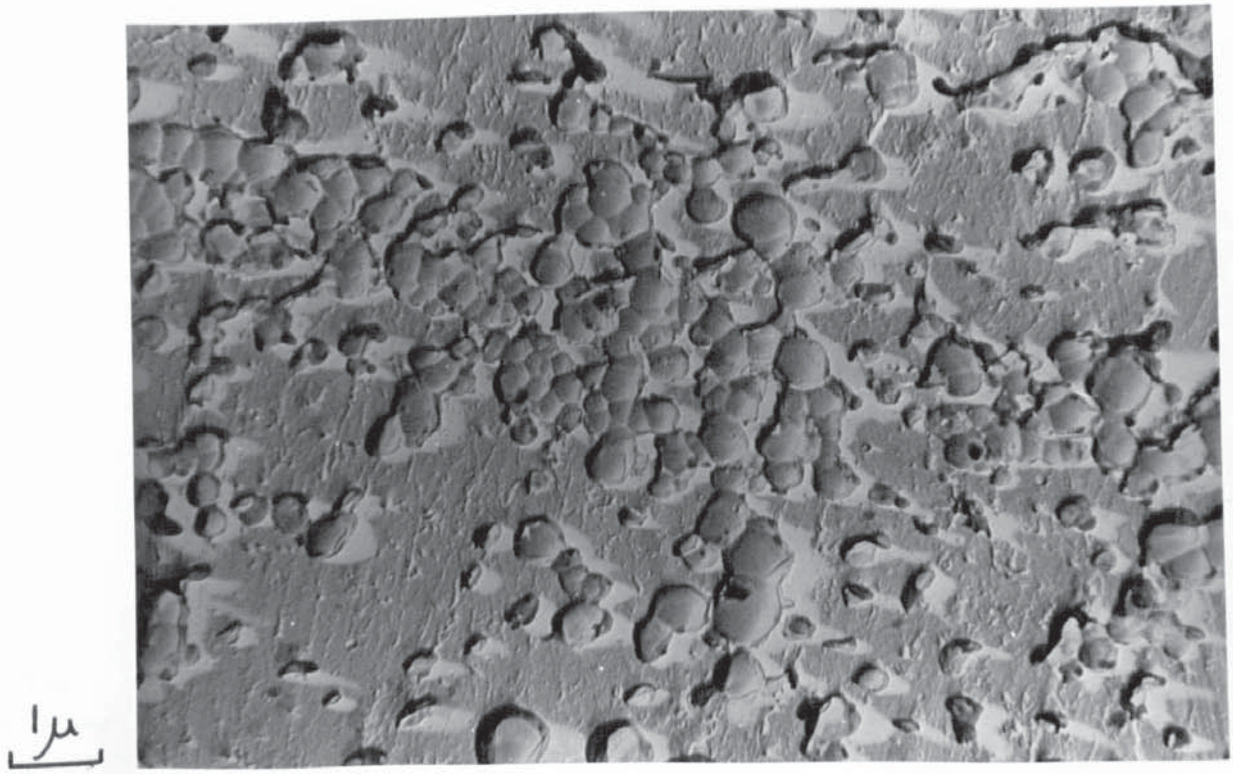


Fig. 3.36. Aluminium Chemically Polished in Solution E (No Copper) for 10 Seconds.

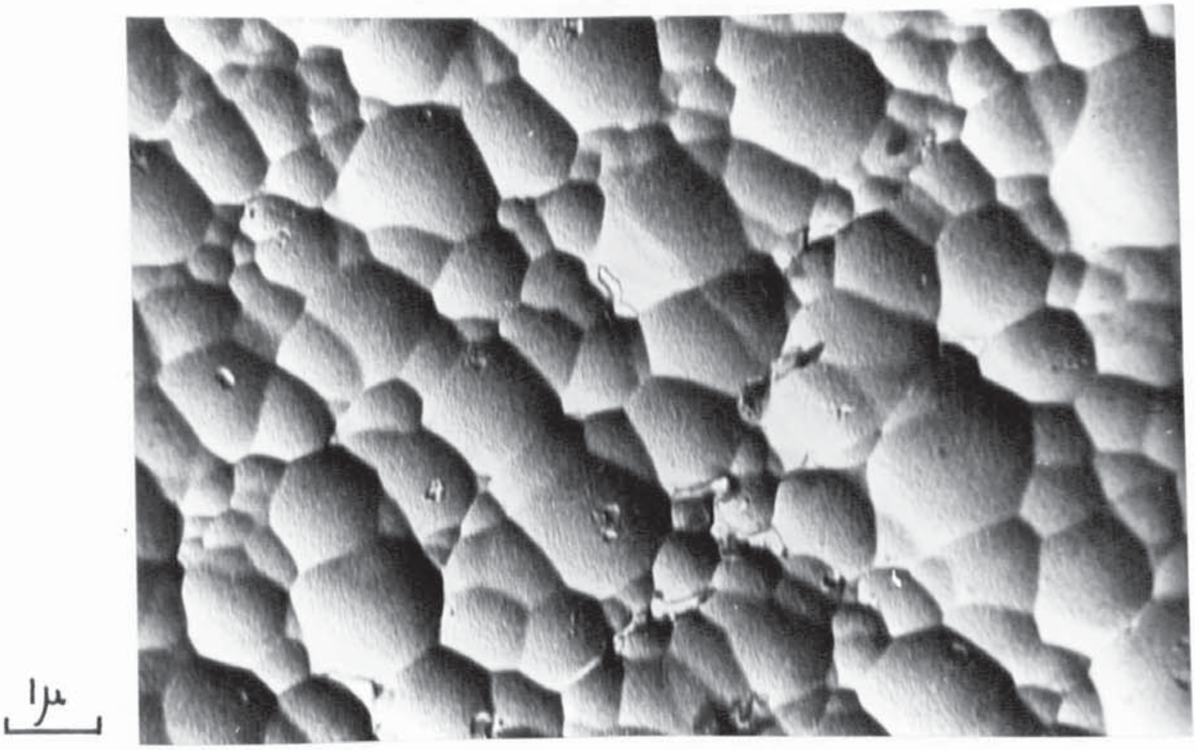


Fig. 3.37. Aluminium Chemically Polished in Solution E (No Copper) for 20 Seconds.

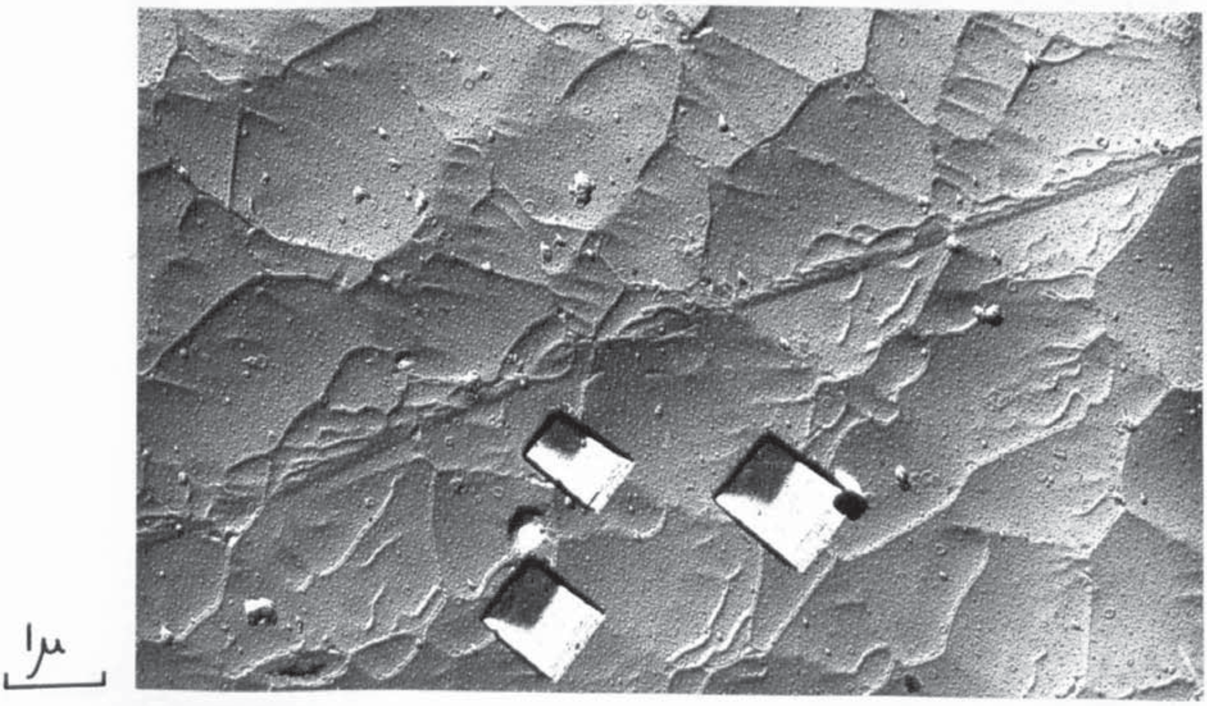


Fig. 3.38. Aluminium Chemically Polished in Solution E (No Copper) for 40 Seconds.

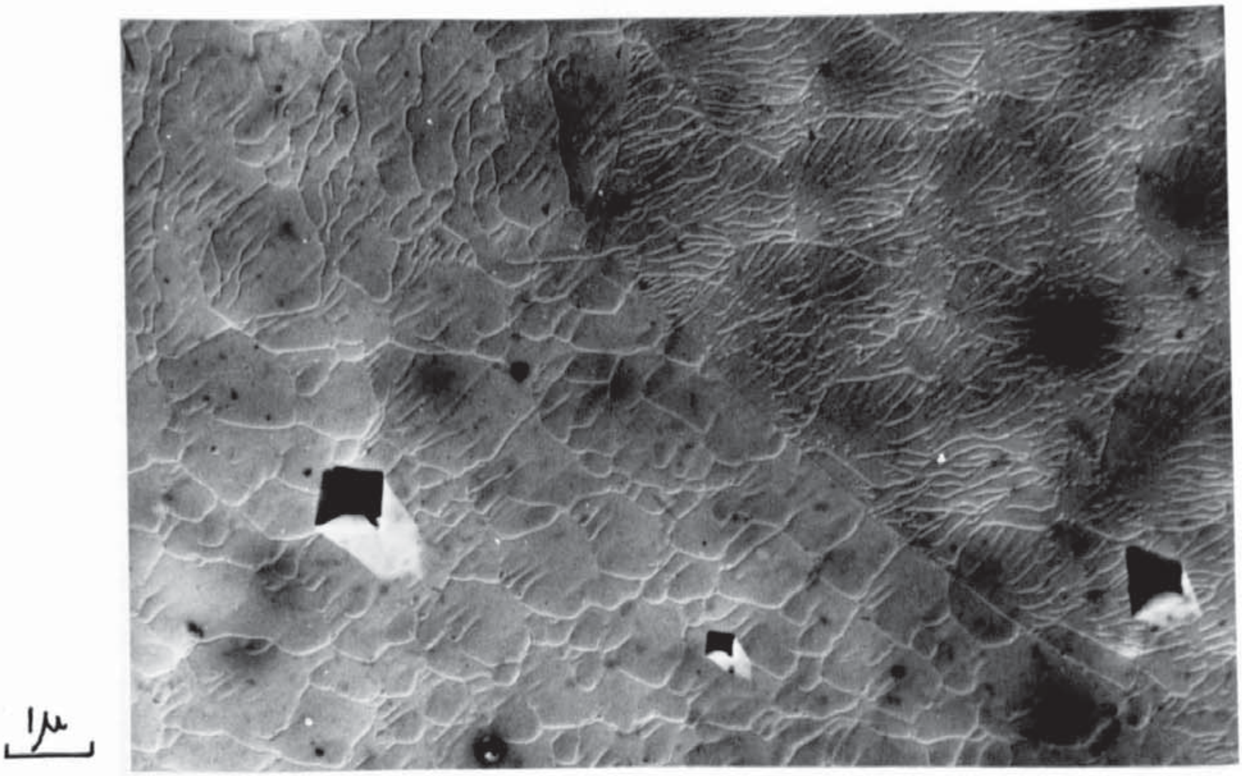


Fig. 3.39. Aluminium Chemically Polished in Solution E (No Copper) for 1 Minute.

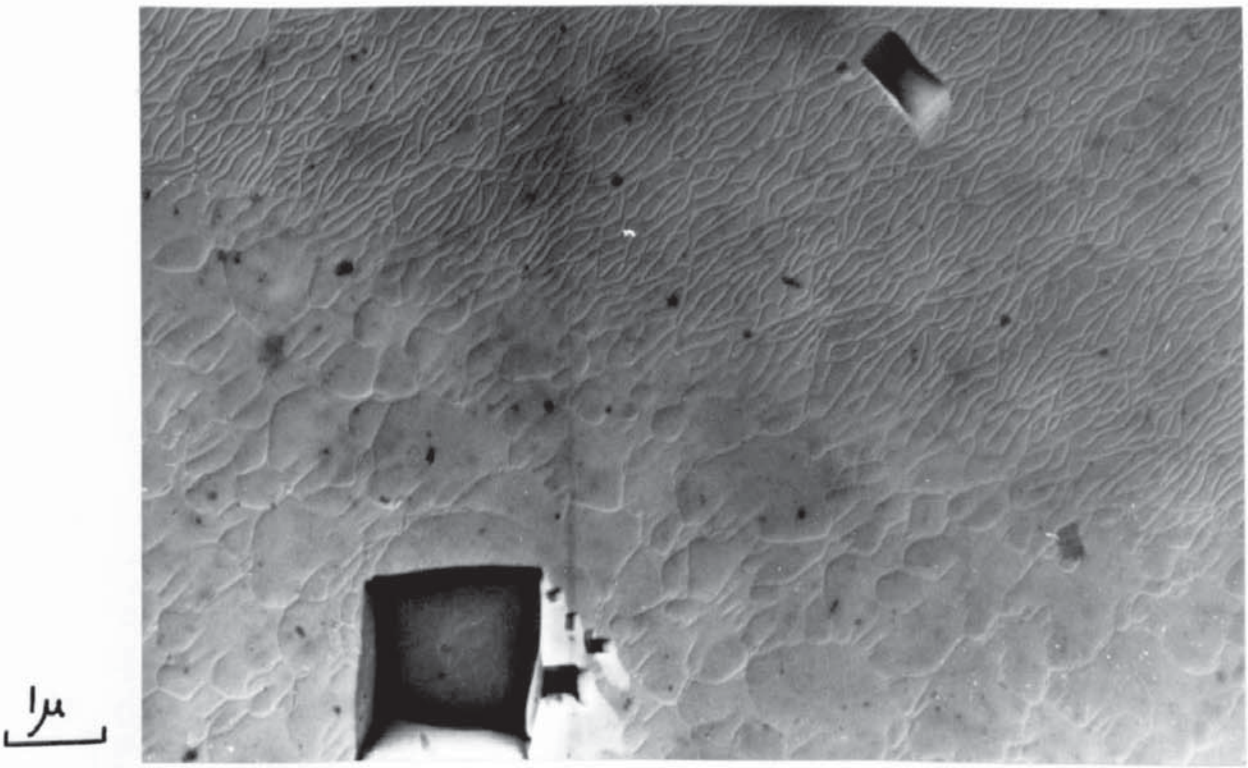


Fig. 3.40. Aluminium Chemically Polished in Solution E (No Copper) for $1\frac{1}{2}$ Minutes.

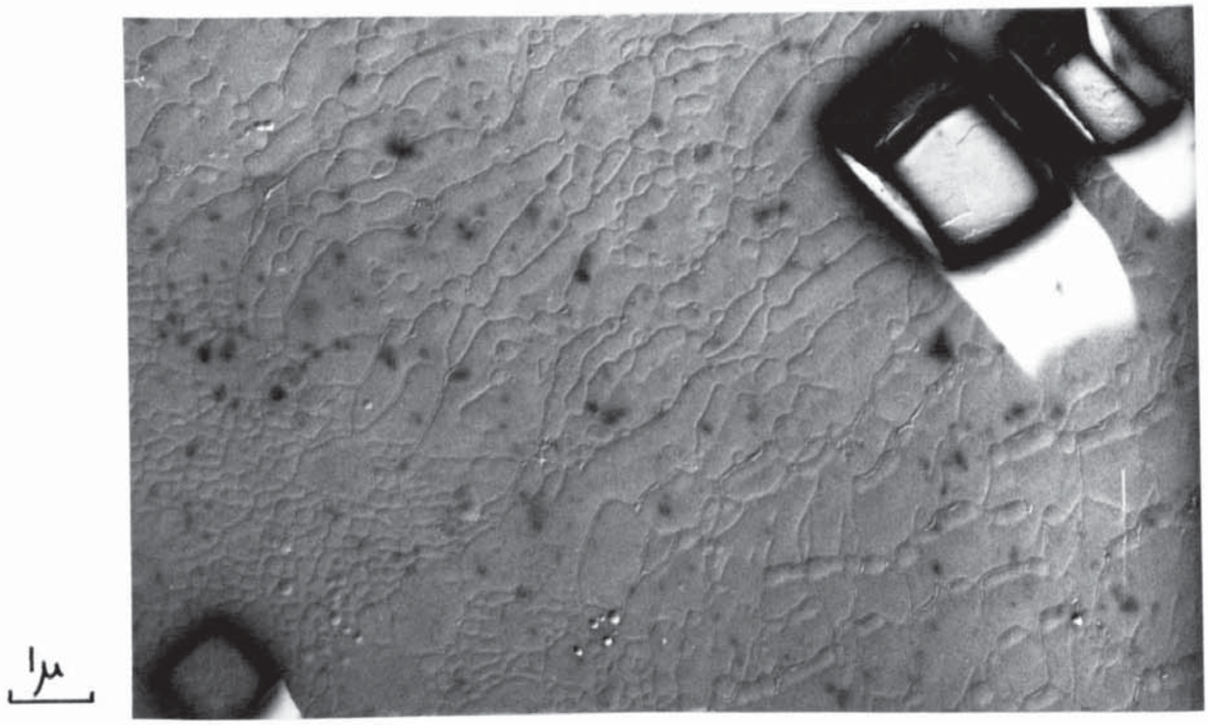


Fig. 3.41. Aluminium Chemically Polished in Solution E (No Copper) for 2 Minutes.

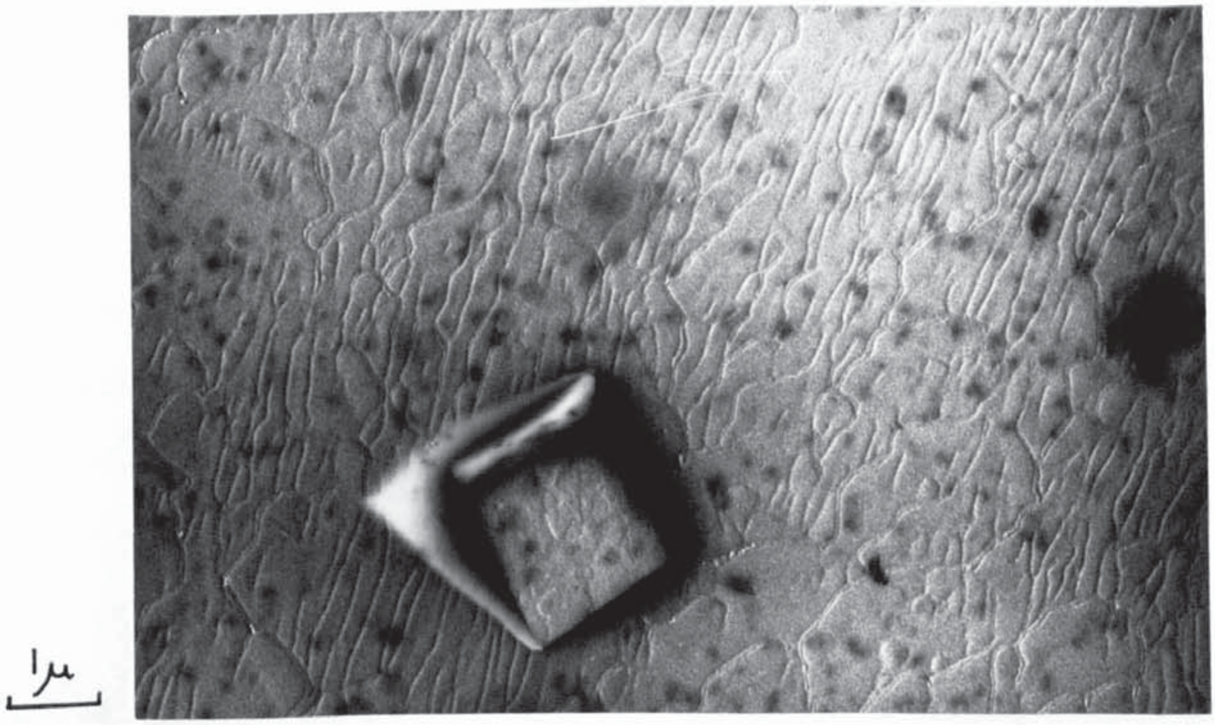


Fig. 3.42. Aluminium Chemically Polished in Solution E (No Copper) for 3 Minutes.

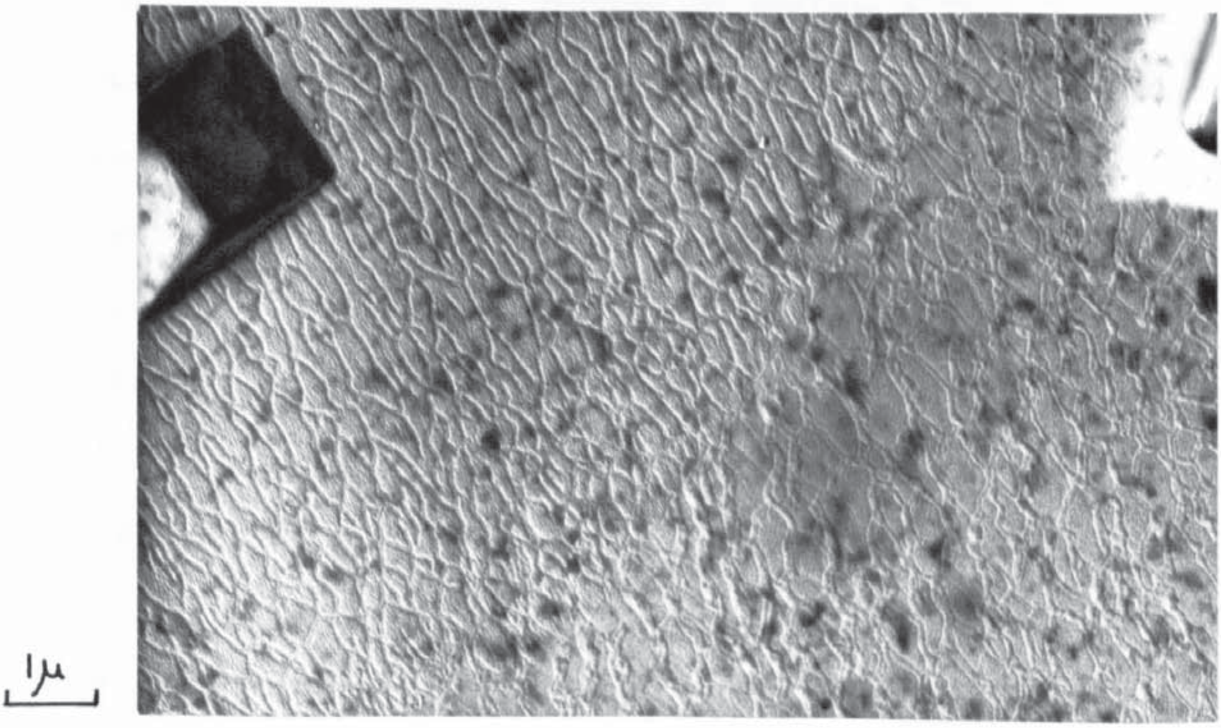


Fig. 3.43. Aluminium Chemically Polished in Solution E (No Copper) for 4 Minutes.

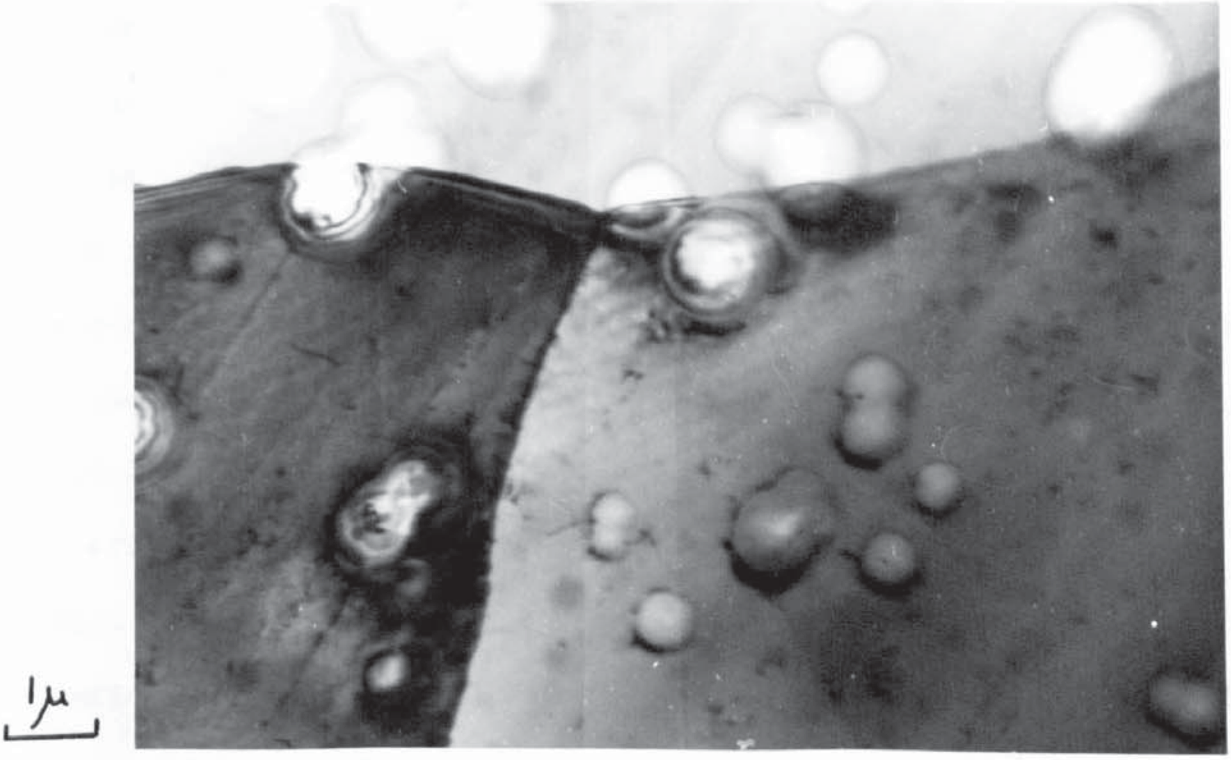


Fig. 3.44. Transmission Electron Micrograph of Aluminium Chemically Polished for 2 Seconds.

structure, although some changes in surface structure are observed on some grain orientations. These structures closely resemble those described by Cuff and Grant(67) and other workers(61,66) who confined their experiments to polishing solutions with no heavy metal additions. Further polishing action for 3 and 4 minutes shown in Figs. 3.42 and 3.43, results in a gradual coarsening of the surface structures.

3.5. Transmission Electron Microscopy

The features observed by transmission electron microscopy are common to all the solutions containing copper. Therefore, only the micrographs taken of specimens polished in solution B are illustrated in this section.

Fig. 3.44 is a typical transmission electron micrograph of an aluminium foil, one side of which was chemically polished for two seconds. This shows the random nucleation of spherical pits, which appear light on the micrograph as the absorption of electrons at these areas is low. Also visible are the boundaries of the aluminium subgrain structure, these are comprised of dislocation walls and appear as electron optical fringes. It can be seen that there is no preferential attack at the subgrain boundaries, in fact, Fig. 3.45, which is taken of a foil polished for four seconds, indicates that pits are formed more readily at defects such as scratches on the original surface. Figs. 3.46 and 3.47

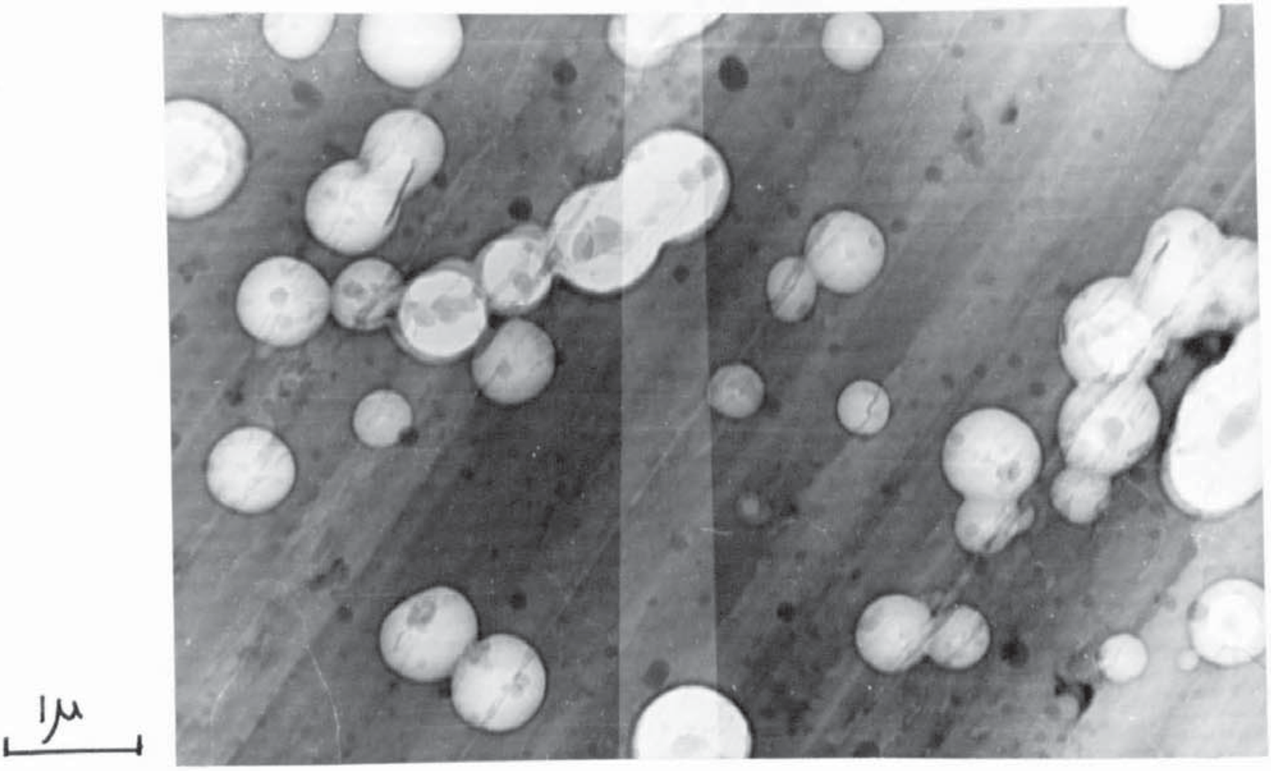


Fig. 3.45. Transmission Electron Micrograph of Aluminium Chemically Polished for 4 Seconds.

Fig. 3.46. Transmission Electron Micrograph of Aluminium Chemically Polished for 10 Seconds.

Fig. 3.47. Transmission Electron Micrograph of Aluminium Chemically Polished for 10 Seconds.

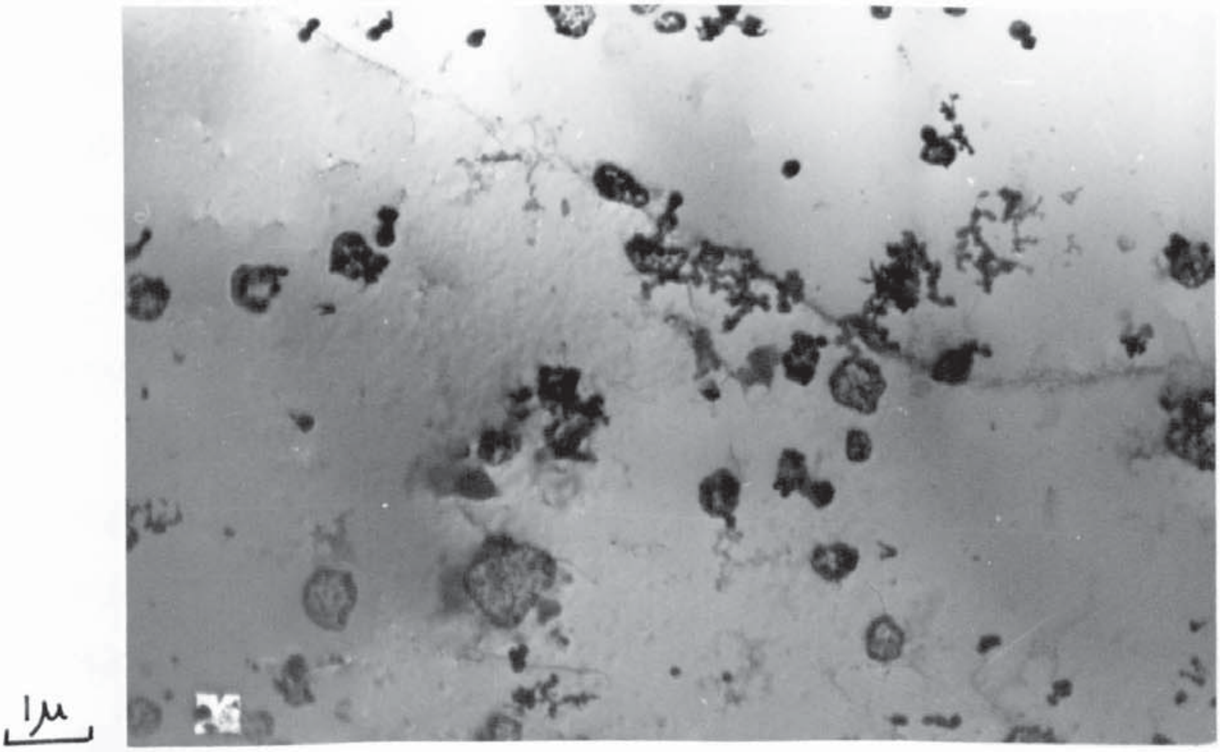


Fig. 3.48. Transmission Electron Micrograph of Aluminium Chemically Polished for 1 Minute.

illustrate the etch structure produced after polishing for 10 seconds, superimposed on the subgrain structure. A number of fine particles are visible, usually around the surface ridges, these appear dark in the electron micrograph as there is greater electron absorption in these areas. The particles are presumably copper deposited on the surface, as the method of preparation would preclude any contamination. It is clear that the sites of copper deposition and the etched cell structure, are unrelated to the underlying metal structure. In fact, on subgrain boundaries the surface cell structure passes without interruption from one subgrain to the other.

Fig. 3.48 shows a foil polished for one minute, here the original etched cell structure has been removed and the polished structure established. The diffraction pattern of the area in Fig. 3.48 is shown in Fig. 3.49 and is of the (100) type. On this plane the copper appears to be deposited mainly around the peripheries of the depressions.

Coarsening of the surface structure is illustrated in Fig. 3.50, which is a foil polished for two minutes. Electron diffraction patterns shown in Figs. 3.51 and 3.52 indicate that the grain on the right has the (100) plane perpendicular to the electron beam and the grain on the left the (110). The enlarged depressions on the (100) plane can be seen clearly,

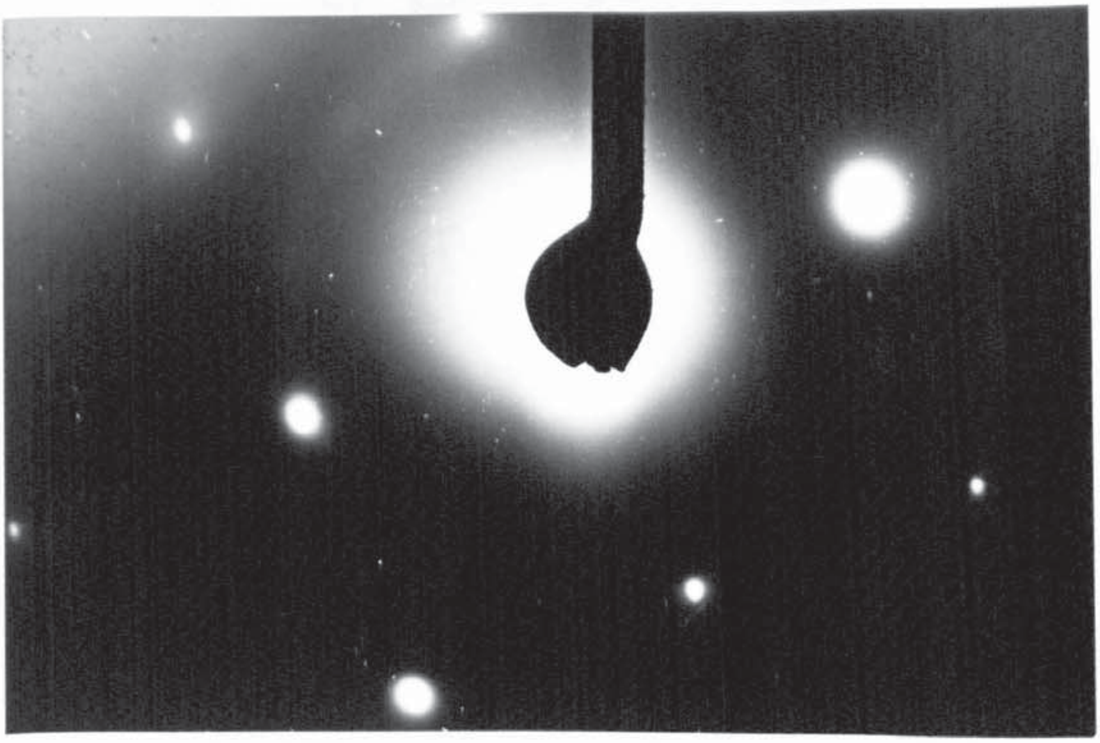


Fig. 3.49. Diffraction Pattern of Area Shown in Fig. 3.48.

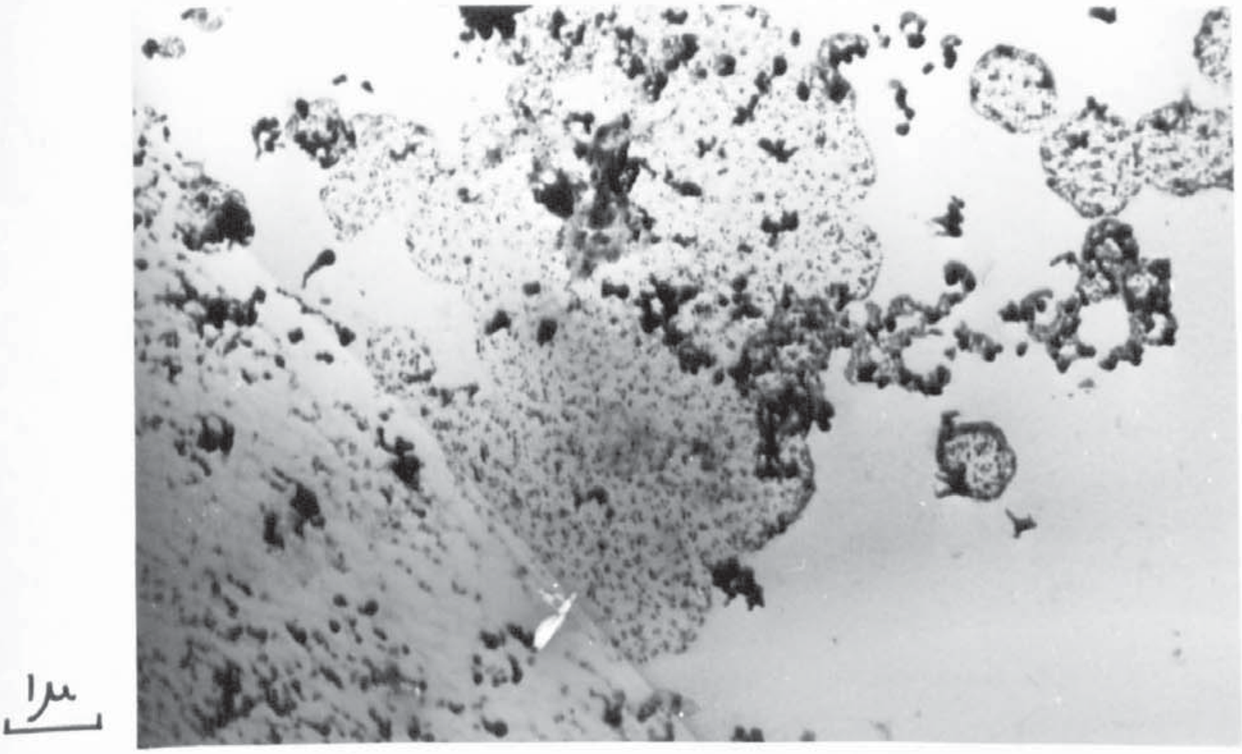


Fig. 3.50. Transmission Electron Micrograph of Aluminium Chemically Polished for 2 Minutes.

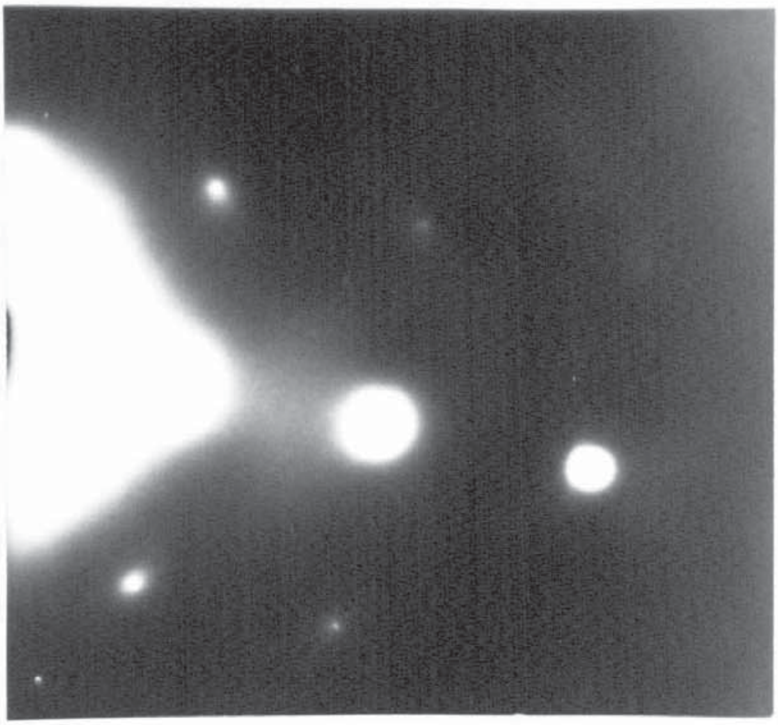


Fig. 3.51. Diffraction Pattern of Area Shown on the Right Side of Fig. 3.50.

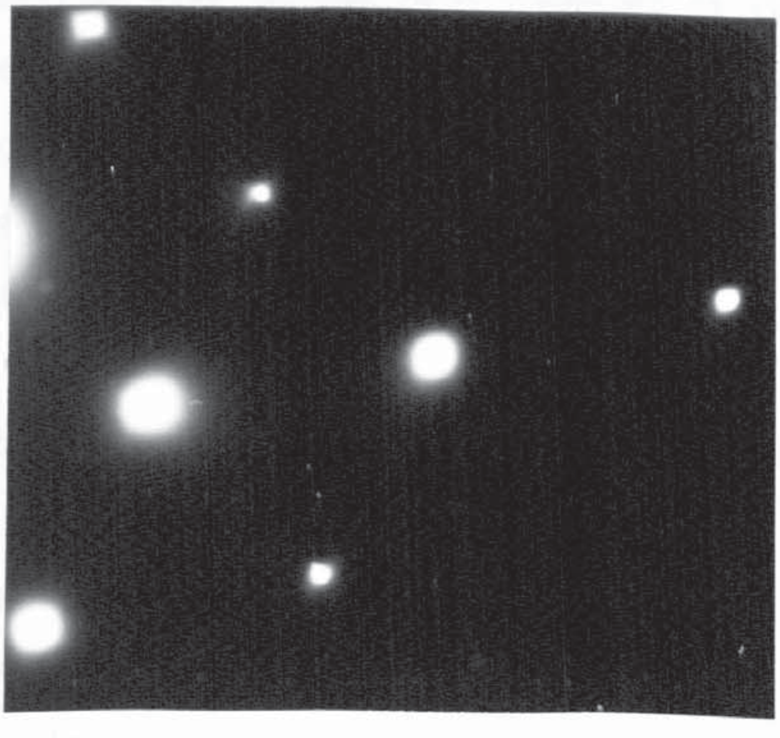


Fig. 3.52. Diffraction Pattern of Area Shown on the Left Side of Fig. 3.50.

together with quite large agglomerations of deposited copper. The laminated structure on the (110) plane is coarse and also has large amounts of deposited copper particularly at the ridge boundaries.

3.6. Scanning Electron Microscopy

The photographs taken of chemically polished aluminium surfaces, using the scanning electron microscope, give direct evidence of the surface structures and copper deposition, described previously in the replica electron microscopy results. Unfortunately, as the definition of this instrument depends on surface projections on the specimen, the results from well polished aluminium were not very good, as the surfaces of these specimens were extremely smooth. The other surfaces examined gave reasonable photographs at magnifications up to about 5,000 times, above which the definition of slight surface imperfections was poor.

The specimens used in this examination did not receive a desmudging dip after polishing so that the sites of copper deposition could be seen.

Fig. 3.53 shows the surface structure of aluminium, chemically polished for 10 seconds in solution B i.e. in the etching region. The photographs show the typical equiaxed etched structure, together with fine globular deposits 0.1 - 0.2 μm. in size, situated at the ridge boundaries. These

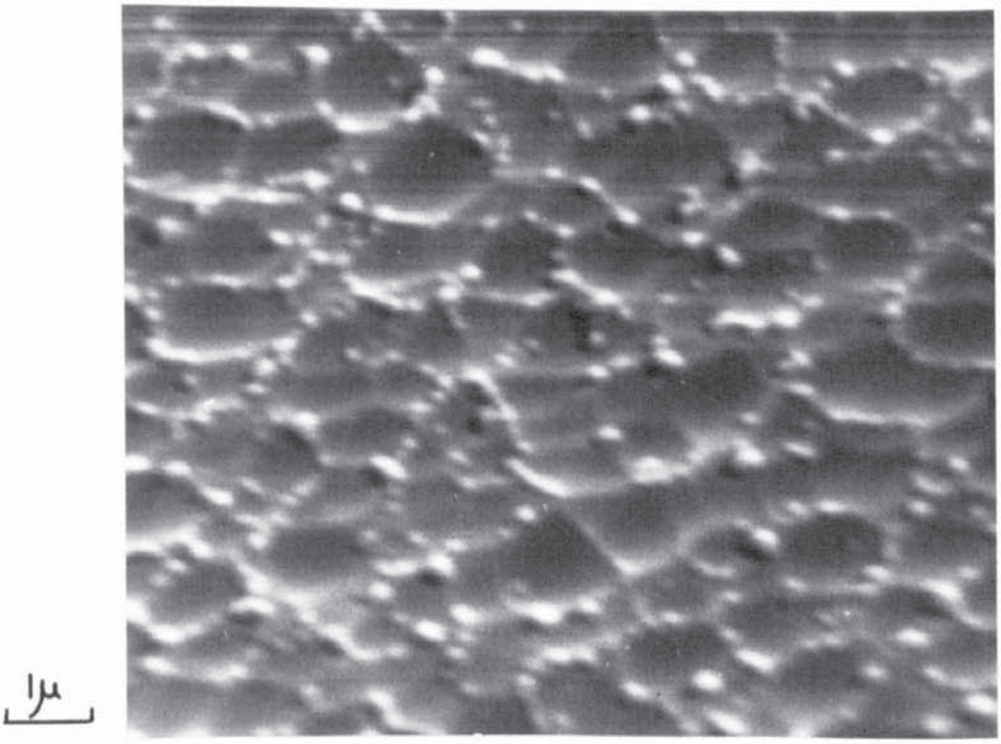


Fig. 3.53. Scanning Electron Micrograph of Aluminium Chemically Polished for 10 Seconds.

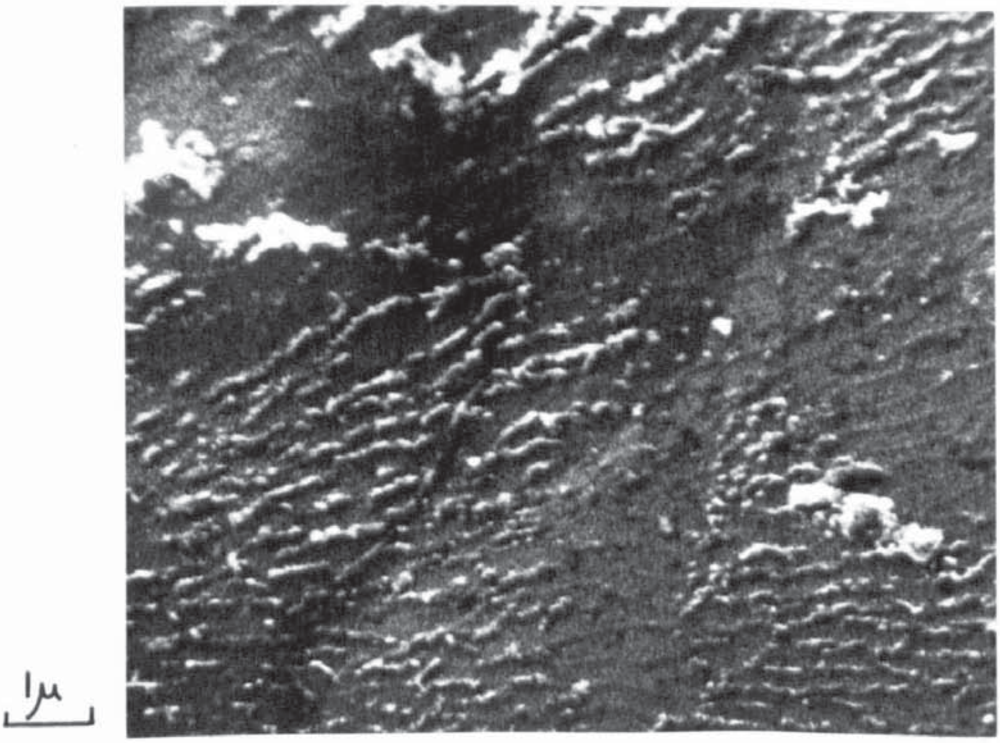


Fig. 3.54. Scanning Electron Micrograph of Aluminium Chemically Polished for 1½ Minutes.

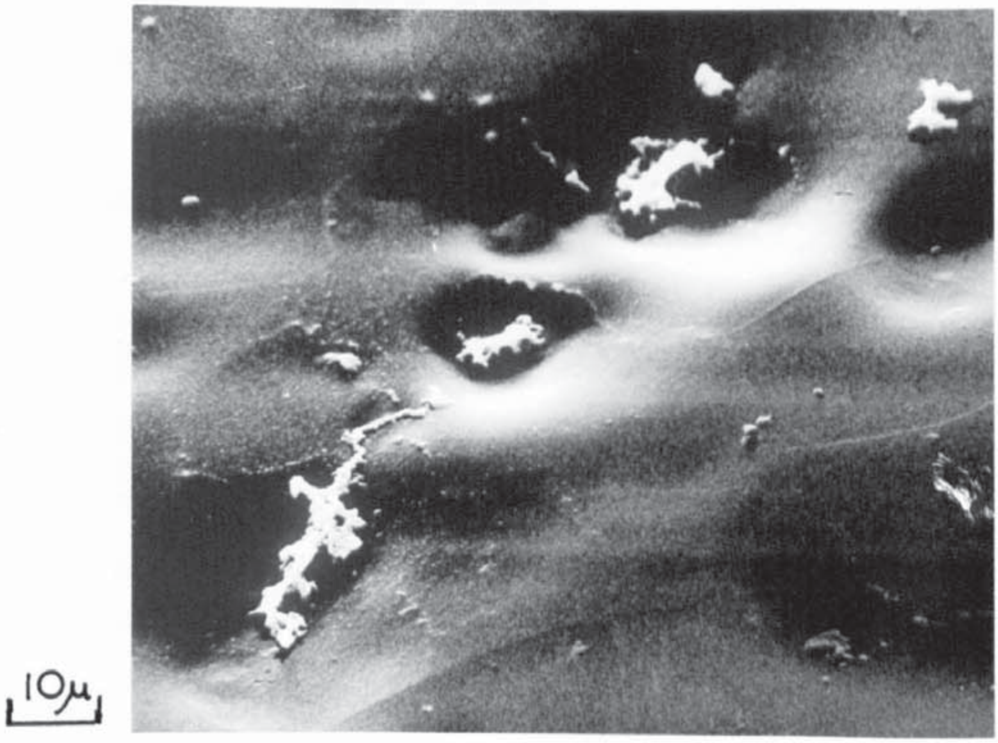


Fig. 3.55. Scanning Electron Micrograph of Aluminium Chemically Polished for 3 Minutes.

deposits are copper, which appear brighter than the aluminium due to the difference in their atomic numbers.

Fig. 3.54 shows a photograph of a specimen polished in the same solution for 1½ minutes. Here the equiaxed structure has been removed and replaced with the fine characteristic polished pattern. The copper deposits now appear as stringers along the chemical polishing pattern and occasionally as larger irregular shaped particles.

Fig. 3.55 shows the surface structure of a specimen polished in the same solution for 3 minutes. This was taken at quite low magnification and it is clear that the copper particles are now very large agglomerates about 5-10 μm. in size and are found in areas of deep etching.

3.7. Weight of Deposited Copper

The weight of copper deposited on aluminium specimens polished for various times in the polishing solutions investigated, are displayed in Fig. 3.56. For each experimental condition, copper determinations were carried out on three aluminium specimens and the average reading used in these results. In all cases it was found that the reproducibility was within ± 5%.

The results show that for all solutions, no copper is deposited on the specimens during the first few seconds of polishing. However, as polishing continues there is a build

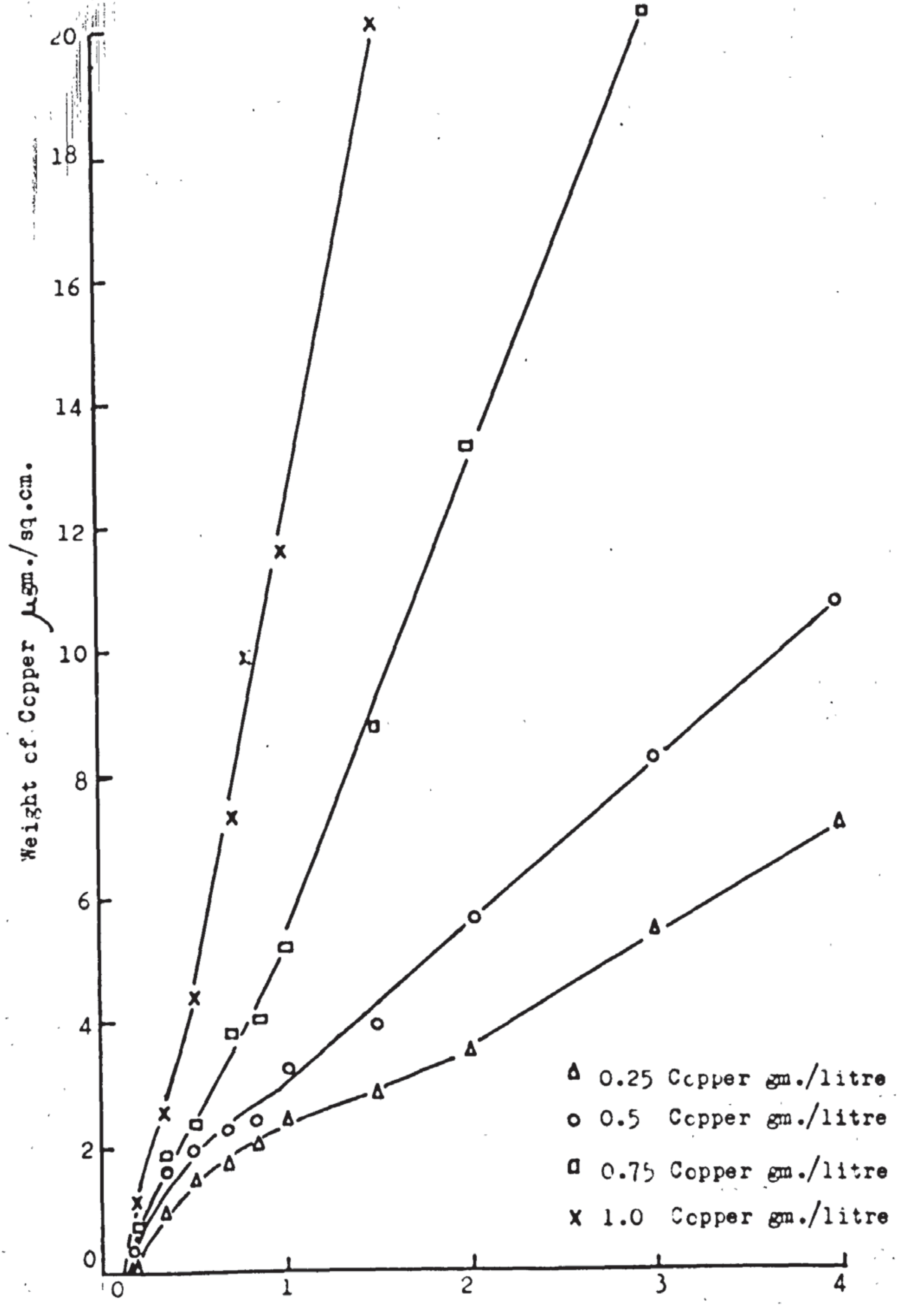


Fig. 3.56 Weight of Copper Deposited vs. Polishing Time

up of copper on the specimens, the rate of which is determined by the concentration of copper in the polishing solution. With solutions A and B, the weight of copper increases rapidly at first then tends to level off after about 45 seconds polishing. With solutions C and D, there is a rapid increase in the weight of copper deposited with increasing polishing time. The slope of the curve for solution D is such that it is soon above the scale of the graph, and maintains this slope until polishing is ceased after four minutes. Although there is no levelling of the curves for solutions C and D, it is clear that there is a slight inflection of the curves in the early part of polishing.

3.8. Electrode Potential Determinations

The change in electrode potential of aluminium specimens with polishing time, in each polishing solution, is shown in Fig. 3.55. Each potential-time curve displayed is representative of three recordings obtained in each solution. In each case the reproducibility was within ± 5%.

It is known that(90,91) the displacement of the electrode potential from the corrected Nernst value is primarily due to the work required to transport aluminium ions through the solid film and into the bulk electrolyte. This must depend on the thickness and defect concentration of the film.

As the exact reference voltage of the calomel electrode

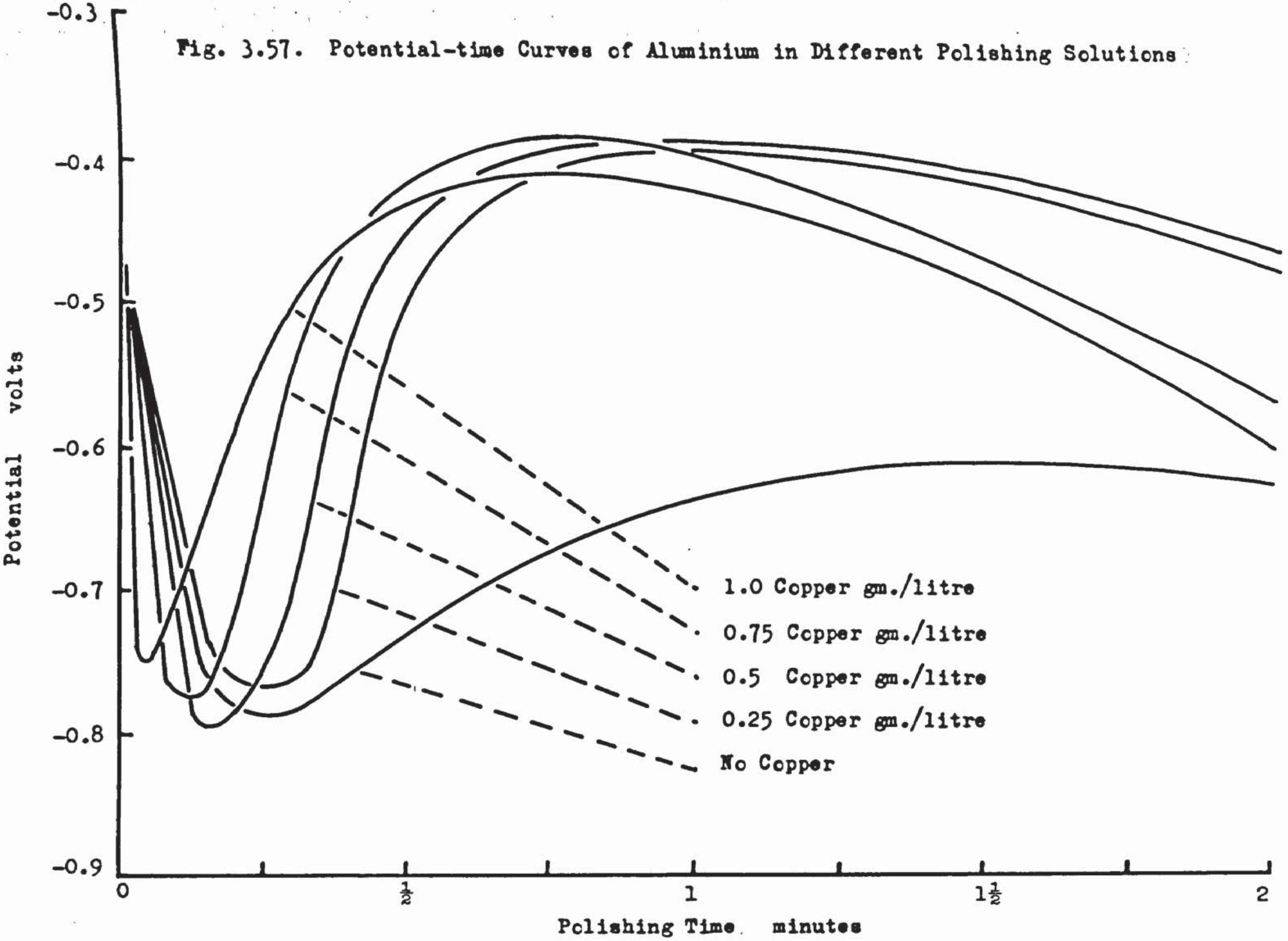


Fig. 3.57. Potential-time Curves of Aluminium in Different Polishing Solutions

operated at this temperature is not accurately known, the results are expressed, for comparative purposes, as the potential difference in mv. between the calomel reference electrode and the specimen. The electrode potential determinations illustrated, although not expressed with respect to the standard hydrogen electrode, do show the change in potential with polishing time and thus can be used to correlate what is happening at the electrode surface with the other parameters involved.

The initial potential of the aluminium in each solution is approximately - 480 mv. This potential value falls rapidly during the initial stage of polishing to a minimum value of about - 800 mv., which coincides with etching of the aluminium. There is then a gradual rise in potential, as the aluminium is polished. The potential value in most solutions remains steady at about - 400 mv. during polishing, then falls gradually after prolonged treatments. However, the potentials of the aluminium specimens polished in the solution containing no copper only increase to about - 640 mv., then remain steady.

3.9. Discussion

3.9.1. Significance of Weight Loss Results

The results of metal dissolution rates obtained in section 3.3, show certain similarities to those obtained by Brace and de Gromoboy(46) and Meyer and Brown(47). These investigators used chemical polishing solutions which did not contain heavy metals for their investigations, although Brace and de Gromoboy stated that additions of copper to the polishing solutions did effect the rate of metal dissolution, but their results were not reproducible. The effect of copper additions to polishing solutions has been extensively studied in the present work, which shows that such additions produce a marked change in the rate of metal dissolution. This is most noticeable with solutions of higher copper contents i.e. 0.75 and 1 gm. of copper per litre, as specimens polished in these solutions have a much greater rate of metal dissolution than specimens polished in the basic solution. The rate of metal removal with the high copper solutions continues with increasing polishing time and is connected with the rapid coarsening of the polished structure, which occurs at these polishing times.

Brace and Kape(43) have stated that additions of copper up to an optimum amount (which was not specified) improves brightness and decreases weight loss, but additions beyond this point give the reverse effect. In the present investigation there was less metal dissolution when specimens were polished in solutions containing 0.25 and 0.5 gms. of copper per litre than in solutions containing no copper, 0.75 and

1.0 gms. of copper per litre. The optimum copper concentration is therefore between 0.25 and 0.5 gms. of copper per litre.

3.9.2. Significance of Specular Reflectivity Results

The results of the variation of specular reflectivity with polishing time, which indicate three stages of polishing, namely etching, polishing and coarsening, have not been reported previously.

Certain investigators(2,6,92) have studied the variation of specular reflectivity with the purity of the aluminium polished, but in each case used a fixed polishing time for their determinations.

The effect of the additions of copper to polishing solutions, on the specular reflectivity obtained, has not been reported previously, although it has been stated that additions of heavy metals improves the surface finish produced by polishing(2,6,43,49).

The effect of the copper additions has been shown to be similar to that described qualitatively by Brace and Kape(43), in that additions of copper up to an optimum amount improve brightness but additions beyond this point give the reverse effect. In the present investigation the specular reflectivity results show that the optimum copper content of the polishing solution is between 0.25 and 0.5 gms. of copper per litre, which is in agreement with the weight loss observations.

The most significant feature of the specular reflectivity results is that increasing the amount of copper in the polishing solution, reduces the treatment time required for optimum brightness and also reduces the interval of time between polishing and coarsening. The practical implications of this are that the use of solutions with high copper contents give the advantage of short polishing treatments with the disadvantages of precise timing and a slight drop in specular reflectivity. Whereas the solutions containing small amounts of copper would be comparatively insensitive to fluctuations in treatment times required for a good surface finish, but with the disadvantage of a longer polishing treatment.

The deterioration of surface finish with increased polishing time, which occurs particularly in solutions of high copper contents, is due to the build up of copper on the aluminium surface. When this occurs there will be appreciable local currents from the galvanic cells produced, which cause etching of the aluminium in the vicinity of the deposit.

The effect of copper additions will be discussed in detail later in this report.

3.9.3. Significance of Electrode Potential Results

These results show that, with most of the polishing solutions investigated, there is a compact solid film present on the aluminium during chemical polishing.

It is apparent that the rapid drop in potential of each specimen during the initial stage of polishing is due to the removal of the air formed oxide film, which results in etching of the metal. There is then a rise in potential, which in each case occurs approximately at the polishing times corresponding to an increase in specular reflectivity. Thus, there appears to be some compact film formation as polishing takes place. This is also indicated by the decrease in the rate of metal dissolution that occurs during polishing. It is significant that specimens polished in the solution containing no copper, which are not brightened satisfactorily, do not show the usual rise in potential.

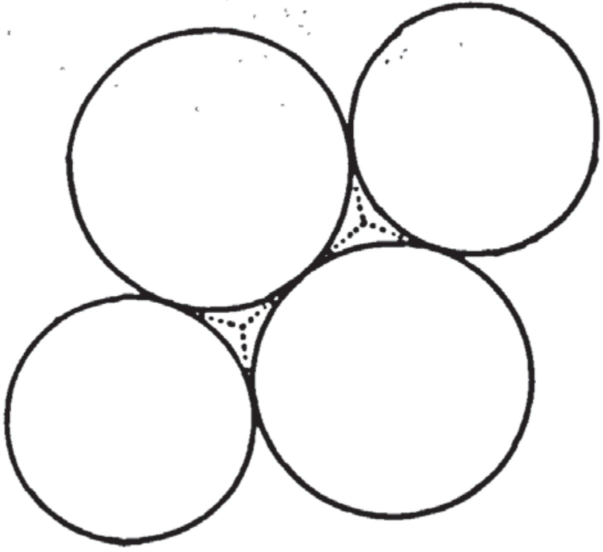
The decrease in potential, which occurs towards the end of the polishing treatment, indicates a decrease in the soundness of the film present on the aluminium. This coincides with the deterioration in surface finish of the specimens investigated.

3.9.4. Significance of Electron Microscopy Results

The electron micrographs taken during this investigation confirm that for specimens polished in solutions containing copper additions, the polishing cycle has three distinct stages and that the polishing times at which these stages are reached, depend on the copper content of the solution.

The surface structures obtained from specimens after short polishing times, indicate that the initial etched cell structure is produced by the merging of laterally growing etch pits. The etch pits which begin to form in the first seconds of polishing are not crystallographic and the etched cell pattern is independent of the grain orientation of the aluminium. The etch pits are in fact initially spherical and similar in appearance to the pits described by Hoar(93) which were produced at areas where the breakdown of passivity has taken place. The etch pits appear to be nucleated at defects in the original oxide such as scratches or at grain boundaries, and their size and distribution are roughly the same on each grain orientation. The change from the initial spherical etch pits to a straight sided cell network takes place by a dissolution process similar to that which exists when porous anodic oxide films are produced on aluminium(11). Consider four spherical pits in contact, shown schematically in Fig. 3.58. Due to the nonhomogeneous nucleation of the etch pits, these will normally be of different sizes when contact takes place. When this occurs, further dissolution will take place at the triangular area remaining between the pits. This will continue

Fig. 3.58



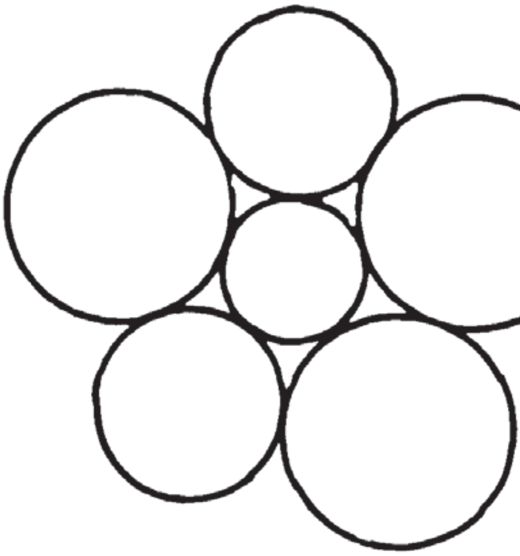
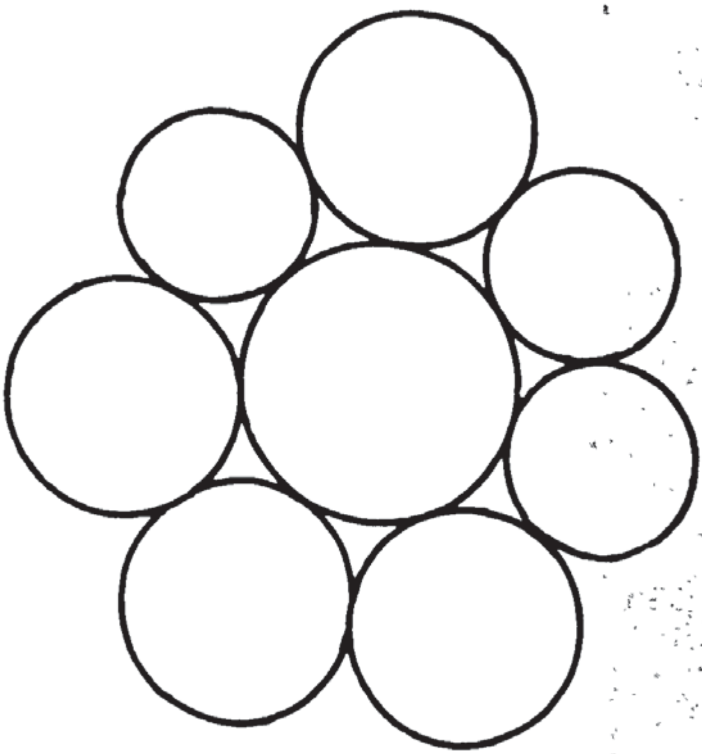


Fig. 3.59

Fig. 3.60



until the boundary between the cells is represented by the dotted line in Fig. 3.58. The above process is repeated whenever the spherical pits contact, to give a network of straight sided cells.

The number of sides of each individual cell will depend on the size of its neighbouring cells. This is illustrated in Figs. 3.59 and 3.60. A small cell surrounded by larger cells, shown in Fig. 3.59 will have less sides than a large cell, surrounded by smaller cells, shown in Fig. 3.60.

The thin foil electron micrographs show conclusively that the nucleation of the etch pits is not connected with the internal structure of the metal, such as dislocations or subgrains.

The etched structures observed on the thin foils of specimens in the present investigation, are similar to those obtained by Philips and Welsh(65) who etched aluminium in a 1% hydroflouric acid solution. In both cases the etched surface structure is independent of the grain orientation and the subgrain boundaries of the aluminium.

It is interesting at this stage to note the similarity between the surface etched patterns produced in the first stage of chemical polishing and those produced in relatively mild etching solutions, such as in dilute (1%)

hydroflouric acid, Fig. 3.61, a 10% sodium hydroxide solution, Fig. 3.62, or the etching region of the "Brytal" electropolish, Fig. 3.63. The surface structure obtained when aluminium is etched in more aggressive reagents, is totally different to the etched cell pattern. Fig. 3.64 shows the typical stepped structure produced by etching in dilute hydrochloric acid which attacks the cube planes to give a crystallographic pattern.

The similarity between the former solutions indicates that the chemical polishing solution acts like any anodic dissolution process during the etching stage, to remove the original oxide film and to give a uniform mildly etched surface. The constituents in polishing solutions then ensures that this etched structure is removed and replaced with a finer structure, the surface morphology of which is dependent upon the crystallographic orientation of the aluminium grains.

Transmission electron microscopy and scanning electron microscopy examinations, indicate that during the etching stage the copper additions are deposited at the ridge boundaries. The deposited copper is in the form of fine particles 1,000 - 2,000 Å in size. This is not consistent with the theories of Brace and Kape(43) who suggested that the aluminium surface is covered with copper to a thickness

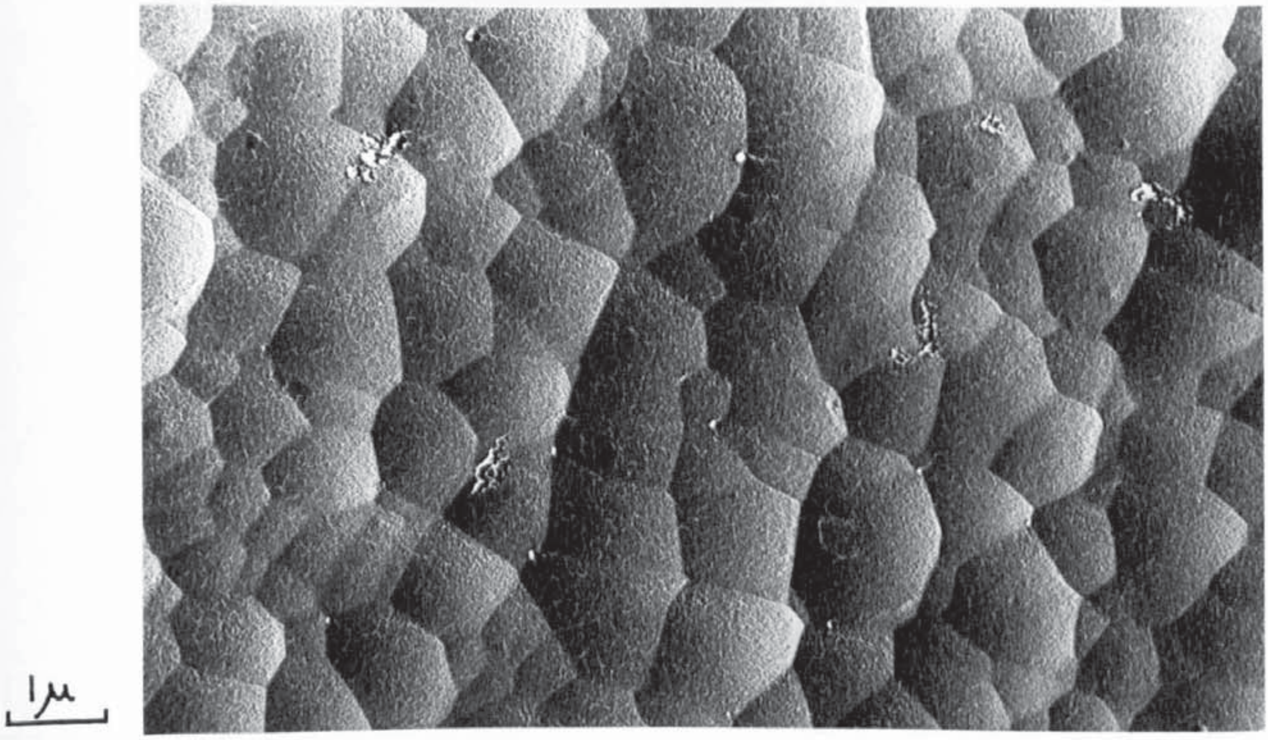


Fig. 3.61. Replica Electron Micrograph of Aluminium Etched in 1% Hydroflouric Acid.

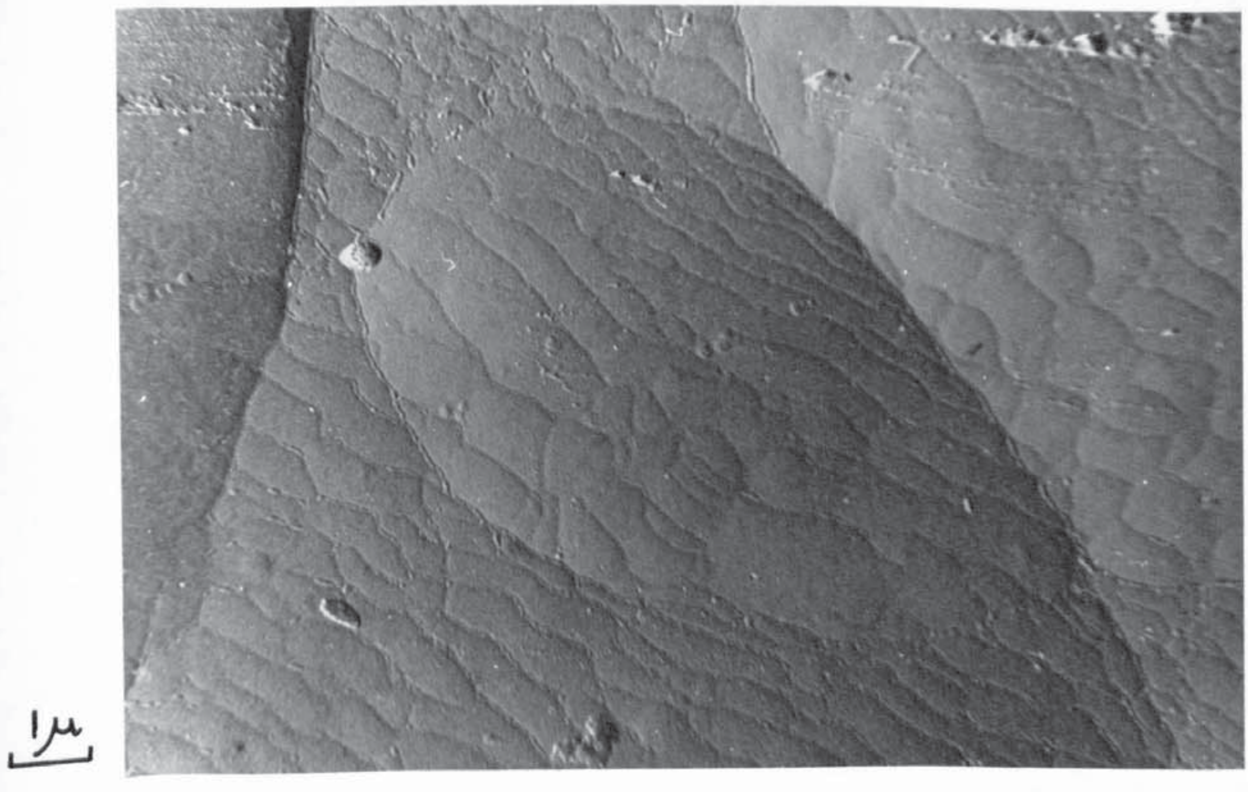


Fig. 3.62. Replica Electron Micrograph of Aluminium Etched in 10% Sodium Hydroxide Solution.

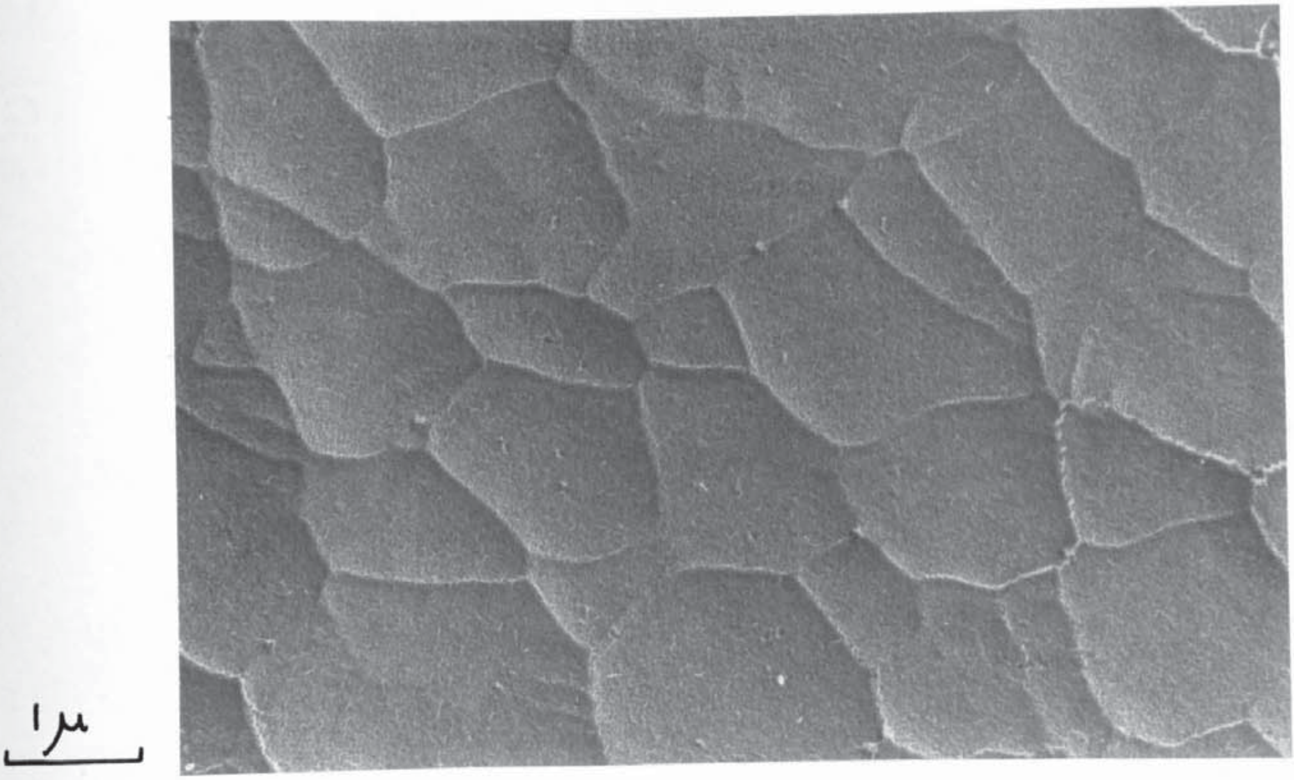


Fig. 3.63. Replica Electron Micrograph of Aluminium Polished in the Etching Region of the "Brytal" Electropolish.

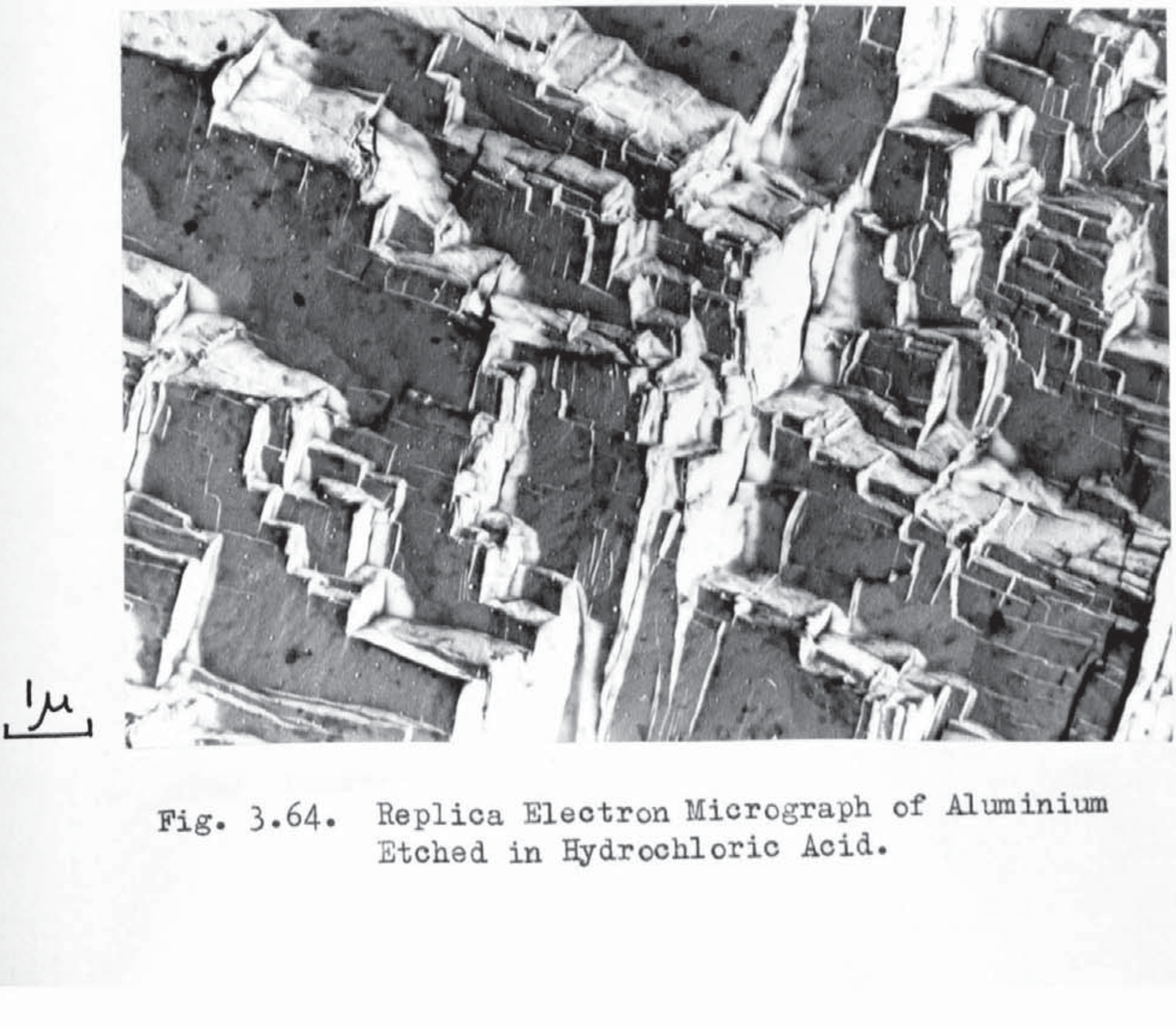


Fig. 3.64. Replica Electron Micrograph of Aluminium Etched in Hydrochloric Acid.

of several atomic layers. It was also observed during this investigation that the copper deposit was easily removed by a nitric acid dip. This observation differed from that of Brace and Kape who experienced difficulty in dissolving the copper and suggested that it may be present as an oxide. The present investigation supports the theory that copper is deposited in its pure state as suggested by Pinner(53). As polishing takes place the amount and size of the deposited copper particles increases. The copper is usually found at the ridge boundaries and at the edges of the polishing depressions, thus forming the cathodic areas for metal dissolution.

When specimens are polished for longer than the optimum polishing time, a roughening and etching of the aluminium surface takes place, which coincides with the build up of large agglomerated particles of copper on the surface. Sub-micro transmission electron microscopy examination indicates that most of these large particles are to be found on protuberances in similar positions to the smaller particles observed during polishing and thus appear to be formed by the preferential deposition at these areas. This results in rapid metal dissolution between the copper deposits with considerable roughening of the surface. The low magnification scanning electron micrograph shows the same effect on a micro scale, as quite large particles of copper about 5-10 μm. in size are visible, each surrounded by an area where considerable metal dissolution has taken place.

The differences in surface structure between the solutions containing no copper and those containing copper additions, are clearly shown by the replica electron microscopy results. The polishing solution containing no copper does not completely remove the original etched pattern and form the characteristic polished structure, although some changes in surface structure are observed on some orientations. The structures observed with this polishing solution closely resemble those described by Cuff and Grant(67), Bichsel(66) and other workers(61,64) who confined their investigations to polishing solutions with no heavy metal additions.

It is not possible at this stage to account completely for the mechanism by which the polished patterns are produced on the aluminium surface. It is interesting however, in view of the results obtained during this investigation, to consider the theories put forward by previous workers to explain the patterns formed by solutions with no heavy metal additions.

Hunter and Robinson(61) considered that these substructures, formed in some chemical polishing solutions, represent the subgrains of the aluminium, however, the results of this investigation and that of other workers(62,63,64) indicate that this suggestion can be discounted. Cuff and Grant(67) suggested that the cell ridges are part of a three dimensional network to which impurity atoms have segregated. As these impurity atoms would be cathodic to the aluminium, they would be left as ridges after the polishing process. Cuff and Grant do not however, explain the mechanism of this segregation nor on to which planes the segregation occurs. The hypothesis also does not explain the observations of the present investigation, which show the differences in surface morphology when the times of polishing are changed and when copper is added to the chemical polishing solution. Bichsel(66) noted that there was a relationship between surface cell structure and the crystallographic orientation of the aluminium and that the structure was apparently not connected with the subgrains of the metal. The author did not comment on the origin of this surface structure but suggested that it was associated with the surface reactions.

3.9.5. The Dependence of Surface Finish on Surface Morphology

It is obvious that there is a close relationship between the surface structure of a chemically polished metal and its measured specular reflectivity and this relationship is clearly shown using replica electron microscopy. The aluminium specimens exhibit a low specular reflectivity during the initial etching stage of polishing. This is due to the very rapid formation on the surface of a relatively coarse cell structure, which is apparently independent of the crystallographic orientation of the grains of aluminium. During the first seconds of polishing the aluminium appears not to have been attacked and there is only a small decrease in its specular reflectivity. Electron micrographs taken at this stage of polishing indicate however, that extremely fine etch pits are produced apparently at random on the aluminium surface with the remainder of the surface not attacked. The specular reflectivity falls rapidly as polishing proceeds, as the initial etch pits become more numerous and grow laterally until the etched cell network is complete. Each cell in the network is about 0.5- 1 μm. across.

When the polishing time is increased the specular reflectivity of the aluminium increases progressively until it reaches a maximum. This increase is due to the gradual removal of the coarse etched cell structure and its replacement by a finer structure which appears to be dependent on the crystallographic orientation of the aluminium. By comparing the amount of shadowing on the replica electron micrographs produced by the cell boundaries, in both the etched and polished conditions, it can be seen that polishing not only produces a finer structure, but also there is less difference in height between the elevations and the depressions. The surface, therefore, has been smoothed. This is shown schematically in Fig. 3.65. The relative amounts of shadowing indicates that the difference between the elevations and depressions in the etched structure is approximately 2,000 Å, whereas in the polished structure it is 500 Å. The initial etch pits appear to be approximately 5,000 Å deep. The gradual replacement of the original etched structure with a finer structure, together with the smoothing of the surface, results in the improvement of surface quality as the polishing time is increased. By comparing the results of specular reflectivity vs. polishing time and the replica electron micrographs, it is clear that the maximum specular reflectivity is attained when the etched cell structure has just been replaced by the polished structure. Prolonged polishing results in a gradual decrease in specular reflectivity, which is due to a coarsening of the surface structure. This appears as an enlargement of the structural features on the surface and pitting attack on the remaining areas.

It was observed that specimens polished in the solution containing no copper additions did not exhibit high specular reflectivity results. This is because the etched cell pattern is not completely removed from the surface of these specimens. Further polishing in this solution also produces

INITIAL ETCH PIT, APPROXIMATELY 5,000 Å DEEP

COMPLETE ETCH NETWORK, APPROXIMATELY 2,000 Å DEEP

POLISHED STRUCTURE, APPROXIMATELY 500 Å DEEP

Fig. 3.65. Schematic View of the Differences in Height of Elevations during the Polishing Process.

a coarse structure, which results in a deterioration in surface quality.

3.9.6. The Dependence of Surface Finish on the Deposited Copper.

The effect of additions of copper to the chemical polishing solution is to promote the formation of the fine surface structure, characteristic of a polished surface, and thus obtain a surface with a high specular reflectivity. The larger the amount of copper in the solution the shorter the polishing time required to produce this polished structure and also the shorter the length of time before the surface coarsens.

The amount of copper deposited on the specimens during polishing, changes with polishing time and with different concentrations of copper in the chemical polishing solutions. It is therefore likely that there is a strong relationship between the amount of copper deposited on the surface of a specimen and the surface structure produced on that specimen. This, as discussed previously, will govern the surface finish produced during polishing.

This relationship can be seen by comparing Figs. 3.1 and 3.2, the values of specular reflectivity with polishing time, against Fig. 3.54, the amount of copper deposited with polishing time, for the polishing solutions used in this investigation. During the initial etching of the surface very little copper is deposited on the specimens, however, as polishing continues the amount of copper deposited increases with a corresponding increase in specular reflectivity. As further polishing takes place it is apparent that the amount of copper deposited is in excess of that required for the polishing process and coarsening of the surface occurs which reduces the specular reflectivity. This effect explains the observed short polishing cycles with solutions containing high copper contents. When specimens are polished in these solutions, there is a rapid rate of copper deposition, which results in the polished structure being formed after short polishing times. Similarly, the rate of deposition is such that the amount of copper required for optimum polishing is soon exceeded and coarsening results. With the solutions containing lower copper contents, there is a more gradual increase in the amount deposited, so that polishing takes place after longer polishing times. As the amount deposited does not increase rapidly, there is a longer interval of time during which the polished structure is maintained, before the surface coarsens.

It is apparent from Fig. 3.54 that for optimum polishing to take place, that is, specular reflectivities greater than 80%, the amount of copper deposited on the specimen must be in the range 2 to 5.5×10^{-6} gms./sq.cm. High specular reflectivity results were not obtained with the solution containing no copper, as although some polishing took place, the original etched structure was not completely removed, confirming that a minimum amount of heavy metal is necessary on the specimen surface for optimum polishing. The slight polishing action which took place in this solution may be due to the presence of extremely small amounts of cathodic impurities in the super-pure aluminium.

CHAPTER 4

THE EFFECT OF SURFACE PRETREATMENTS ON THE CHEMICAL POLISHING OF ALUMINIUM

4.1. Introduction

The object of the work in this chapter was to evaluate quantitatively and structurally, the effect of the initial surface preparation on the chemical polishing of aluminium. The different surface preparations used were; electropolishing in perchloric acid/alcohol; etching in sodium hydroxide and anodising to produce a barrier oxide film. The anodised specimens were separated into two groups, in one the specimens were electropolished before anodising and in the other group the anodising was carried out on the original surface. The aluminium specimens were annealed before each of the above pretreatments. The experiments were also carried out on 60% cold worked aluminium specimens to show the effect of working on the chemical polishing process.

The chemical polishing solution used in all the above experiments was the basic solution plus 0.5 gms. of copper per litre. This solution has been previously shown to give the most satisfactory polishing results, of the solutions investigated.

4.2. Specular Reflectivity Results

The specular reflectivity results obtained with each pretreatment at differing polishing times are shown in Fig. 4.1. An enlargement of the curves from 0 to 80 seconds polishing time is shown in Fig. 4.2. The specular reflectivity readings obtained with the annealed specimens used in chapter three, polished in this solution, are included for comparison.

It is apparent from these results that the effect of different pretreatments is most pronounced in the early stages of polishing and the results obtained with polishing times longer than one minute are very similar to those obtained previously using annealed specimens having the as-rolled surface finish.

The electropolished specimens show a similar curve to those with the original surface. However, the electropolished surface is not etched as heavily in the first stage of polishing, and the specular reflectivity drops to 60% compared with 20% in the case of the original surface specimens, after 10 seconds treatment. The specular reflectivity of both specimens then rises with increasing polishing time and both have similar results after one minutes polishing.

The etched specimens have a low specular reflectivity initially and this increases slowly with polishing time. The curve levels out at about 80% specular reflectivity, which is somewhat below the other results obtained.

Anodising the specimens prior to chemical polishing,

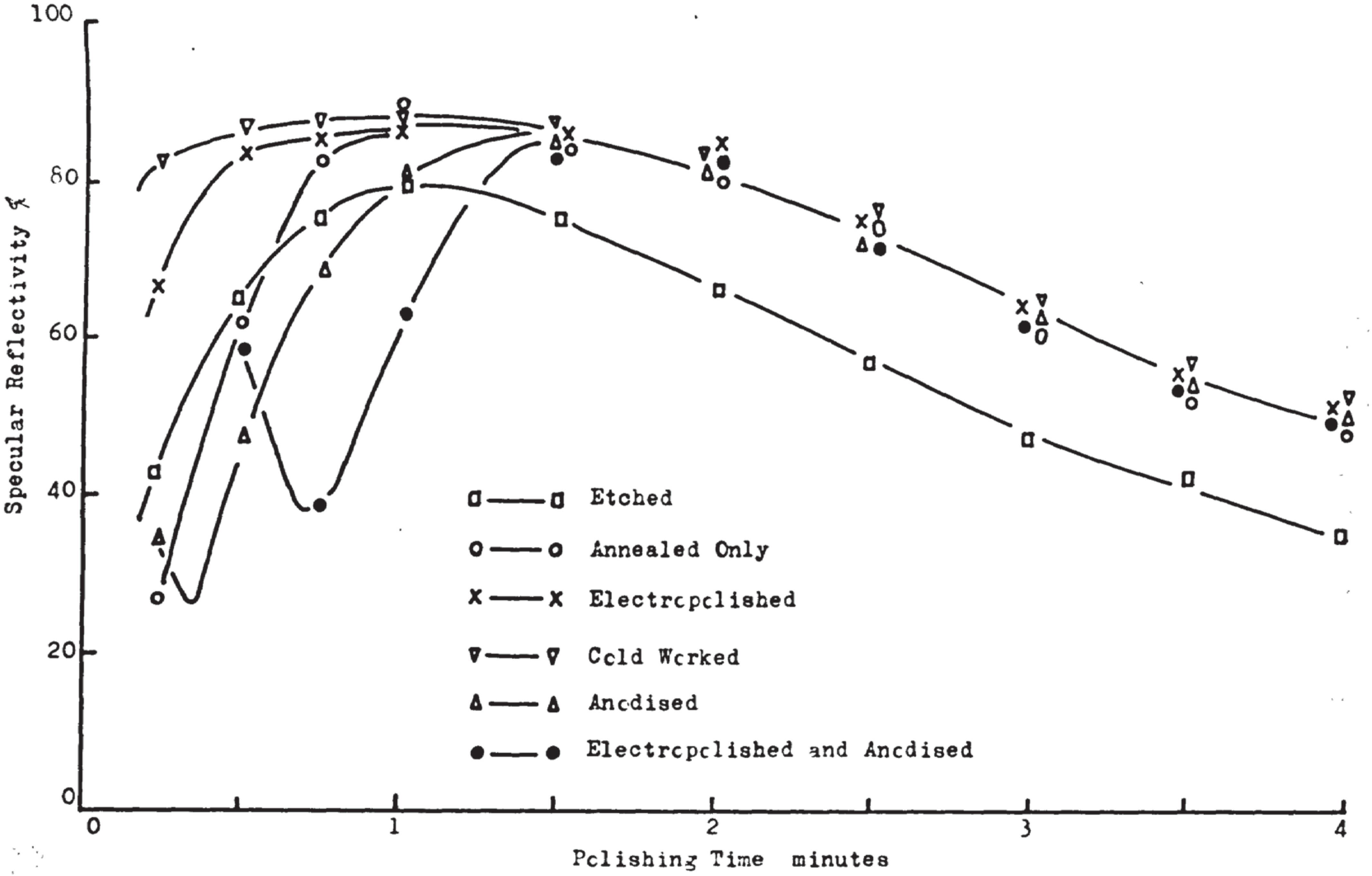


Fig. 4.1. Specular Reflectivity vs. Polishing Time

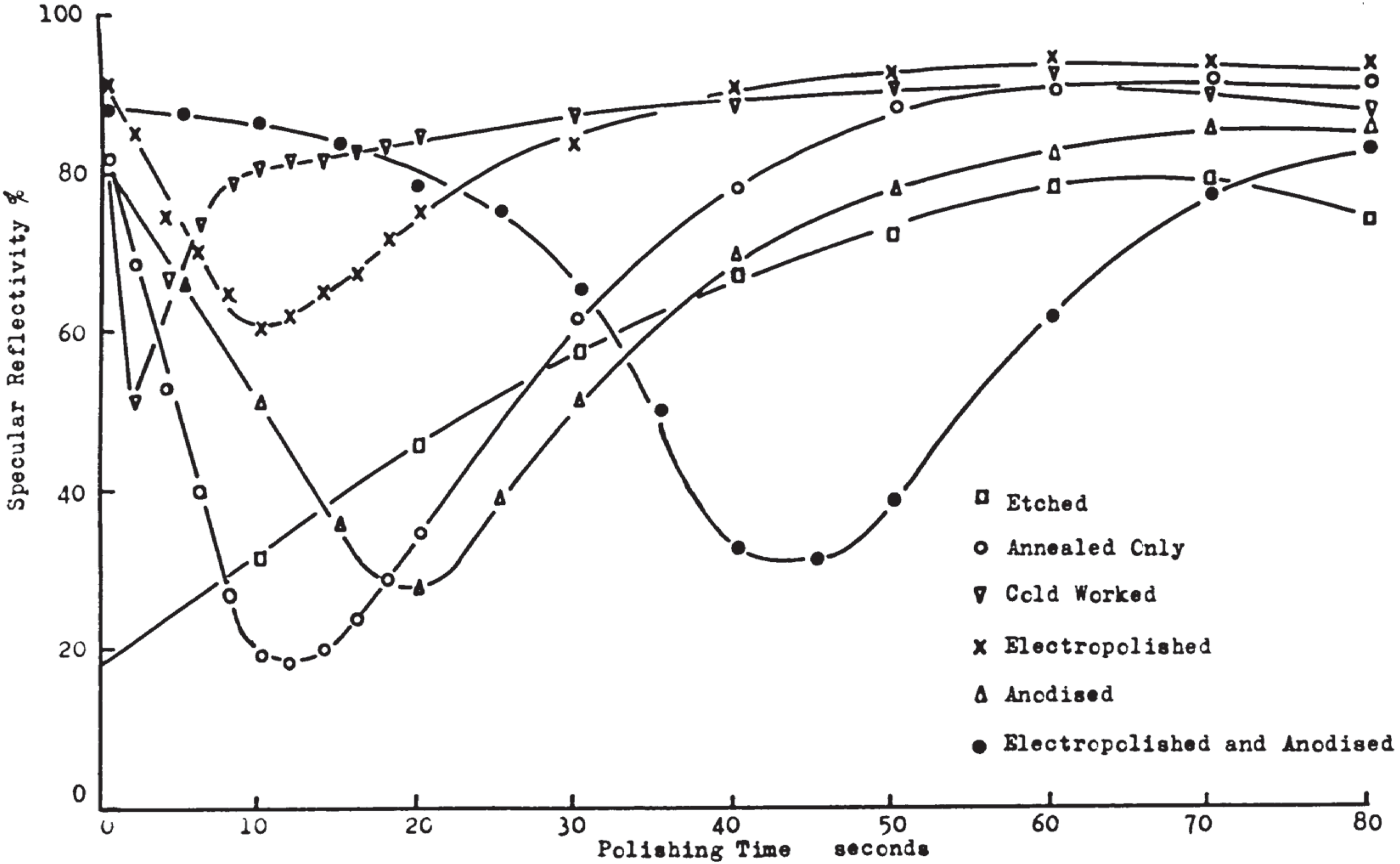


Fig. 4.2. Specular Reflectivity vs. Polishing Time

results in a move to the right of the specular reflectivity results. The specimens which have been anodised on the original surface prior to chemical polishing, are etched initially then polished. The lowest specular reflectivity is recorded after 20 seconds polishing time compared with 10 seconds with the original un-anodised specimens.

The electropolished and anodised specimens gave results more delayed in time, the lowest reflectivity occurring after 40 seconds treatment.

The specular reflectivity readings of the cold worked specimens indicate a very short polishing cycle. With these specimens etching took place after two seconds immersion and polishing after twenty seconds.

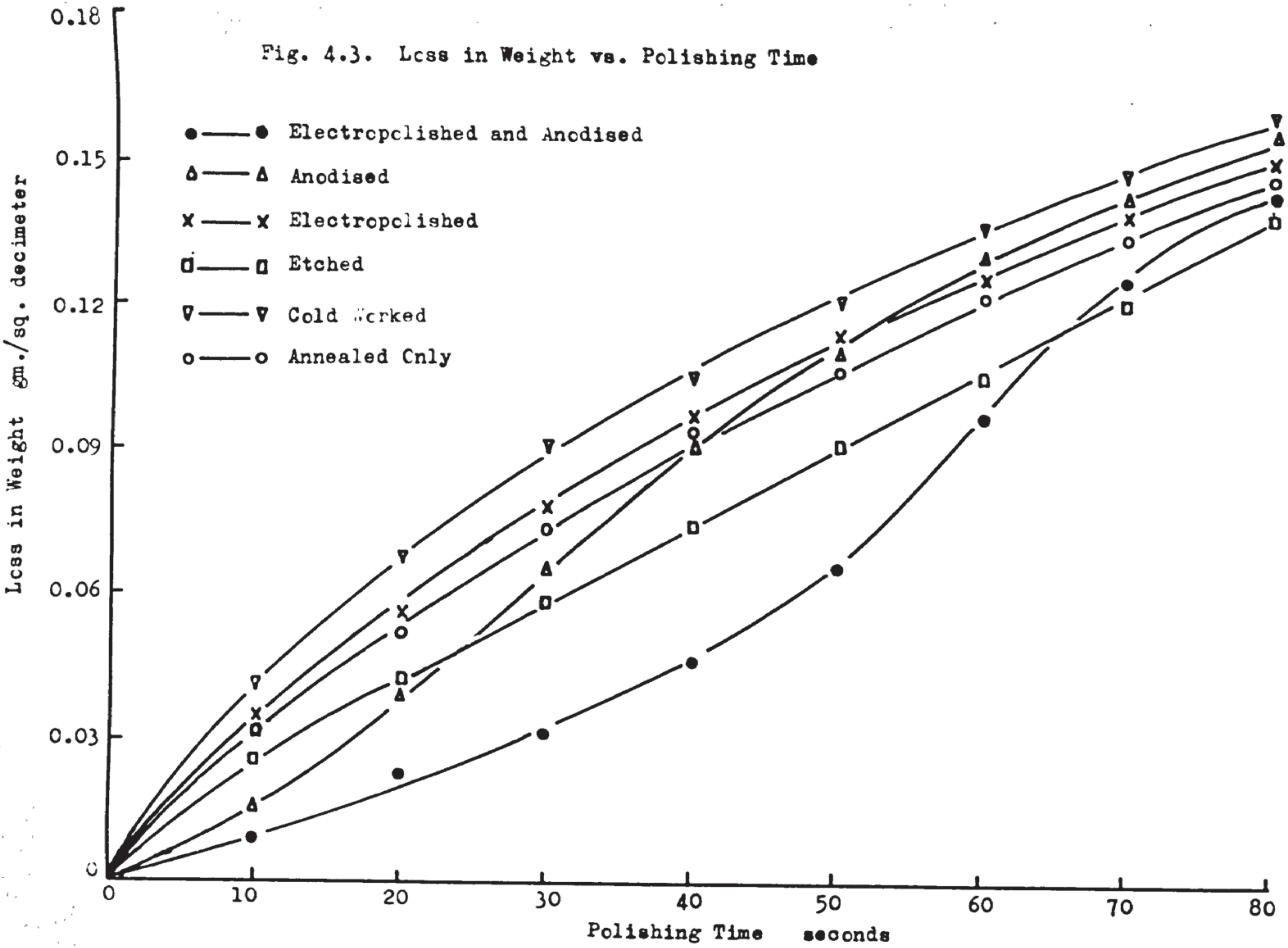
4.3. Weight Loss Results

The weight loss results during the chemical polishing of pretreated samples are shown in Fig. 4.3. These results do not show a great deal of variation between the forms of pretreatment.

The exceptions are the anodised specimens and the electropolished and anodised specimens, which show a low rate of dissolution initially.

All the results obtained after 1 minutes polishing time are similar to the results of variation in weight loss with polishing time for the original annealed

Fig. 4.3. Loss in Weight vs. Polishing Time



specimens which are included in Fig. 4.3 for comparison.

4.4. Replica Electron Microscopy Results

4.4.1. Electropolished Specimens

Replica electron micrographs taken from specimens which have been electropolished then chemically polished for 5, 10, 20, 30, 45 and 60 seconds are shown in Figs. 4.5 - 4.10. A typical electron micrograph of the electropolished surface is shown in Fig. 4.4.

This electropolished structure, which has been commented on by earlier workers(57,58,59) appears to show the same orientation dependence as the chemical polishing structures. The structure is however, on a much finer scale, as the cells and "furrows" are about 200 Å across.

The subsequent electron micrographs show that the characteristic electropolished structure is rapidly removed by chemical polishing and is replaced by a fine structureless pitting of the surface. As polishing continues this structureless pitting is gradually replaced by the characteristic chemical polished structure, described previously.

This structure has similar features to that of the electropolished surface, particularly the laminations on the $\{110\}$ planes, however, a close examination of the magnifications of the electron micrographs indicates that the chemically polished structures are larger by approximately a factor of ten.

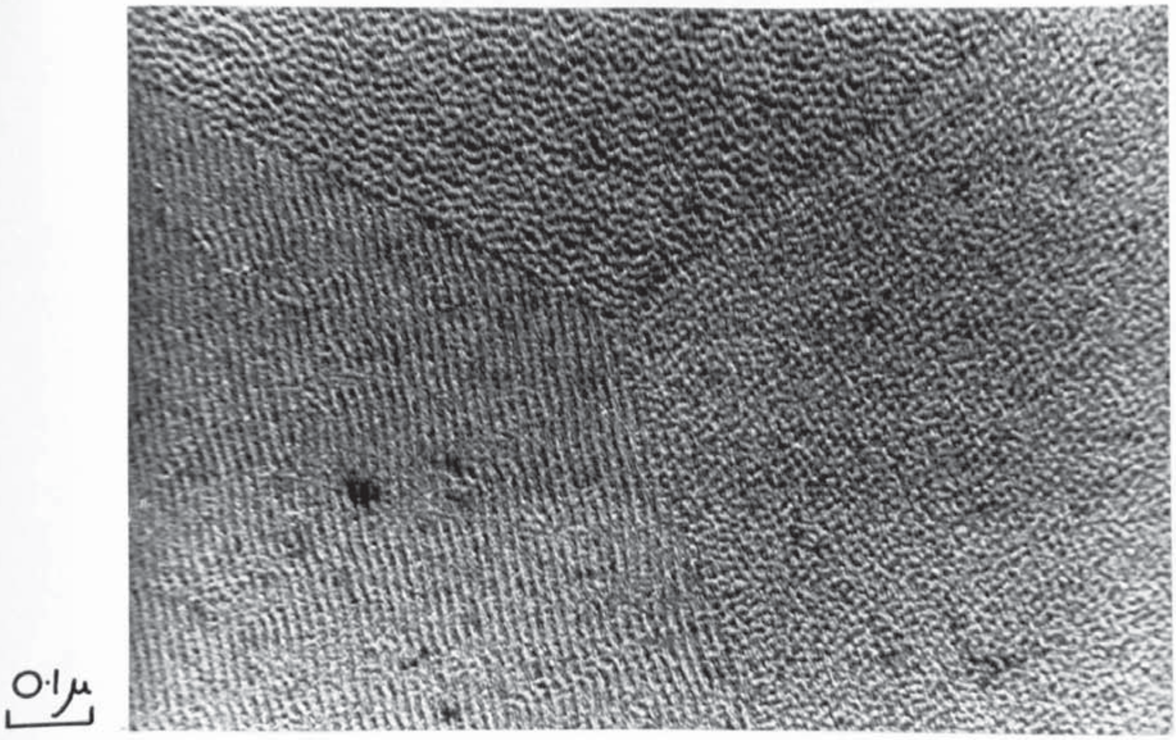


Fig. 4.4. Replica Electron Micrograph of the Electropolished Aluminium Surface

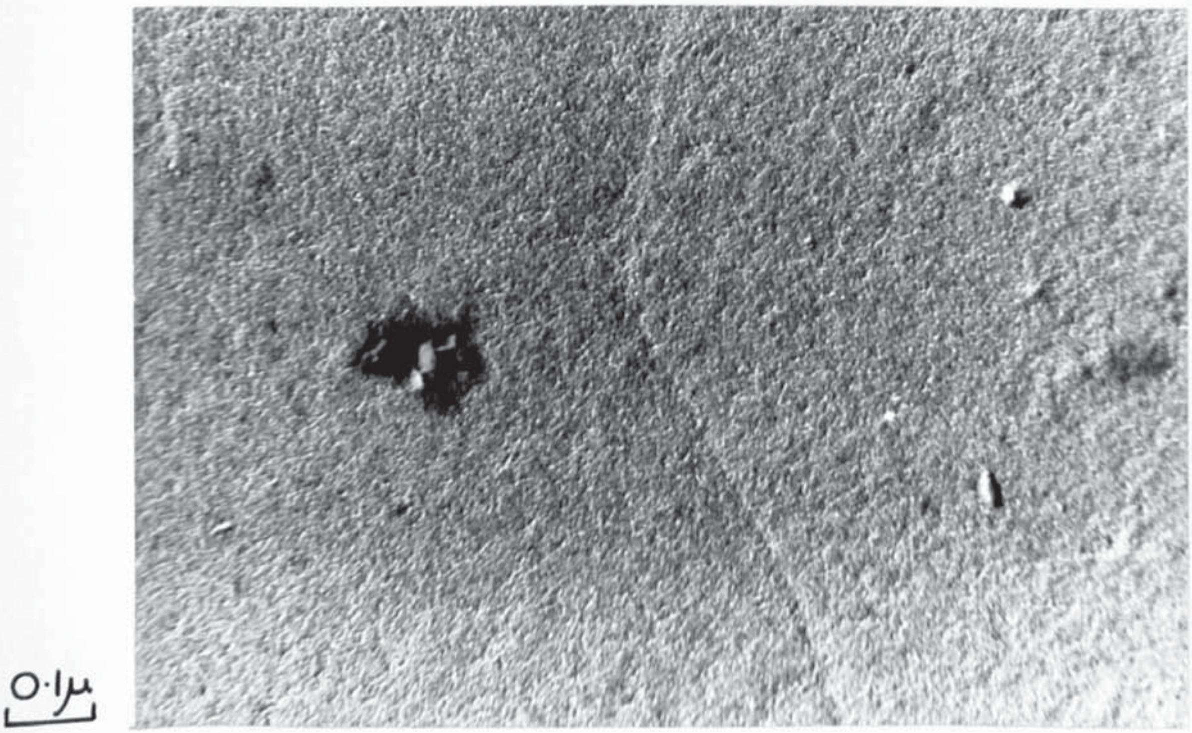


Fig. 4.5. Electropolished Aluminium Chemically Polished for 5 Seconds.

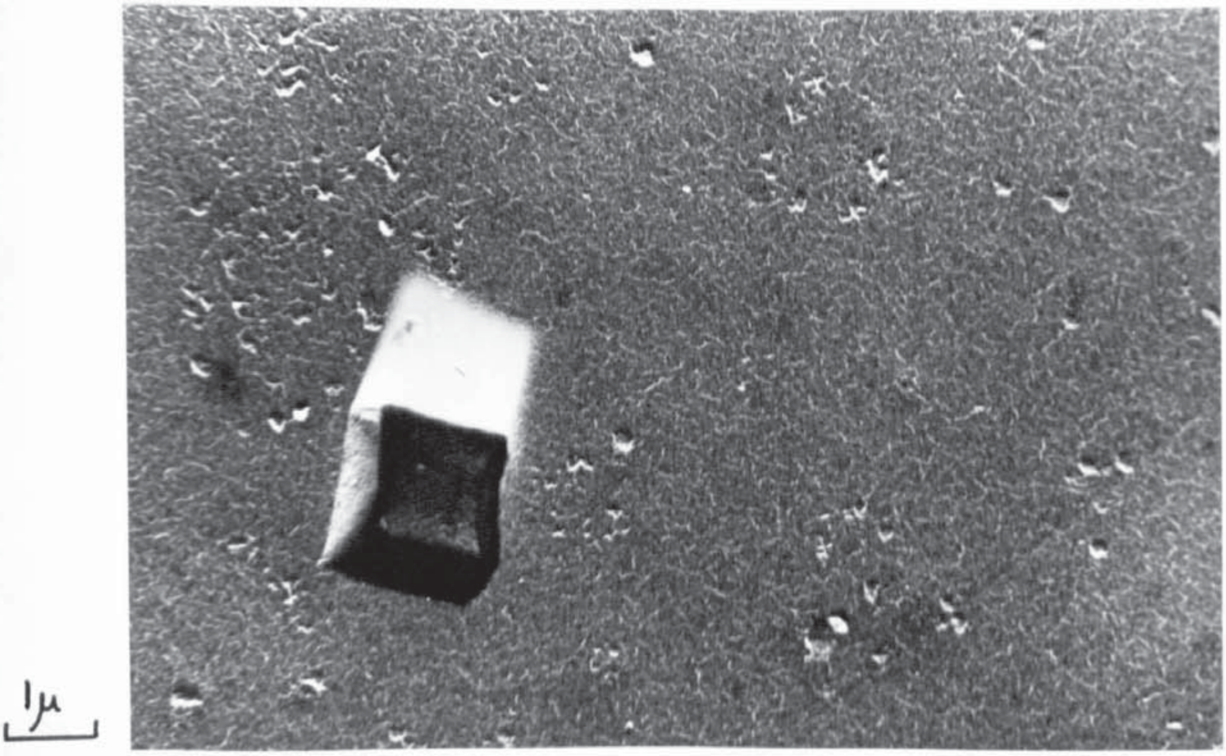


Fig. 4.6. Electropolished Aluminium Chemically Polished for 10 Seconds.

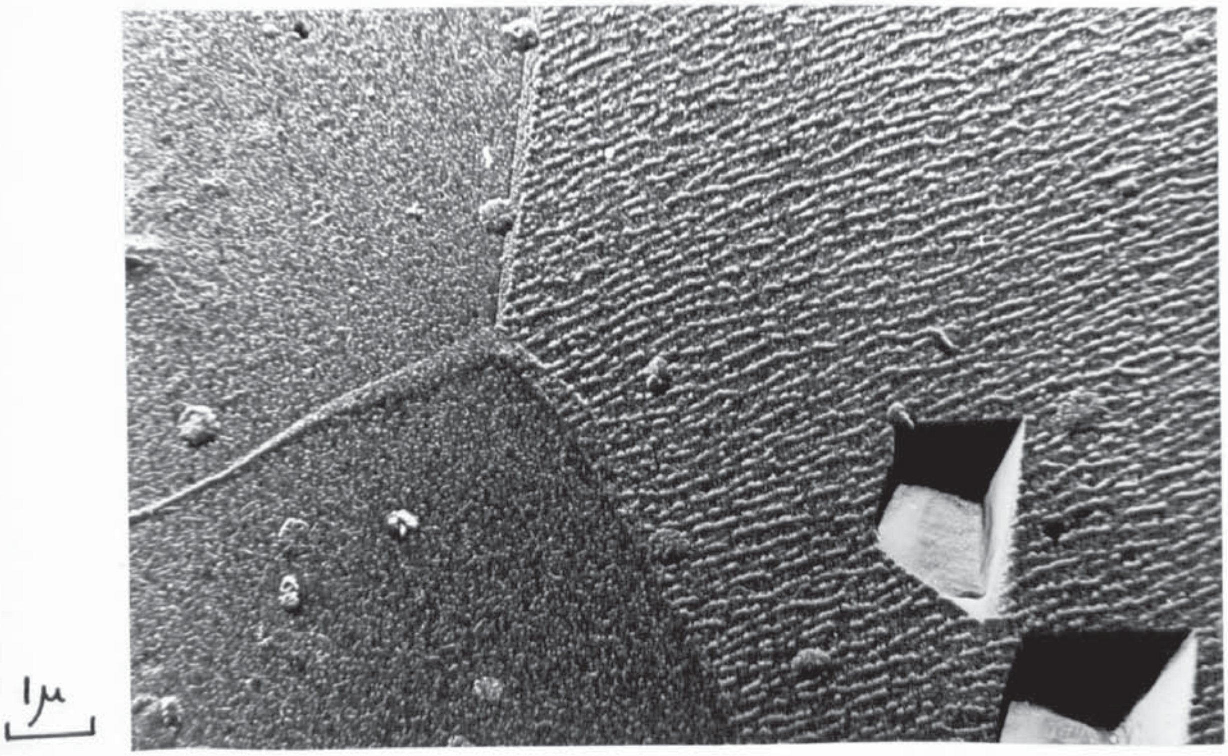


Fig. 4.7. Electropolished Aluminium Chemically Polished for 20 Seconds.

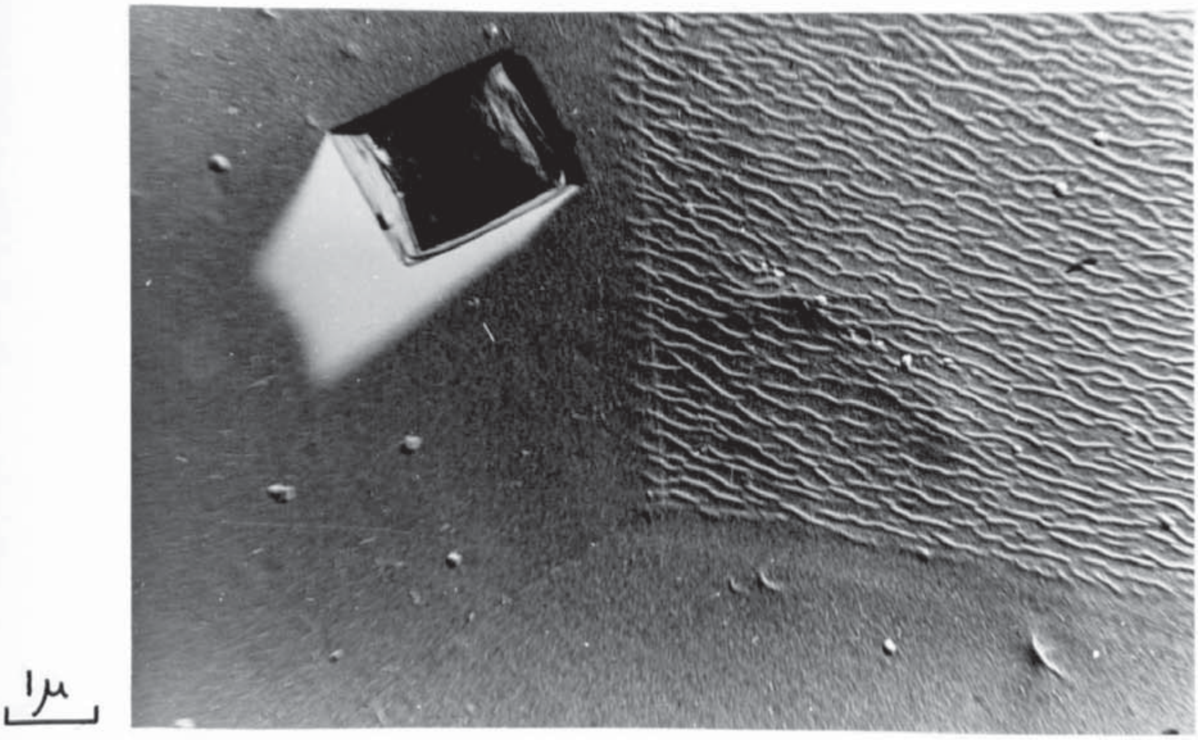


Fig. 4.8. Electropolished Aluminium Chemically Polished for 30 Seconds.

Fig. 4.9. Electropolished Aluminium Chemically Polished for 45 Seconds.

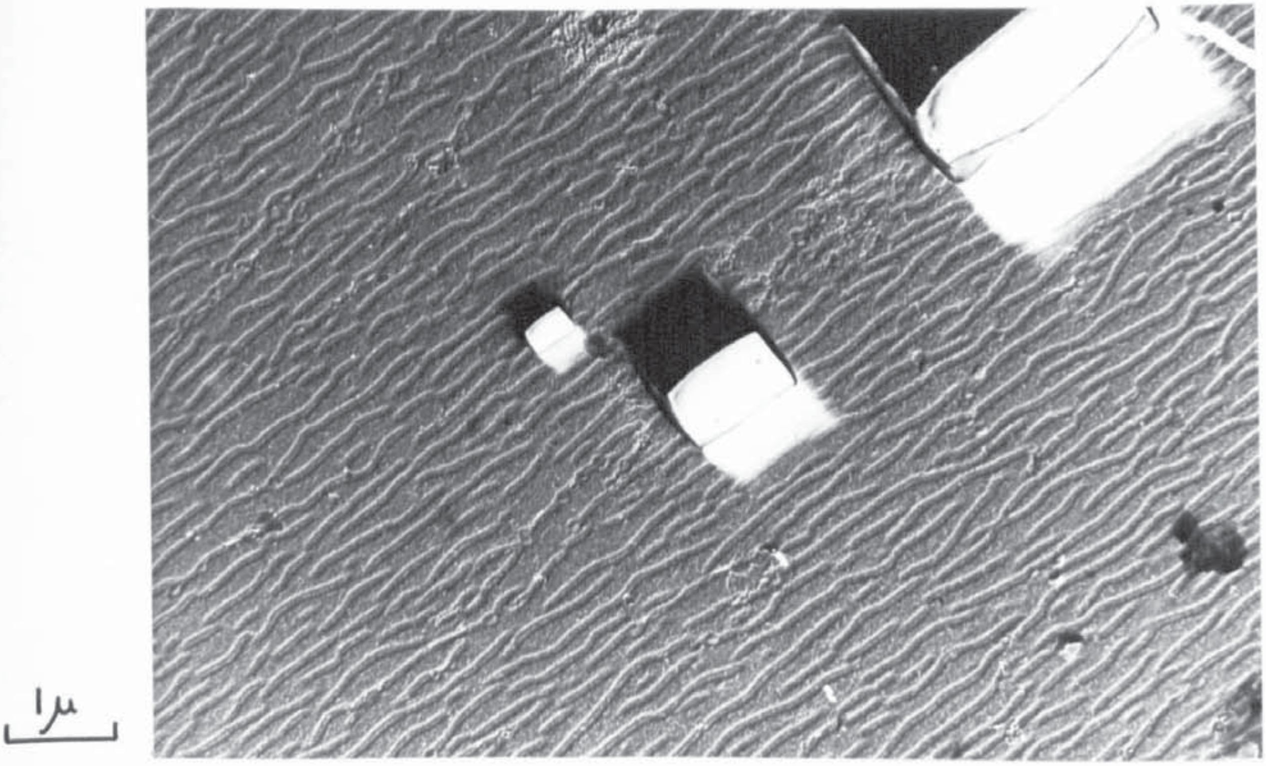


Fig. 4.10. Electropolished Aluminium Chemically Polished for 60 Seconds.

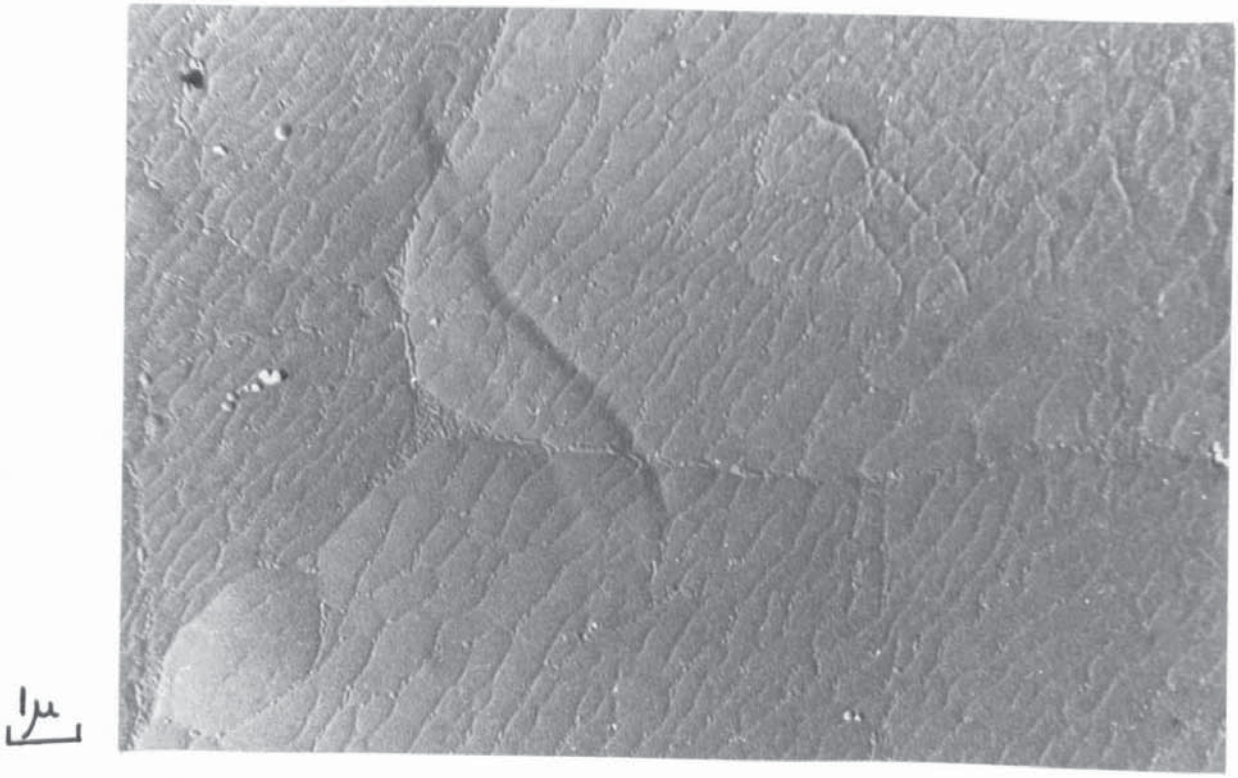


Fig. 4.11. Replica Electron Micrograph of the Etched Aluminium Surface.

4.4.2. Etched Specimens

Figs. 4.12 - 4.19 display replica electron micrographs taken from specimens which have been etched then chemically polished for 2, 10, 20, 30, 45, 60 seconds, $1\frac{1}{2}$ minutes and 3 minutes respectively. An electron micrograph of the etched surface structure is illustrated in Fig. 4.11.

The etched structure consists of large, approximately spherical depressions, superimposed on which is a finer network of irregular cells. These have ridge boundaries similar to the etched structure that occurs in the initial stages of chemical polishing, described previously.

As chemical polishing proceeds there is dissolution from the ridge boundaries and particularly at the boundaries of the large depressions. With longer polishing times the surface structures become dependent on the grain orientation of the base metal. These structures are similar to the normal chemical polishing structure, particularly at polishing times of one minute and longer, when the structure begins to coarsen. There is also some smoothing of the surface with increasing polishing time, the larger etched depressions becoming less clear as polishing proceeds, until they are not noticeable after 20 seconds treatment.

4.4.3. Anodised Specimens

Electron micrographs taken from specimens of aluminium

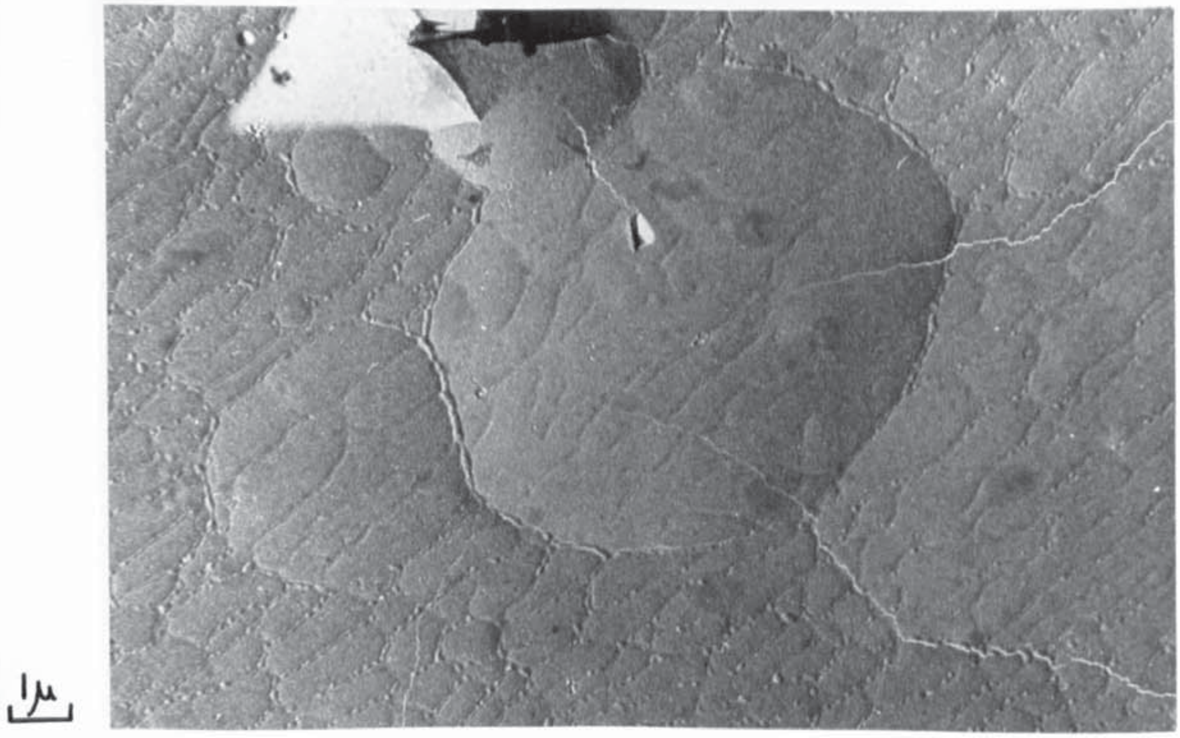


Fig. 4.12. Etched Aluminium Chemically Polished for 2 Seconds.

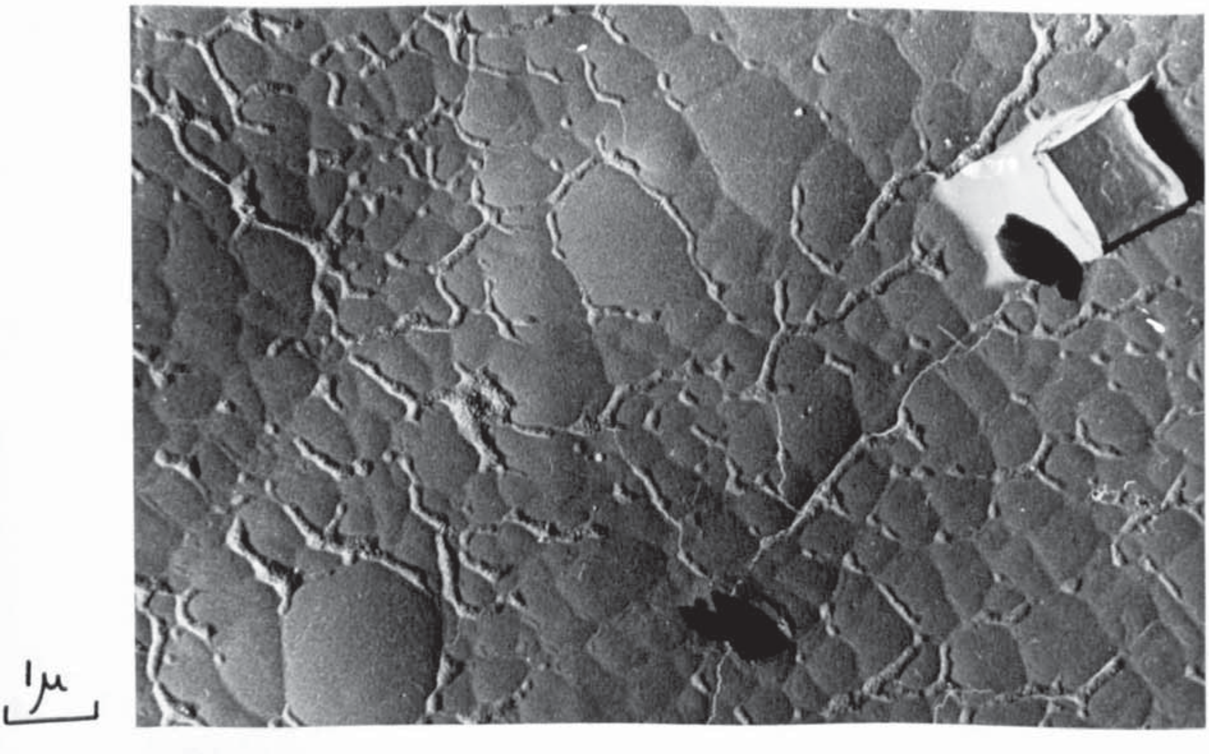


Fig. 4.13. Etched Aluminium Chemically Polished for 10 Seconds.

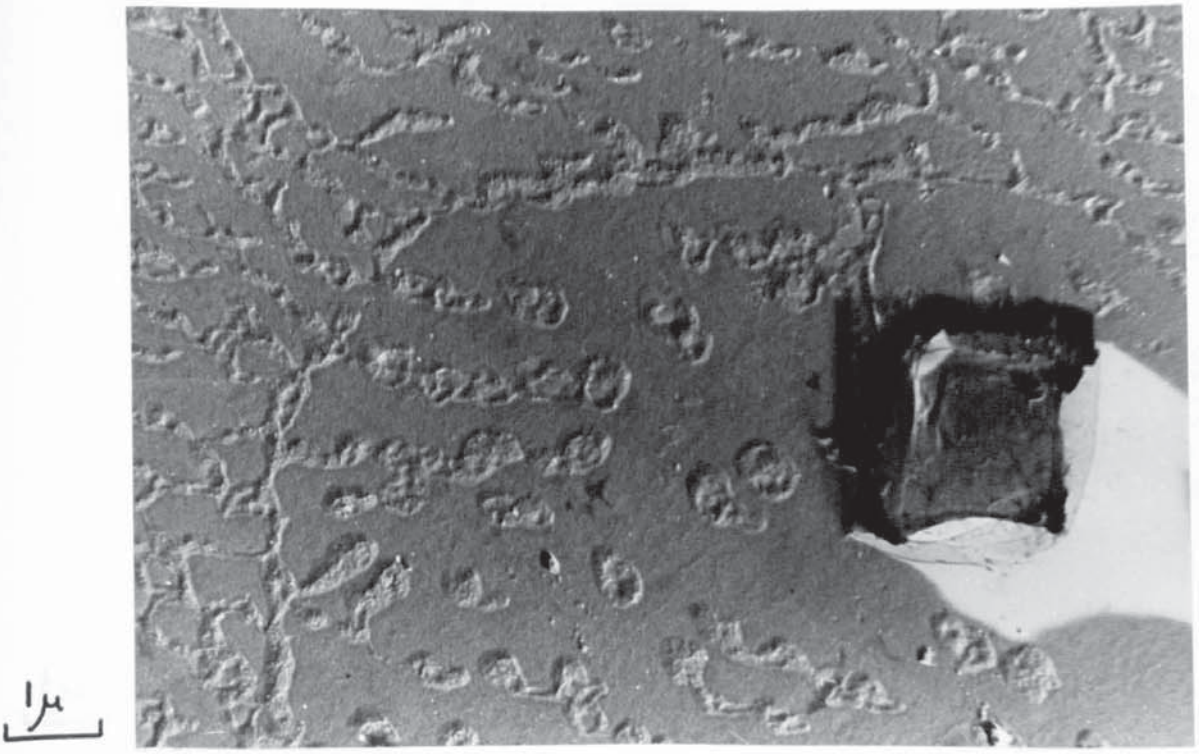


Fig. 4.14. Etched Aluminium Chemically Polished for 20 Seconds.

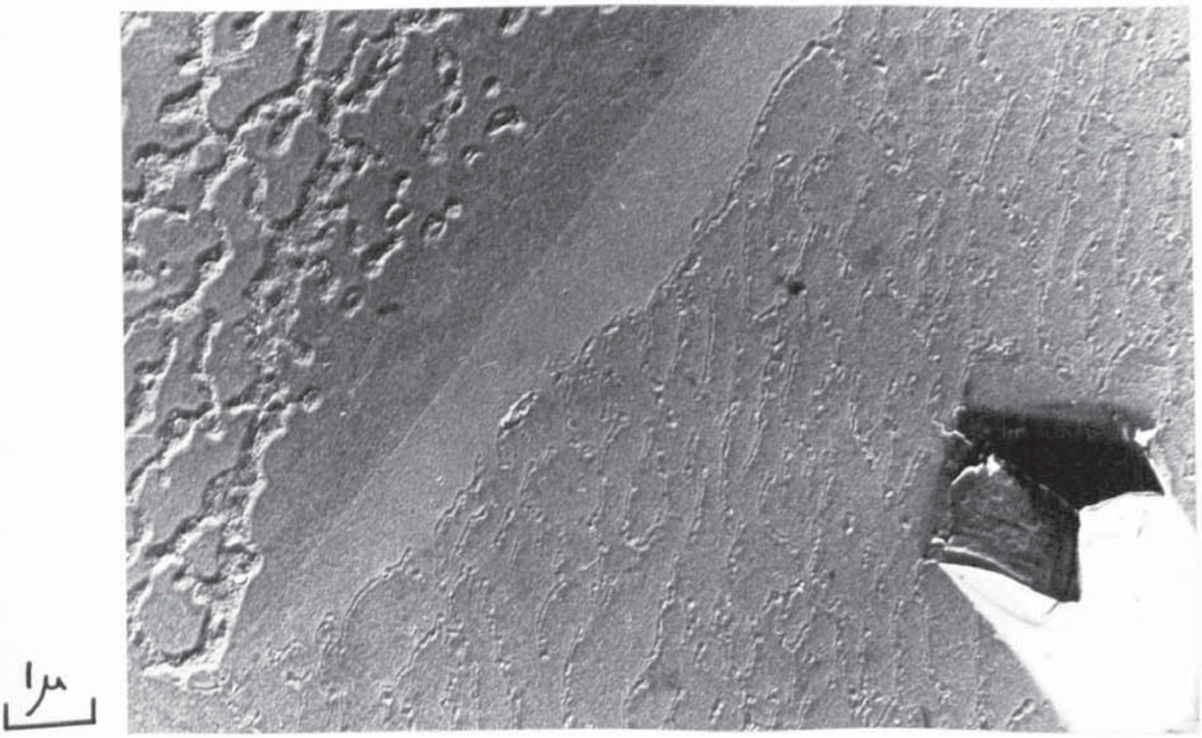


Fig. 4.15. Etched Aluminium Chemically Polished for 30 Seconds.

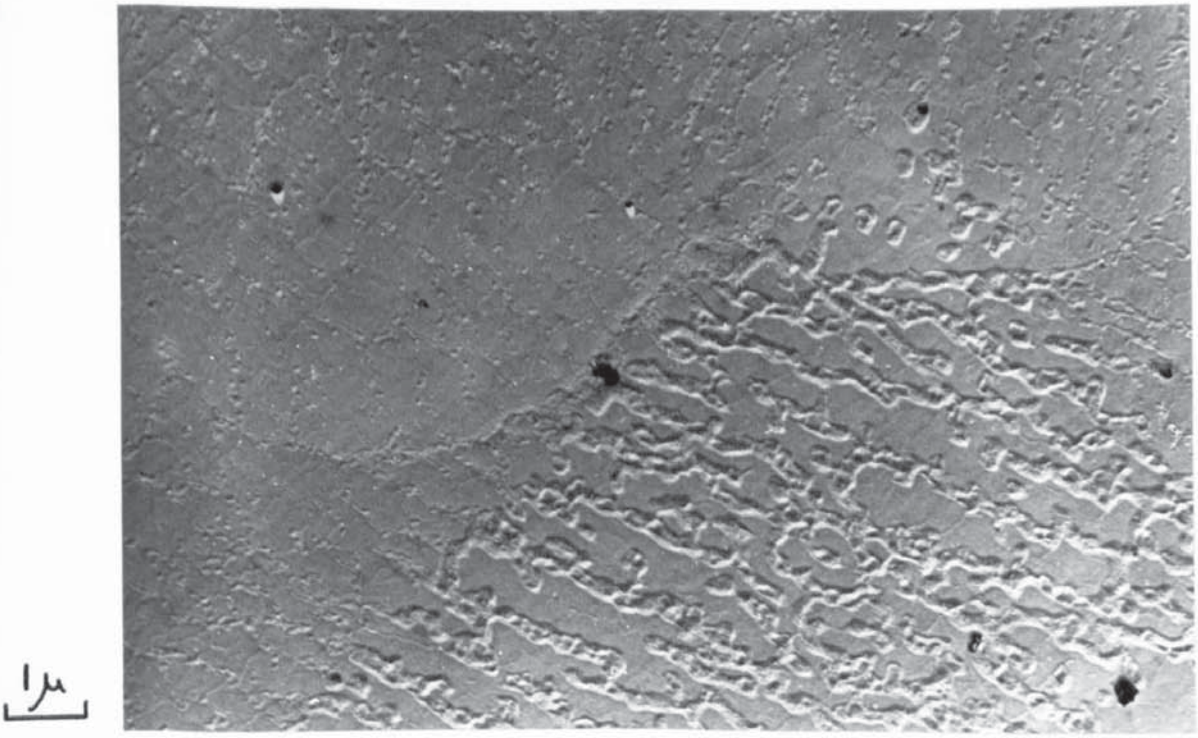


Fig. 4.16. Etched Aluminium Chemically Polished for 45 Seconds.

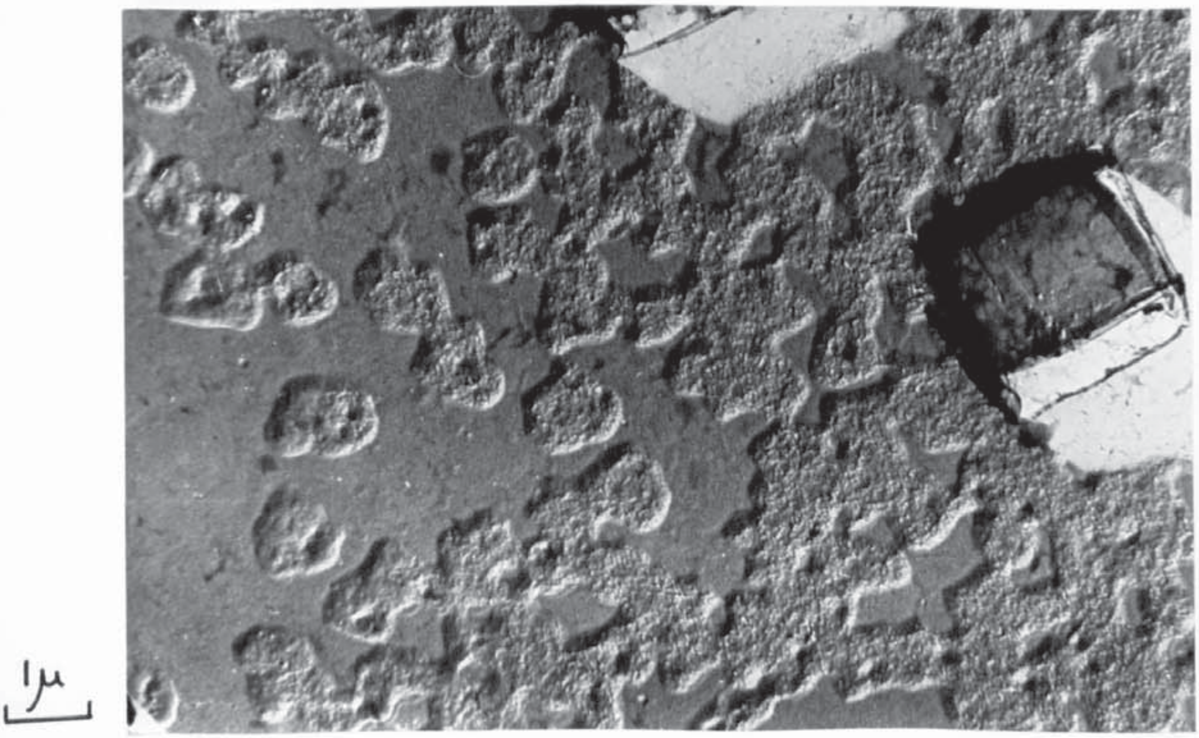


Fig. 4.17. Etched Aluminium Chemically Polished for 1 minute.

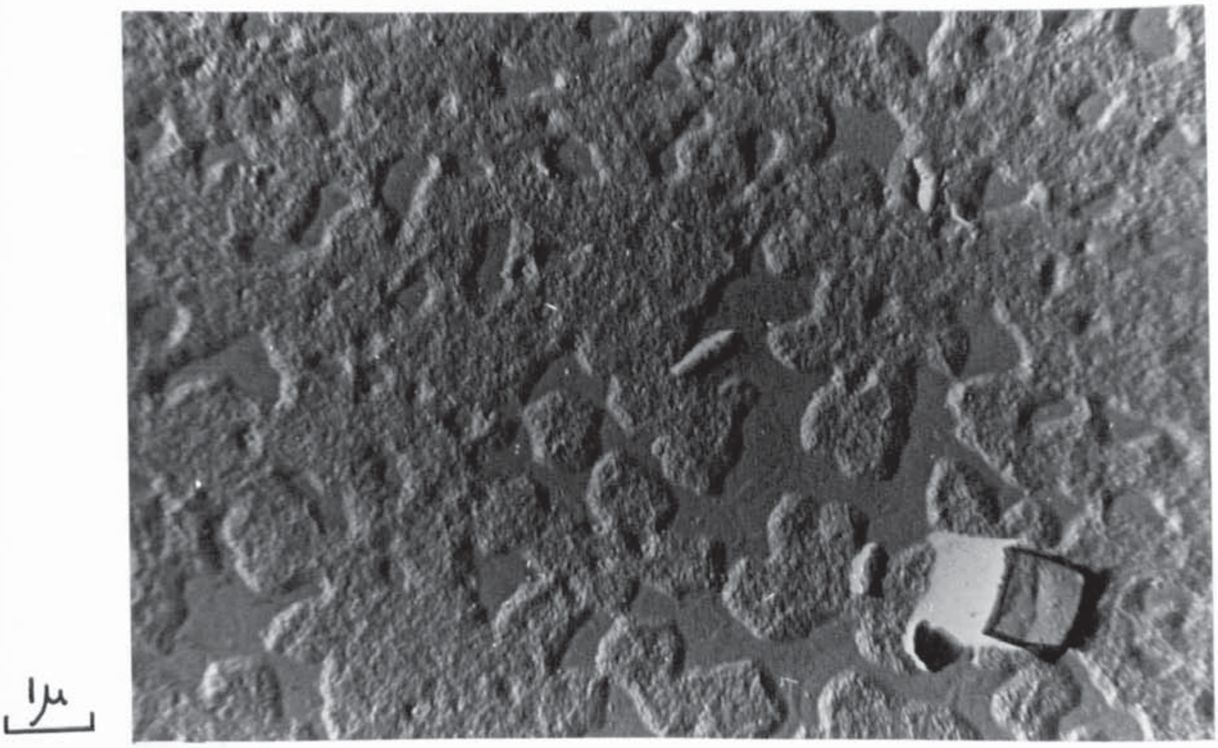


Fig. 4.18. Etched Aluminium Chemically Polished for $1\frac{1}{2}$ Minutes.

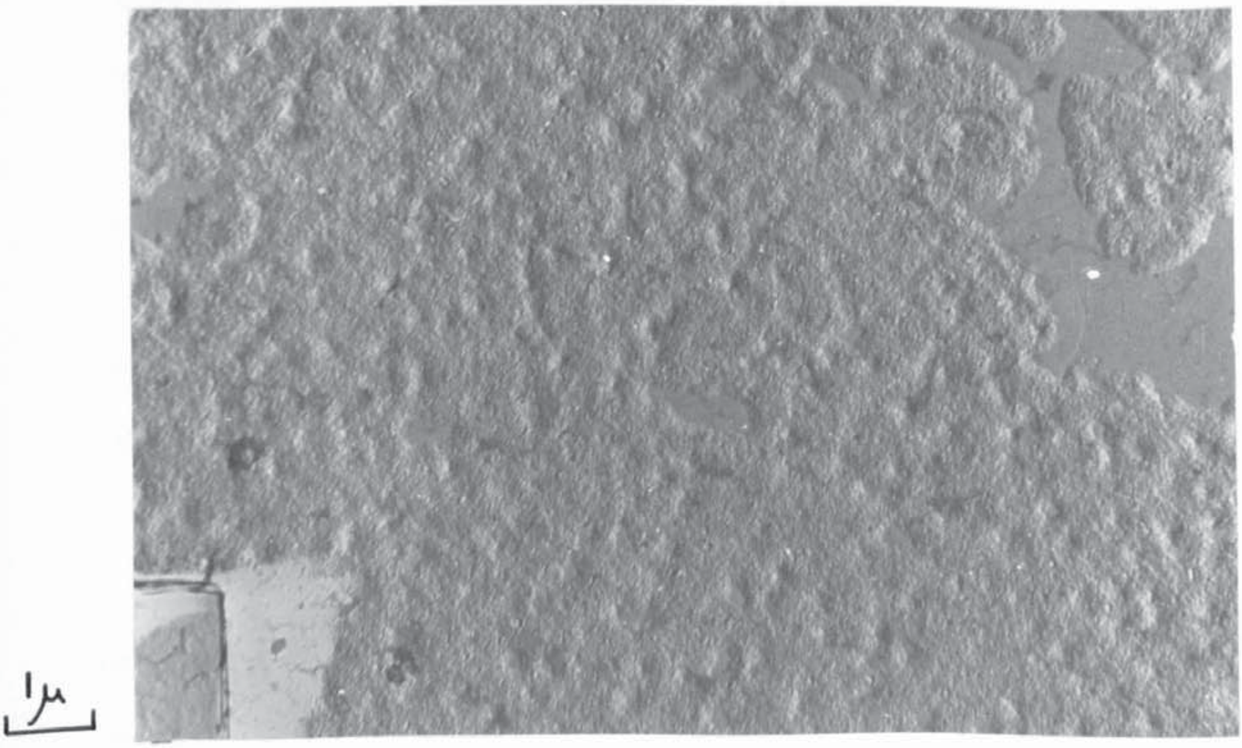


Fig. 4.19. Etched Aluminium Chemically Polished for 3 Minutes.

which have been anodised to give a barrier film approximately 1,400 Å thick, then chemically polished for 5, 10, 15, 30, 45 and 60 seconds, are displayed in Figs. 4.21 - 4.26 respectively; Fig. 4.20 shows the surface structure of an anodised specimen. The barrier film appears to be a structureless film upon the normal as-rolled surface finish shown in Fig. 3.5.

There is little attack on the aluminium surface for the first few seconds of polishing. After five seconds, a few small pits appear and after ten seconds, the number has increased slightly. After twenty seconds polishing, the characteristic etched structure is produced in some areas on the surface, alongside which other areas show little sign of attack. As polishing proceeds the etched structure covers most of the surface with small areas of the original anodic oxide film remaining. The characteristic polished structure then begins to form from the etched structure as before. The areas where the etch attack was rapid, being the first to show the polished structure.

4.4.4. Electropolished and Anodised Specimens

Figs. 4.28 - 4.33 show the surface structures of specimens which have been electropolished and anodised then chemically polished for 10, 20, 30, 35, 40 seconds and 1½ minutes.

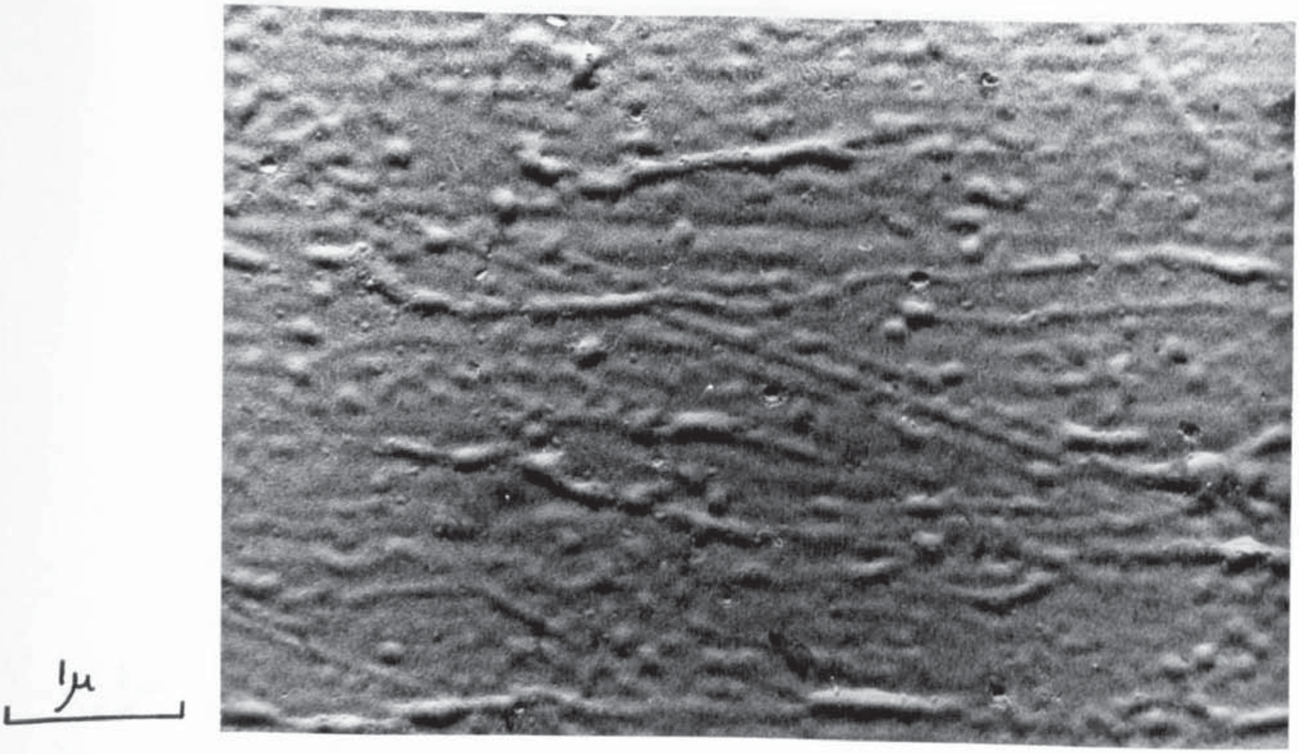


Fig. 4.20. Replica Electron Micrograph of the Anodised Aluminium Surface.

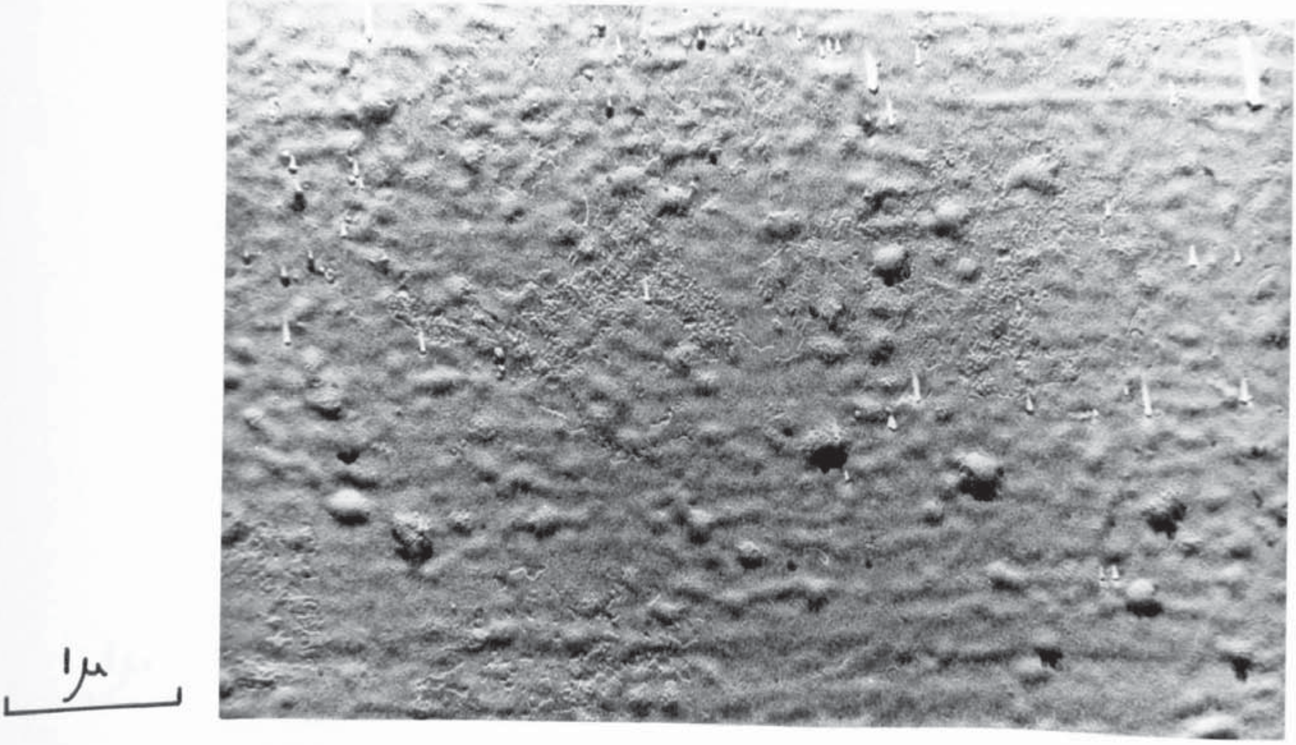


Fig. 4.21. Anodised Aluminium Chemically Polished for 5 Seconds.

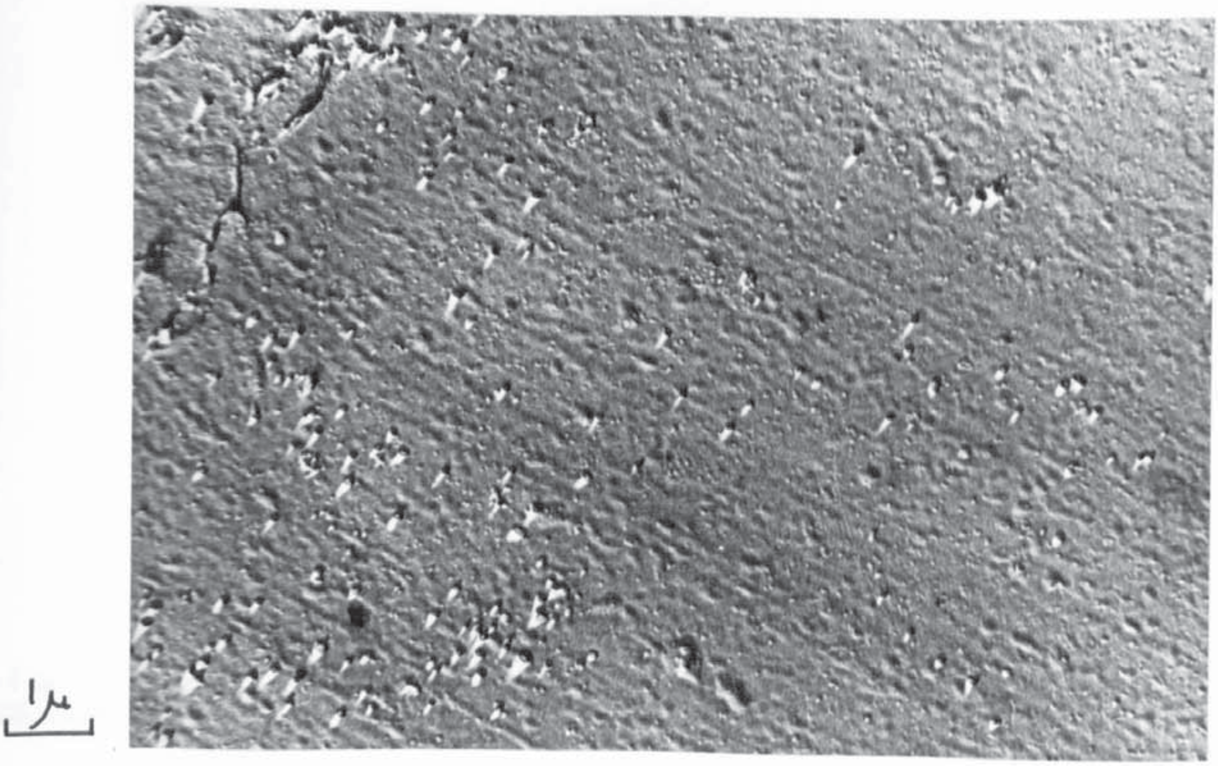


Fig. 4.22. Anodised Aluminium Chemically Polished for 10 Seconds.

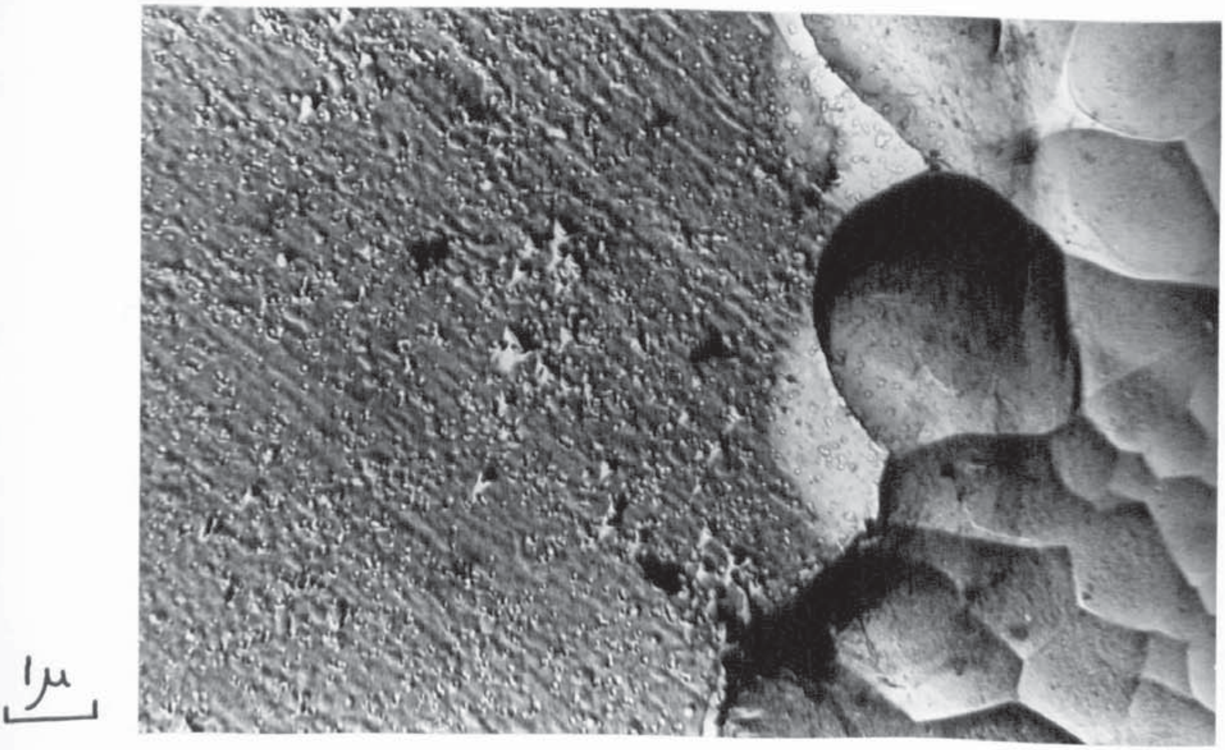


Fig. 4.23. Anodised Aluminium Chemically Polished for 15 Seconds.

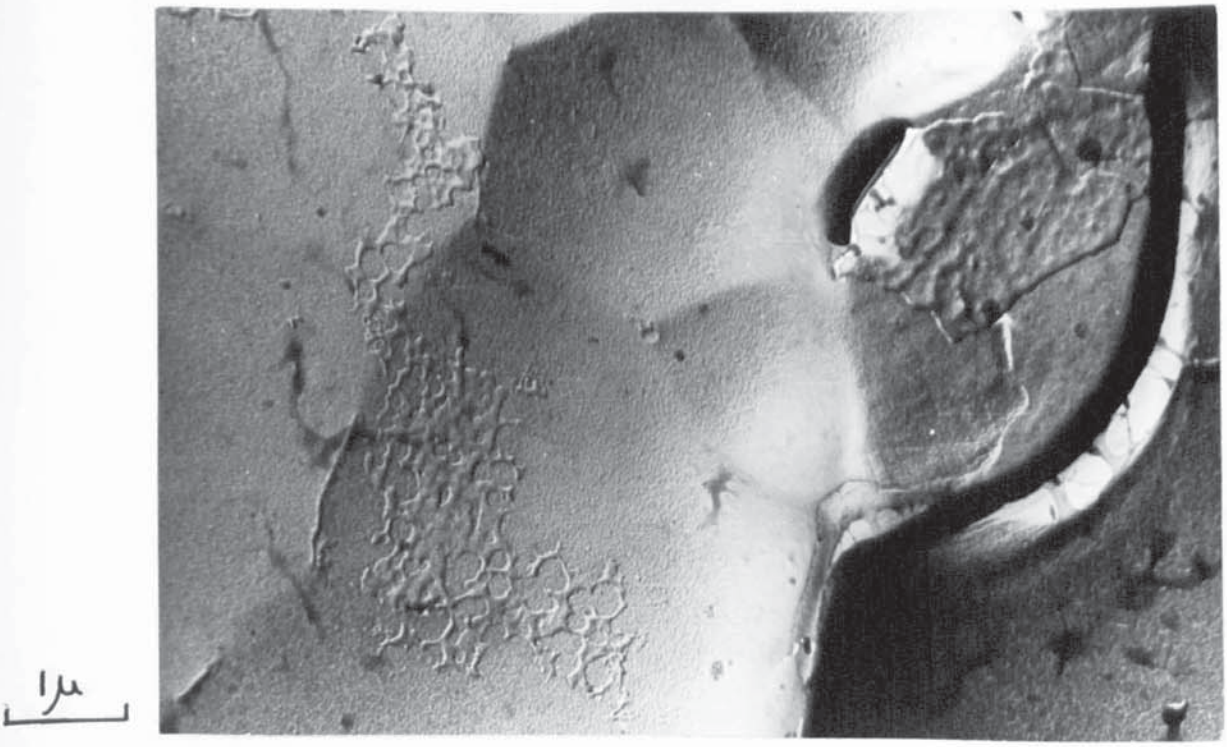


Fig. 4.24. Anodised Aluminium Chemically Polished for 30 Seconds.

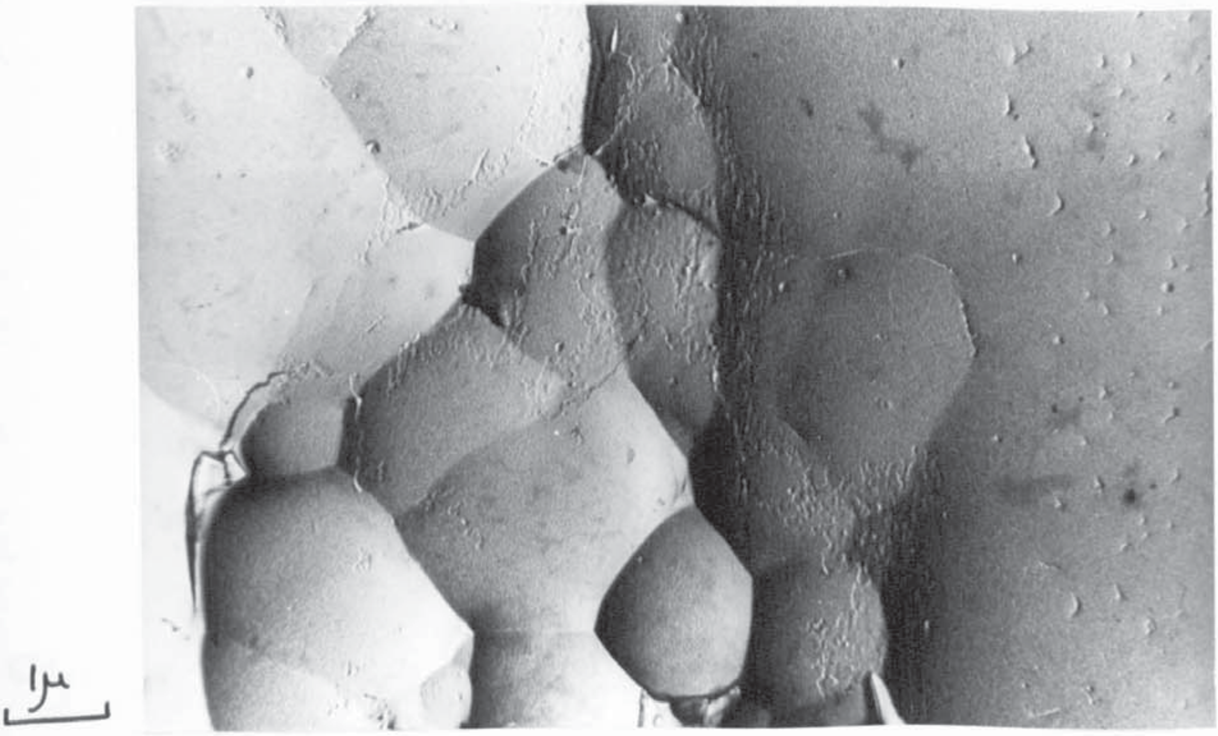


Fig. 4.25. Anodised Aluminium Chemically Polished for 45 Seconds.

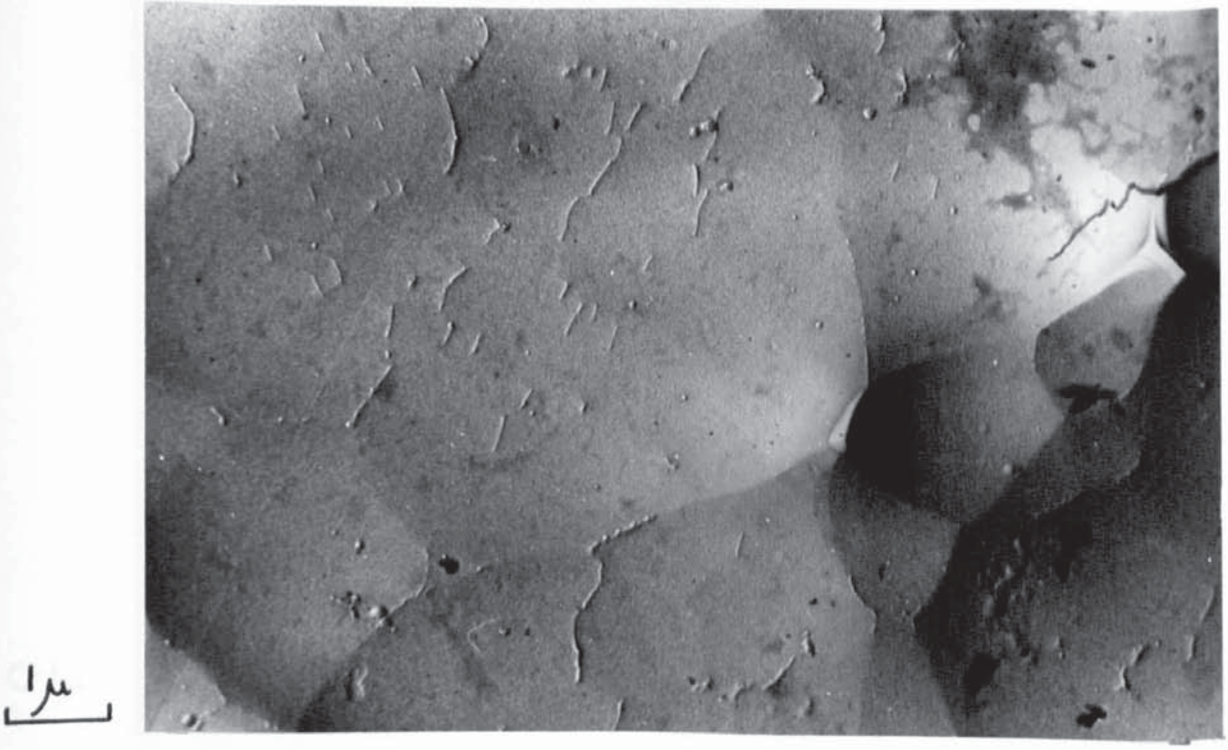


Fig. 4.26. Anodised Aluminium Chemically Polished for 1 Minute.

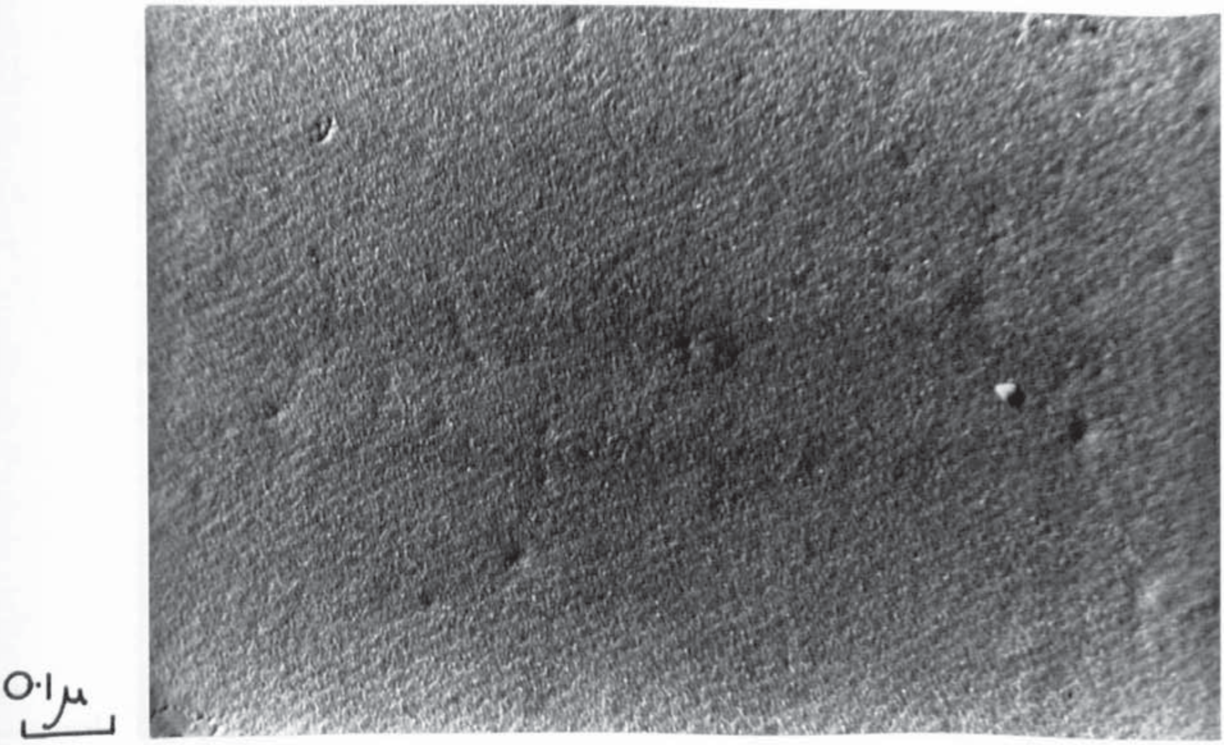


Fig. 4.27. Replica of Electropolished and Anodised Aluminium Surface.

Fig. 4.28. Electropolished and Anodised Aluminium Chemically Polished for 10 Seconds.

Fig. 4.29. Electropolished and Anodised Aluminium Chemically Polished for 20 Seconds.

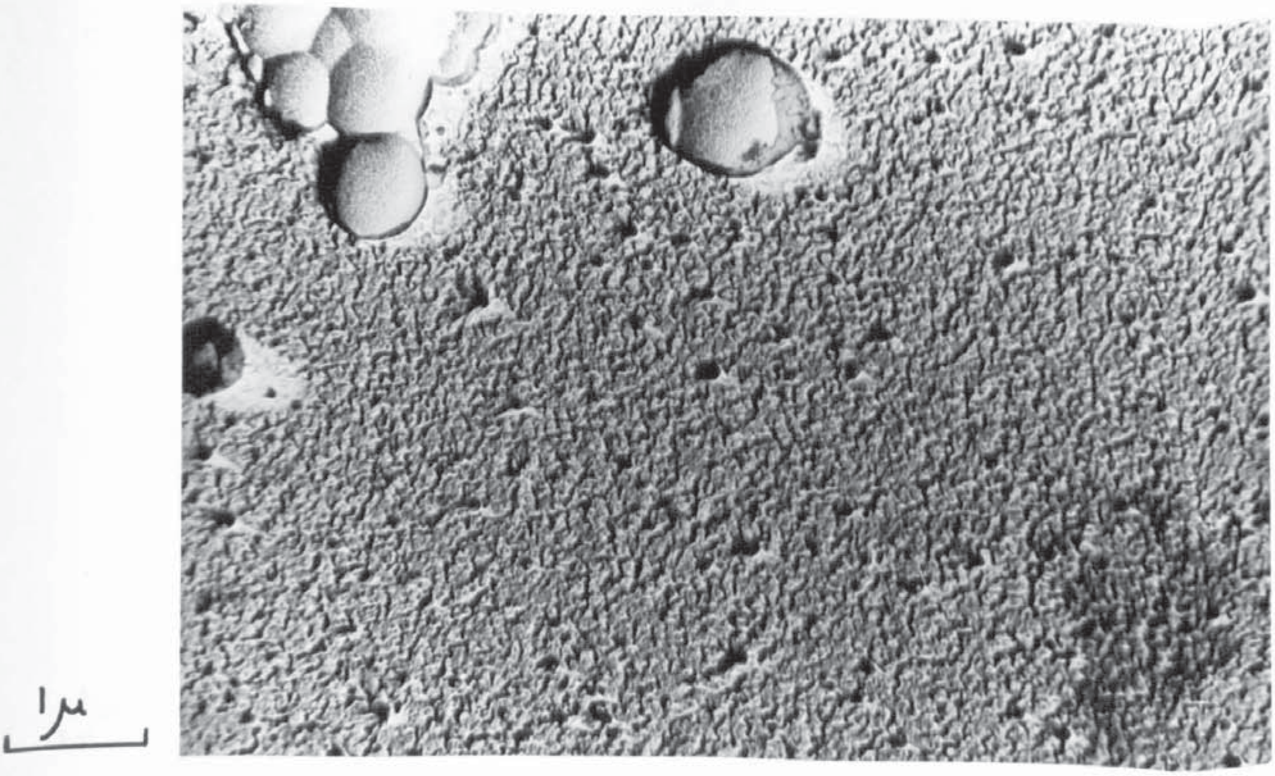


Fig. 4.30. Electropolished and Anodised Aluminium Chemically Polished for 30 Seconds.

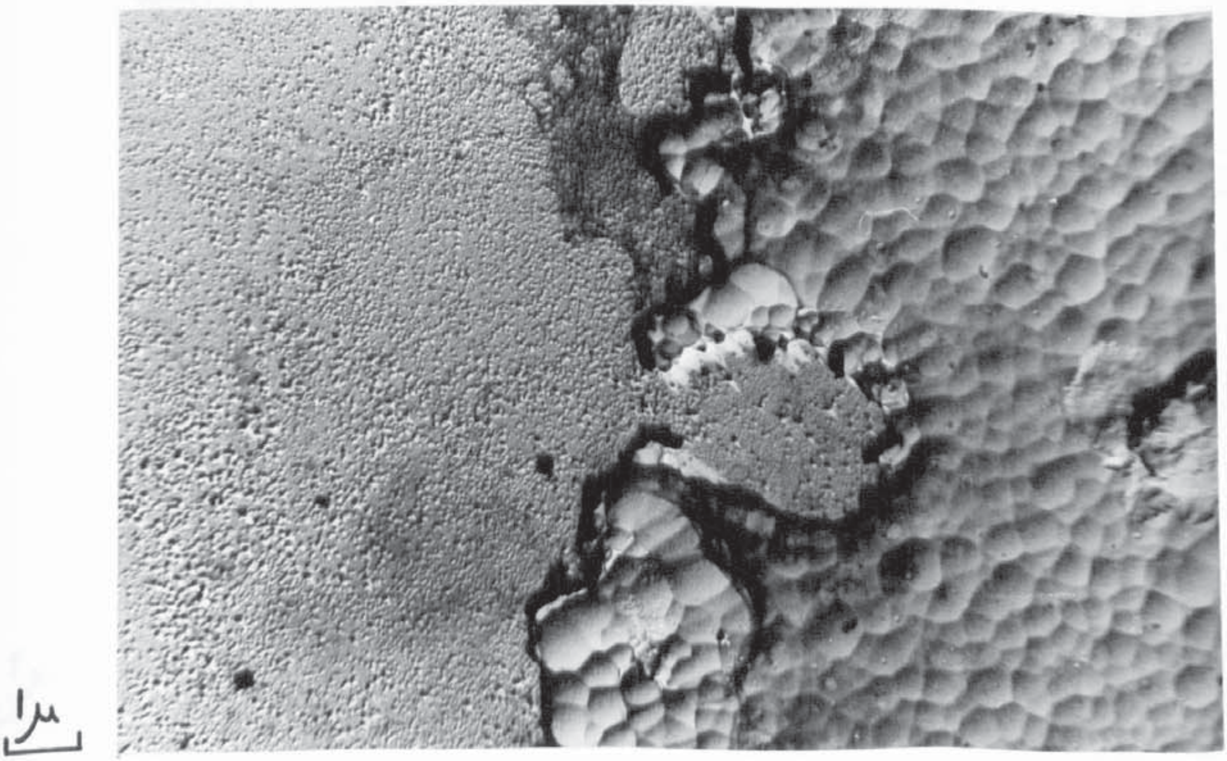


Fig. 4.31. Electropolished and Anodised Aluminium Chemically Polished for 35 Seconds.

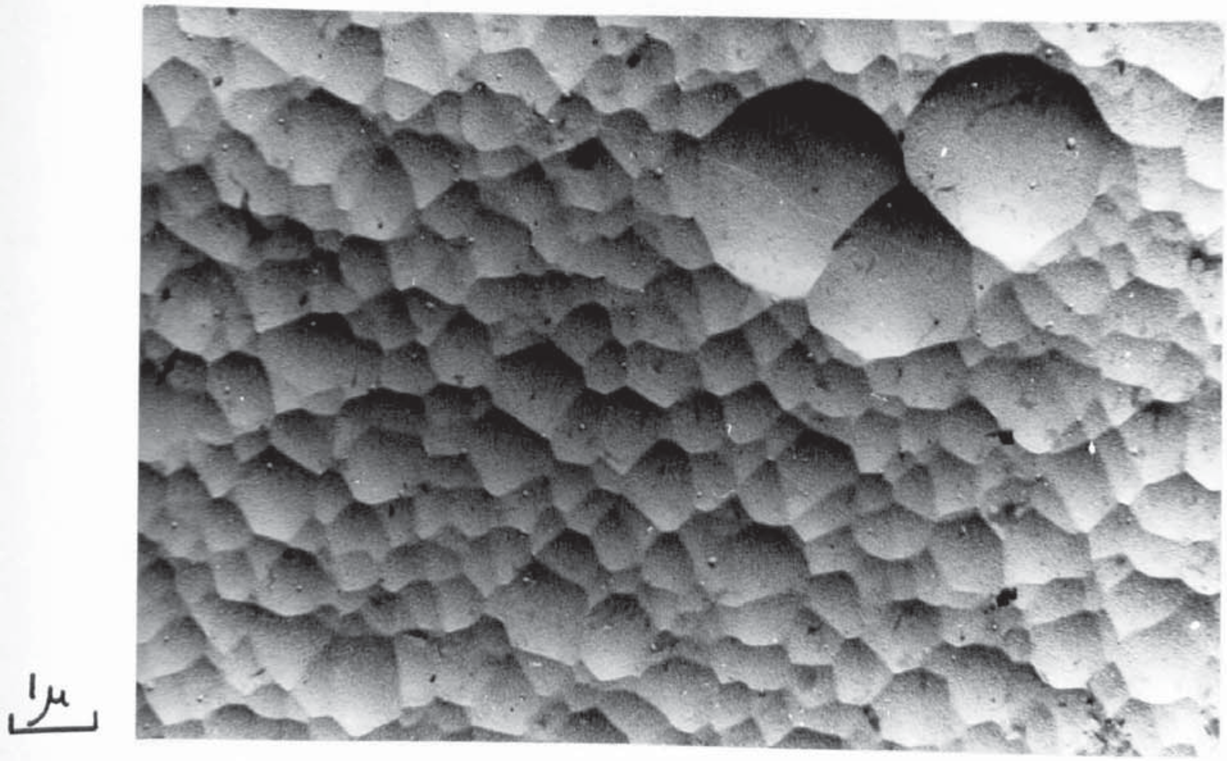


Fig. 4.32. Electropolished and Anodised Aluminium Chemically Polished for 40 Seconds.

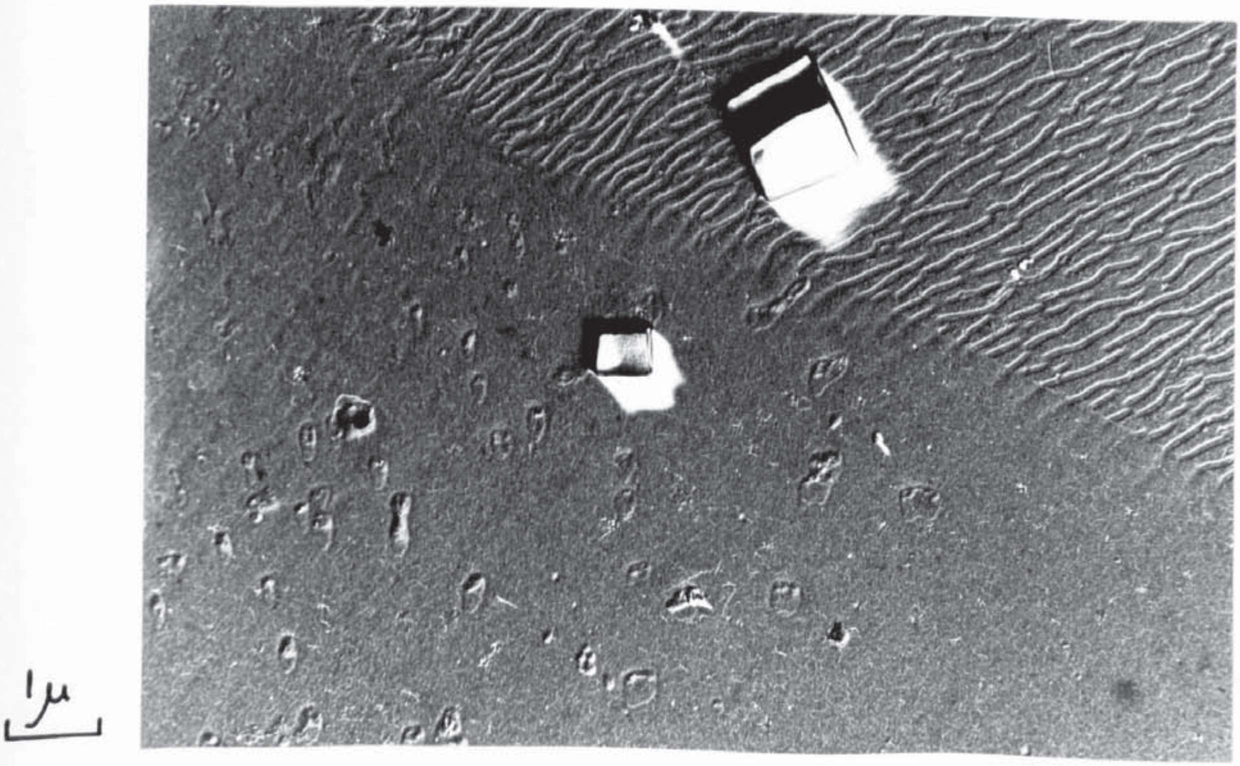


Fig. 4.33. Electropolished and Anodised Aluminium Chemically Polished for 1½ Minutes.

Fig. 4.27 illustrates the surface structure of an electropolished and anodised specimen. The sequence of structures is very similar to those described for the anodised only specimens. The difference being that the amount of polishing time required to produce a given structure is much longer with the electropolished and anodised specimens. It was also noted that the initial electropolished and anodised surface was very smooth and that little structural attack took place until the first area of etched structure was formed after about 30 seconds polishing, whereupon the entire surface was rapidly covered with the network of cells. This is in contrast to the anodised only specimens, in which the transformation from the first etched structure observed, to complete removal of the anodised film, took about 40 seconds.

4.4.5. Cold Worked Specimens

The electron micrographs taken of cold worked aluminium specimens, which have been chemically polished for 2,4,6,10,20 and 30 seconds, are displayed in Figs. 4.34 - 4.39. The electron micrographs show that the cold worked material has the same sequence of etched then polished structures as described previously for the annealed material. However, the polishing time required to produce these structures with the cold worked material is extremely short. The surface is covered with the etched structure after 2 seconds immersion and

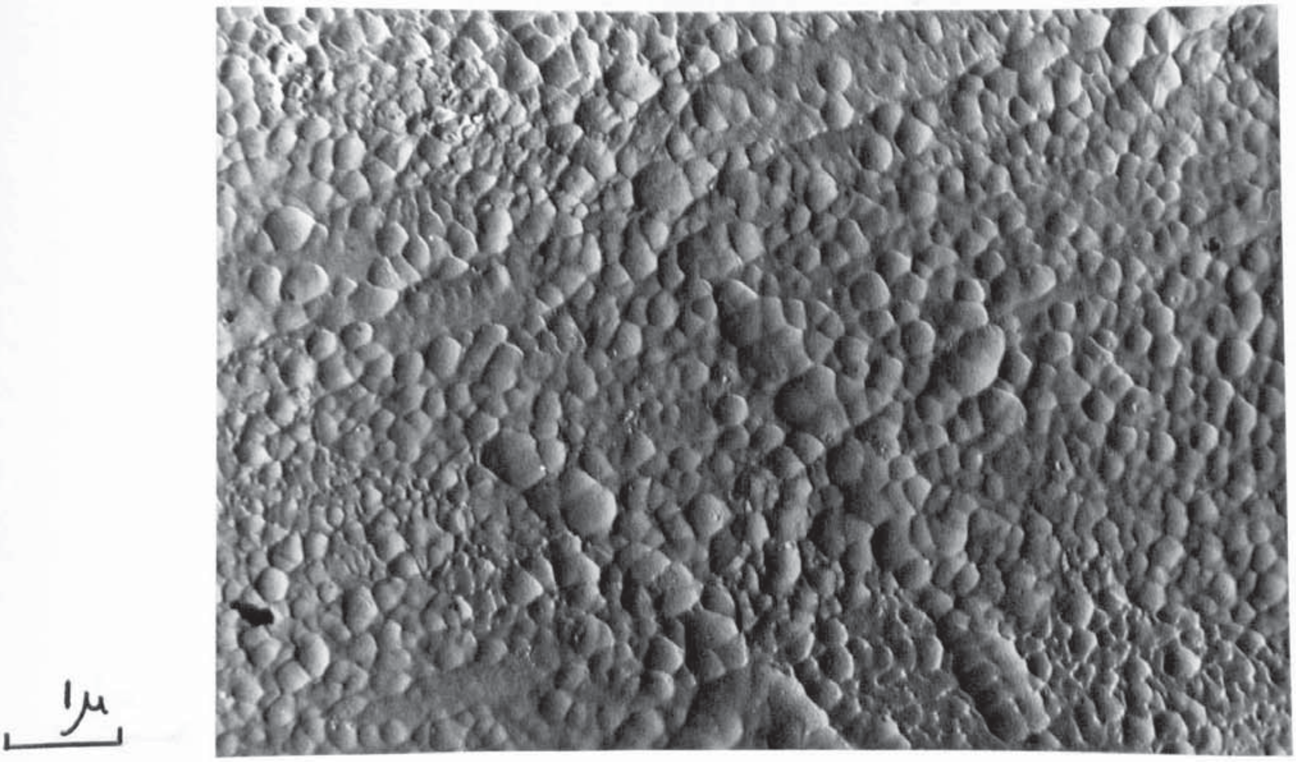


Fig. 4.34. Cold Worked Aluminium Chemically Polished for 2 Seconds.

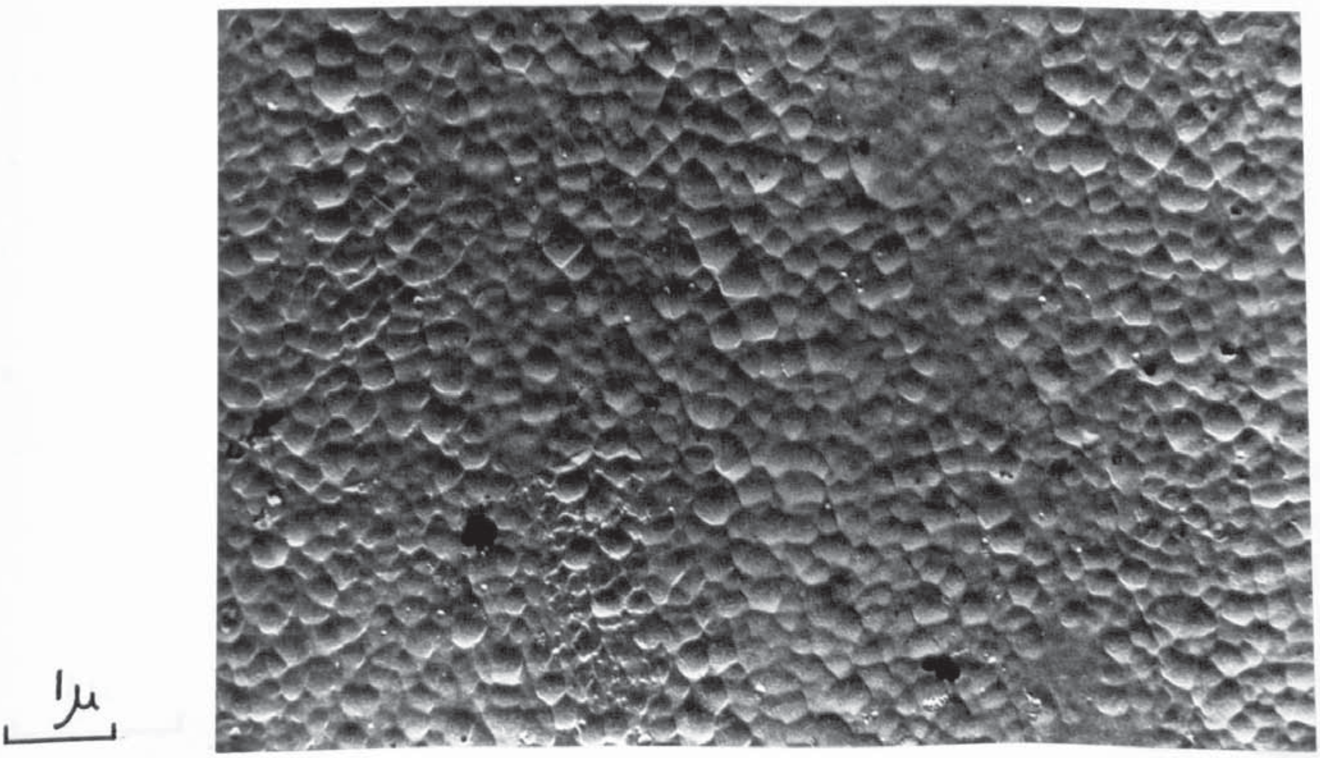


Fig. 4.35. Cold Worked Aluminium Chemically Polished for 4 Seconds.

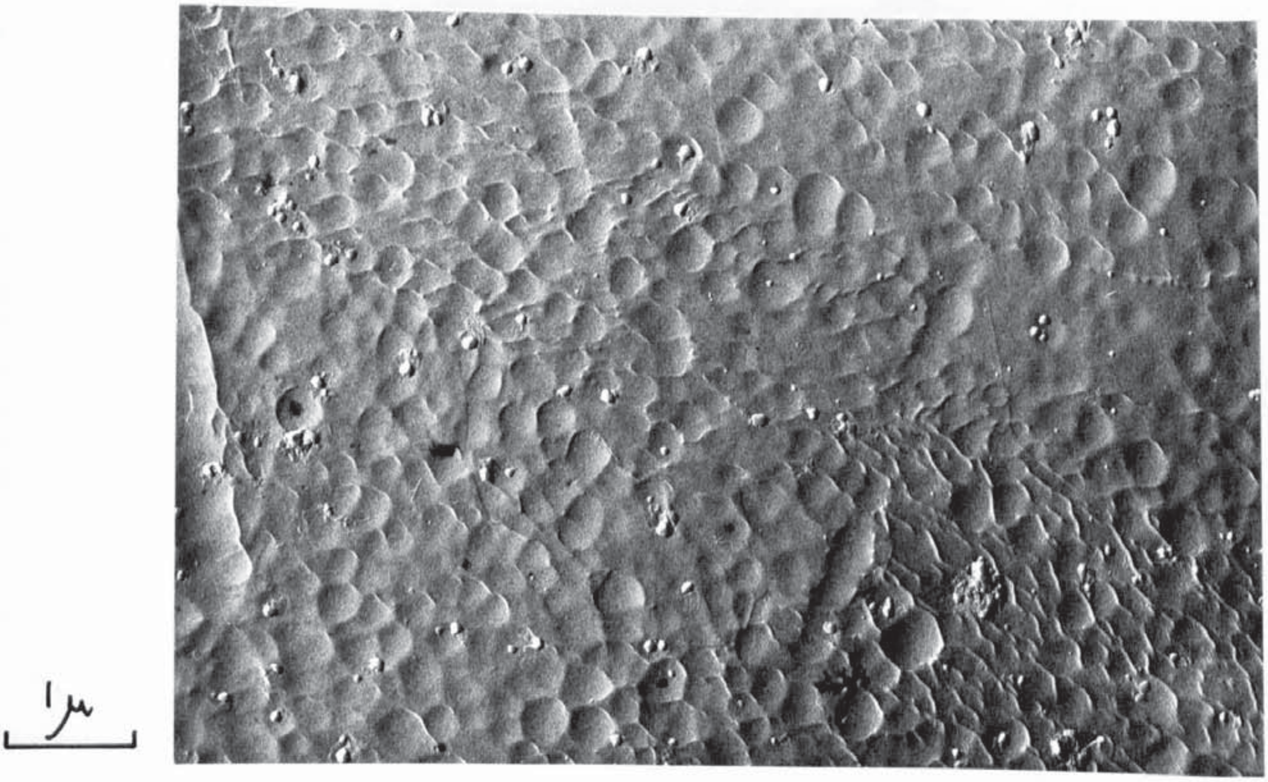


Fig. 4.36. Cold Worked Aluminium Chemically Polished for 6 Seconds.

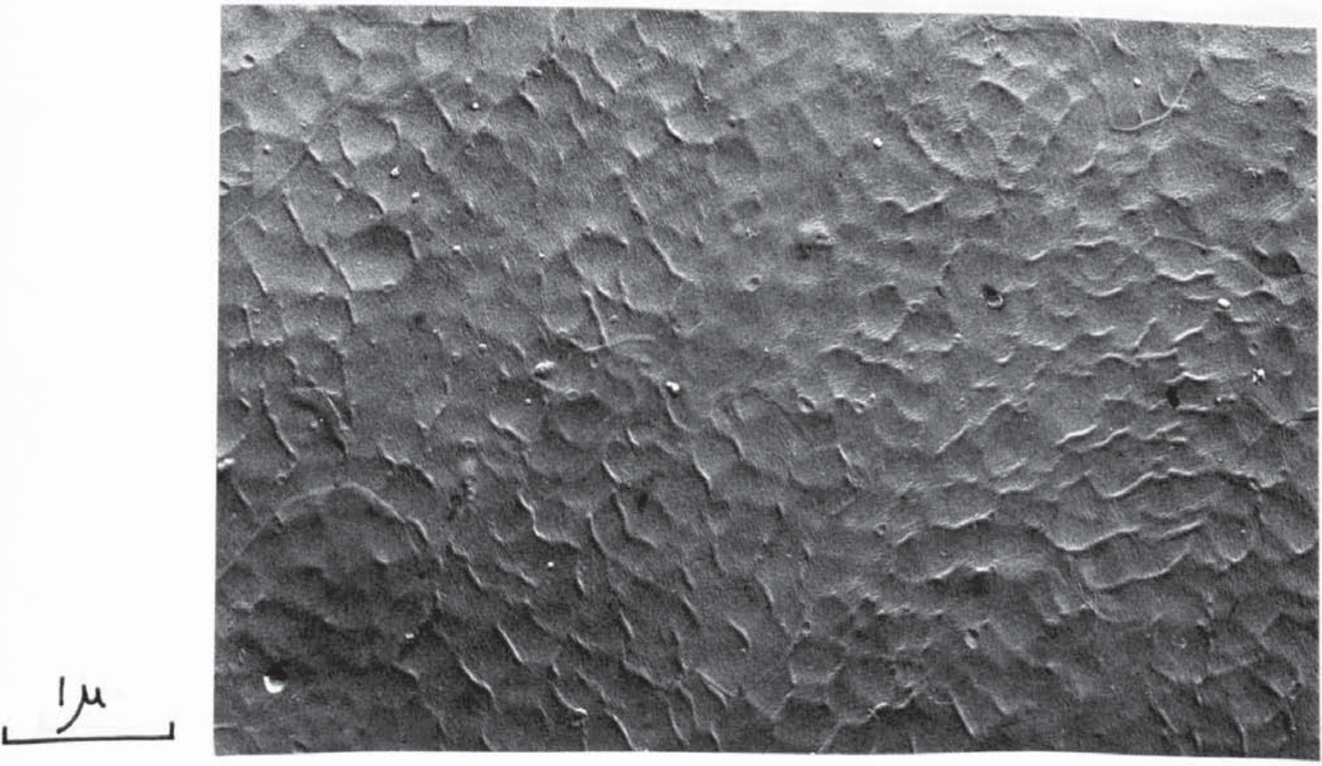


Fig. 4.37. Cold Worked Aluminium Chemically Polished for 10 Seconds.

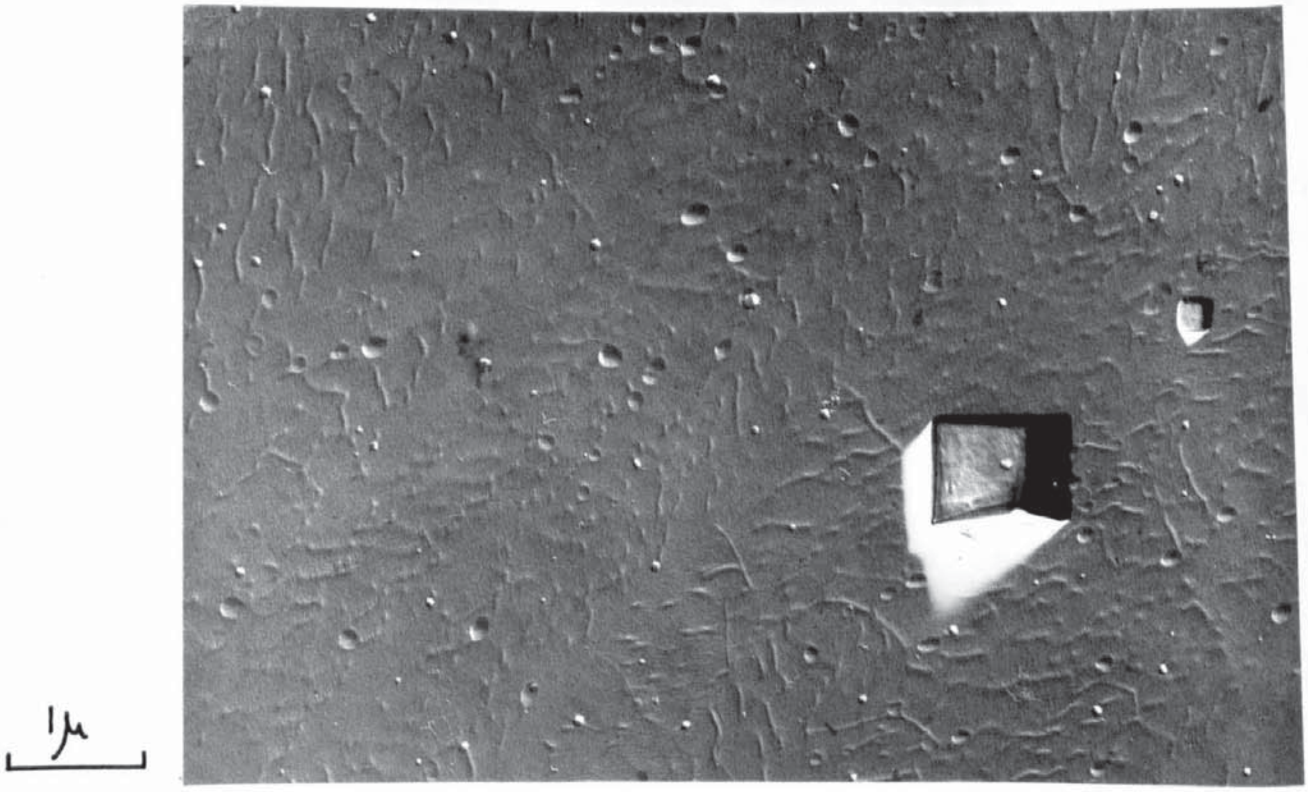


Fig. 4.38. Cold Worked Aluminium Chemically Polished for 20 Seconds.

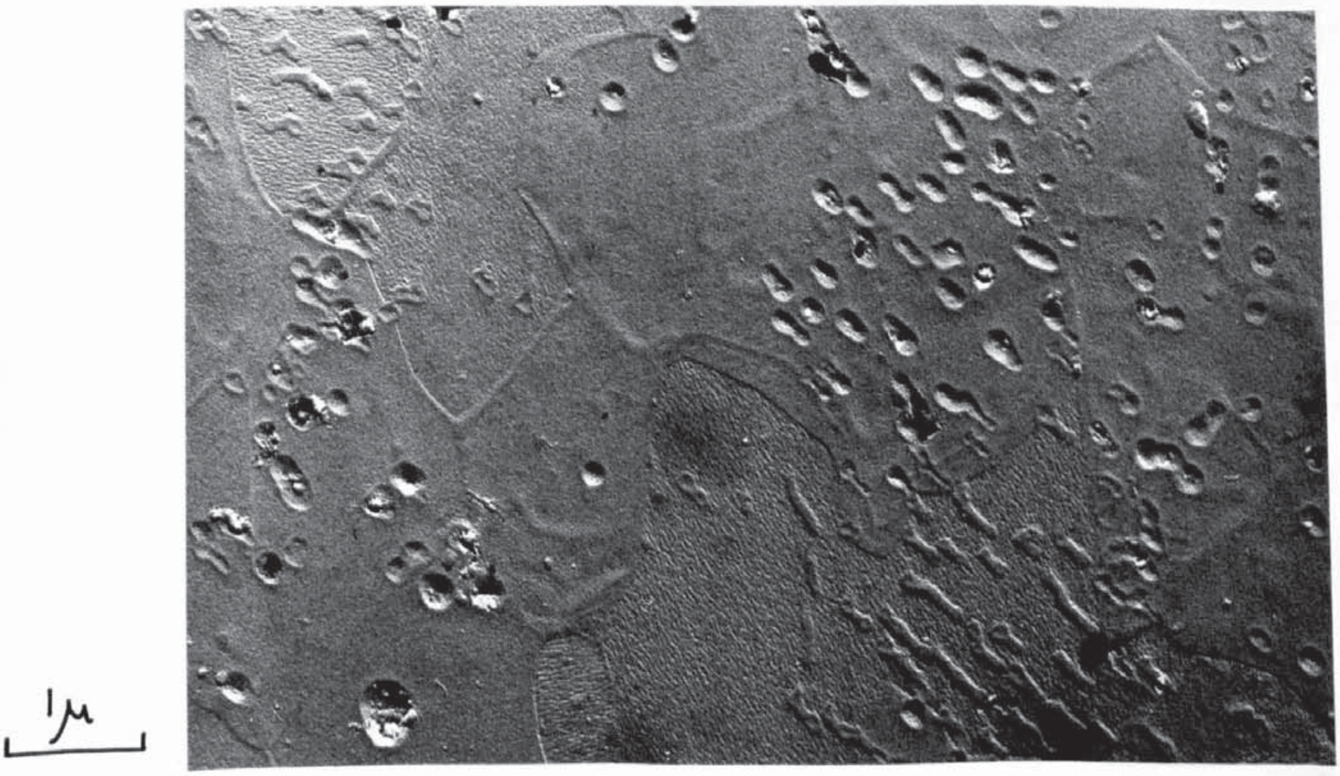


Fig. 4.39. Cold Worked Aluminium Chemically Polished for 30 Seconds.

the polished structure is well established after 30 seconds. It can be seen that the cold worked material has an extremely small grain size, which makes the use of etch pits to determine grain orientation somewhat unsatisfactory. However, it is clear that the usual orientation dependency still applies with these specimens.

The structural features within the grains are the same size as those on the surface of chemically polished annealed material of much larger grain size.

4.5. Weight of Deposited Copper

The amounts of copper deposited on pretreated aluminium specimens during chemical polishing, are shown in Fig. 4.40.

The curve for the weight of copper deposited when the specimens with the annealed, rolled finish, are chemically polished in the same solution, is also shown for comparison.

It can be seen from Fig. 4.40 that the etched aluminium had the most copper deposited during chemical polishing. This was most pronounced with polishing times longer than 30 seconds. The other specimens had a rapid build up of copper during the first 20 seconds of polishing then the rate of deposition tended to decrease with increased polishing time. Both sets of anodised specimens had slightly less copper deposited on them after 30 seconds polishing time, than the normal annealed specimens. The two other types of specimens,

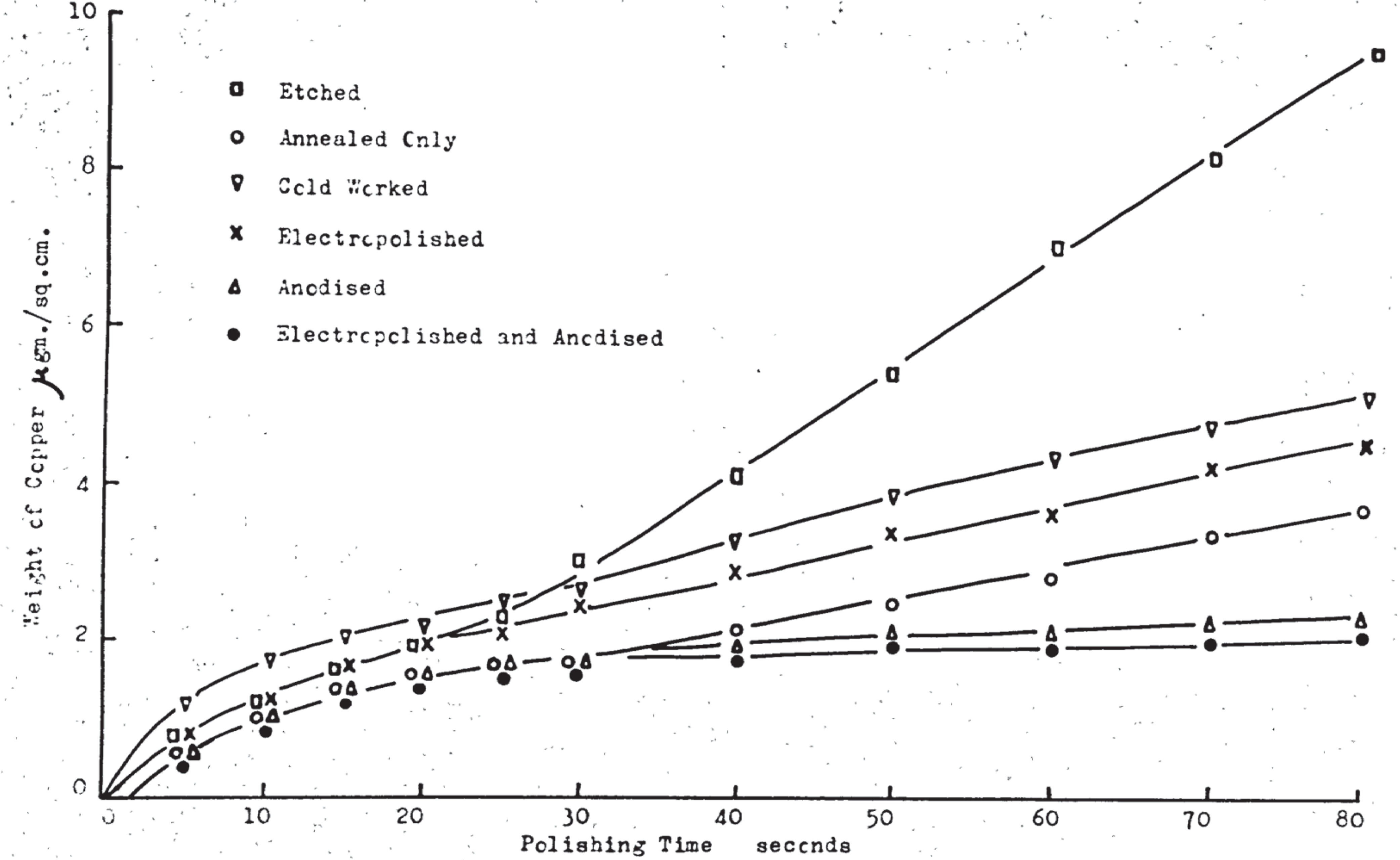


Fig. 4.40. Weight of Copper Deposited vs. Polishing Time

the electropolished and the cold worked materials, had slightly more copper deposited than the annealed specimens.

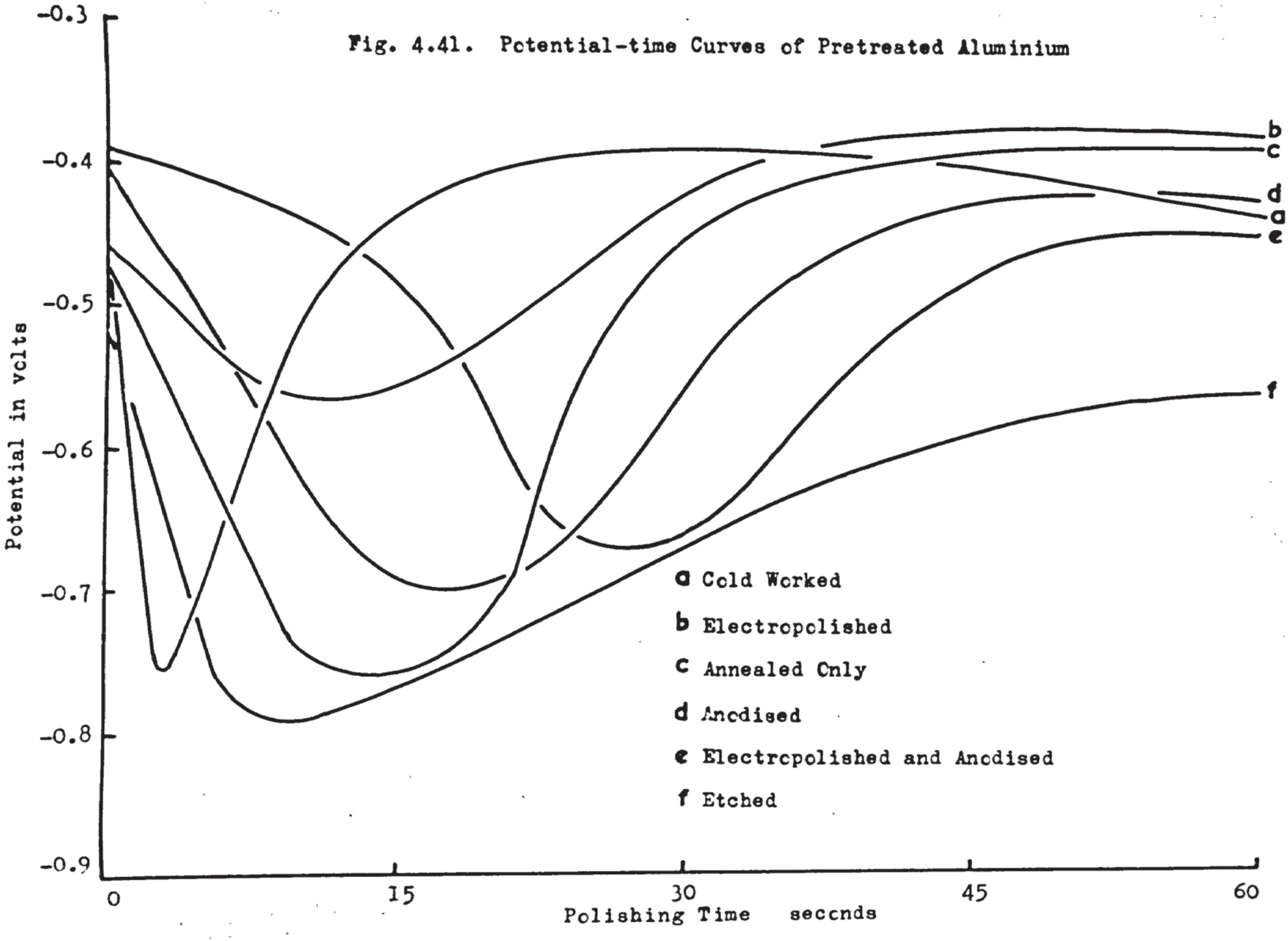
4.6. Electrode Potential Determinations

The changes in electrode potential with polishing time, of pretreated aluminium specimens, are illustrated in Fig. 4.41. Each curve shown is representative of three recordings. The curve obtained previously from the annealed, rolled specimen is included in Fig. 4.41 for comparison.

It is apparent that both sets of anodised specimens have more positive initial potentials than the other samples, due to the presence of the relatively thick compact film. The other specimens recorded initial potentials in the region of – 450 mv. which was similar to that of the annealed specimen.

The effect of polishing time on the potentials of the pretreated specimens is similar to that described previously for the annealed specimens. As before, removal of the original oxide film, however formed, results in a lowering of the potential, which occurs in the initial stage of polishing. There are however, differences in the polishing times at which a drop in potential is observed. This must be related to the soundness of the oxide film on the aluminium prior to polishing. The cold worked specimens show a rapid drop in potential during polishing. The potential of the electropolished and anodised aluminium falls slowly during the

Fig. 4.41. Potential-time Curves of Pretreated Aluminium



initial stage of polishing then drops rapidly after about 20 seconds treatment. The potential of the anodised specimen, however, falls to a minimum after 20 seconds polishing.

The electropolished specimen did not show a large drop in potential during chemical polishing, whereas the potential of the etched specimen falls rapidly then rises to a maximum potential of about - 550 mv., which is somewhat below the maximum potential of the other specimens investigated.

4.7. Discussion

4.7.1. Introduction

When the results obtained in this chapter are compared with those obtained previously using the normal annealed specimens, it is apparent that the effect of the pretreatments is most pronounced in the early stages of polishing. With polishing times longer than 1 minute, there is little difference between the results obtained for the pretreated specimens and the normal annealed specimens, thus only the etching and polishing stages will be considered in this discussion.

It is apparent that the relationship between surface structure and surface quality as described in section 3.9.5. is also exhibited by all the pretreated specimens. In each case, specimens recording low values of specular reflectivity, have surface structures similar to the equiaxed etched structure, whereas specimens which exhibit the polished structure have a high specular reflectivity. The relationship between the amount of copper deposited on the surface and the surface structure obtained is also apparent with the pretreated specimens. It can be seen by comparing Figs. 4.1, 4.2 and 4.40, that at very low amounts of copper deposition, etching results, whereas when the amount of copper increases the specimens are polished. Further increases in the amount of deposited copper eventually result in coarsening of the aluminium surface. As before, high specular reflectivity was obtained when the amount of copper deposited on the aluminium surface was between 2 and 5.5×10^{-6} gm./sq.cm.

The influence of pretreatment of the metal, on the chemical polishing process, appears to either promote or delay the rate of which the characteristic structures are produced. This is due to the fact that each pretreatment process used in this investigation resulted in a modification of the natural oxide film present on the surface of the aluminium.

The implication of this will now be discussed for each set of specimens in turn.

4.7.2. Cold Worked Specimens

These specimens, unlike the others used in this investigation, have not received any surface treatment.

They have however, a worked structure of fine grain size. The fine grain size, together with discontinuities produced in the natural oxide film by working(94,95), explains the rapid formation of the etch structure with these specimens, which is complete after two seconds polishing. As grain boundaries and defects in the oxide are preferential sites for the initial etch pits, these will tend to form rapidly in cold worked material. However, as the many initial etch pits grow laterally, they will soon meet other nucleated etch pits and the network will be rapidly completed. The size of each cell being much smaller than those on the annealed specimens. The small cell size of the etched network indicates the reason for a relatively high specular reflectivity reading for these specimens in the etched condition, compared with the annealed specimens. The subsequent electron micrographs indicate that the removal of the etched structure to produce the polished structure appears to take the same length of polishing time as the normal annealed specimens. Thus it is apparent that the effect of the initial grain size and oxide film becomes insignificant once the etched structure is established and the original oxide film removed.

Electron micrographs taken from polished cold worked specimens show that the features of the polished structure are of a similar size to those obtained on the annealed material, although these latter specimens have a much larger grain size. This gives further confirmation that the polished structure is a surface effect on each particular grain and that the grain size is not important at this stage.

4.7.3. Electropolished Specimens

When the electropolished specimens are chemically polished, the original electropolished structure, observed by replica electron microscopy, is removed very quickly. This indicates that the distance between the elevations and depressions on the electropolished surface is extremely small. This is also indicated by the very high specular reflectivity reading of the electropolished surface. The chemically polished structure subsequently produced, has a larger cell size and is less smooth. This is probably due to the fact that the corrosion cells produced by the heavy metal additions during chemical polishing, are not as uniform as those produced by the applied potential during electropolishing.

The most significant observation with the electropolished specimens, is that during chemical polishing little etching takes place prior to polishing. This is in contrast to the annealed only specimens which show considerable etching in the initial stage of the process. It has been assumed that the etching in the initial stage of chemical polishing is to remove the air formed oxide film, therefore, it is apparent that this is not necessary with electropolished specimens. Several workers(60,96) have detected compact oxide films on aluminium after electropolishing, thus it is probable that the electropolished aluminium already has a smooth surface and oxide film suitable for uniform dissolution during the chemical polishing process. Thus, as the metal surface is already smooth and covered with a compact oxide, little etching takes place and extremely uniform dissolution occurs which does not develop a definite surface structure. The potential-time curves of these specimens, show that there is little drop in potential during the initial stage of chemical polishing. This indicates that the aluminium surface is covered with a compact film throughout the chemical polishing cycle.

As polishing continues it is observed that the structure characteristic of the chemical polishing process is produced. This could be due to the influence of the increasing amount of copper which is deposited on the surface. This would modify the oxide film formed on the surface and produce conditions similar to those operating during normal chemical polishing.

4.7.4. Etched Specimens

The chemical polishing of the etched specimens is markedly effected by the deep etched structure which exists on the surface prior to polishing. The initial polishing stage smoothes the surface as dissolution takes place preferentially at protuberences, particularly those forming the boundaries of the large depressions produced by etching. As smoothing takes place there is a corresponding increase in specular reflectivity, which continues to increase as the characteristic polished structure is formed on the surface. However, as polishing takes place a high concentration of copper is deposited on the surface, which soon results in the surface structure coarsening with a corresponding reduction in specular reflectivity.

4.7.5. Anodised Specimens

The effect of pre-anodising on the chemical polishing of aluminium specimens is to lengthen the treatment time required during the etching stage. This increase in polishing time is presumably the time required to remove the anodised film by chemical dissolution. The time required is longer with the electropolished and anodised specimens than the anodised only aluminium. As the anodised film on the latter specimens is formed on the rolled surface, it will incorporate the defects in the original surface(97,98,99) and will be much less continuous than one grown on a smooth surface. The material which is initially electropolished will however, produce a uniform compact anodic film. This is shown by the differences in the potential-time curves of the specimens. The potential of the anodised only specimen falls gradually to reach a minimum after about 20 seconds polishing. However, the electropolished and anodised specimen shows a slight decrease in potential during the initial stage of chemical polishing, then falls rapidly after about 20 seconds immersion.

The difference in soundness of the anodic films can explain the different modes of dissolution of the specimens during chemical polishing. With the anodised only specimens, dissolution takes place almost immediately and in isolated areas on the surface. Once the anodised film is removed from these areas, the etched structure is produced as usual by the merging of individual etch pits, followed in due course by the polished structure. It is observed that the polished structure is produced in some areas whereas the anodised film remains in adjacent areas.

However, with electropolished and anodised specimens the dissolution appears to be uniform over the anodised film, as initially no structural changes are observed. The dissolution continues until the oxide film finally dissolves, apparently simultaneously over the surface to produce the etched pattern.

It is interesting to note that in both cases dissolution takes place until all the anodised oxide film is removed and the surface is etched. This is in contrast to the electropolished specimens which are only slightly etched during the chemical polishing process. This is to be expected with the anodised only specimens, as the anodised film is not sound and is therefore not thinned uniformly, and so does not provide a smooth surface and oxide film suitable for uniform dissolution. It is also apparent that anodising after electropolishing must modify the compact film remaining after electropolishing, with the result that during chemical polishing, this oxide film, although thinned uniformly is completely removed. Thus these specimens, unlike the electropolished only aluminium, are etched before chemical polishing takes place.

CHAPTER FIVE

FURTHER DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

The results of this investigation indicate that there is a close relationship between electropolishing and chemical polishing, each polishing process consisting of three stages with characteristic surface structures, namely etching, polishing and coarsening.

The surface topography of chemical polished and some electropolished specimens are very similar in form and in size of features during the etching stage.

It is apparent that this structure, which consists of equiaxed cells approximately 0.5 - 1 µm. in size, is produced by the merging of individual spherical etch pits, nucleated at defects and weak points in the original oxide film and not by the presence of subgrains(61) or networks of segregation(67).

There are considerable differences between the respective structures of the specimens in the polished condition. The electropolished structure is extremely fine and regular in appearance, whereas the chemically polished specimens have a somewhat coarser and less regular structure. Both specimens however, have structures which depend on the crystallographic orientation of the aluminium. The chemical polishing structure depends also on the time of polishing and on the concentration of heavy metal in the solution. The dependence of the surface structure upon the amount of copper deposited on the surface has been shown to exist for each polishing solution and for each pretreatment process investigated.

In chemical polishing the deposited copper aids the dissolution of the aluminium for two reasons. First, the potential difference generated between the copper deposit and the aluminium and secondly, because of the lower cathodic polarisation of the evolution of hydrogen on copper than on aluminium (50,97), as hydrogen evolution is very difficult on clean aluminium surfaces.

It is apparent that the difference between the structures of the chemical and electropolished specimens is due to the mode of deposition of the copper particles. In the case of electropolished aluminium, the external potential supplied is uniform over the whole surface, which will lead to an extremely fine and regular surface structure being developed. In the case of the chemically polished specimens, the copper deposition takes place as discrete particles in positions which vary with the grain orientation, thus the potential difference for the polishing process, supplied internally, will vary slightly over the surface of the aluminium.

The morphology of the characteristic polishing structure formed by chemical polishing, can be explained by considering the sites of copper deposition. During the etching stage, the copper particles are deposited on the ridge boundaries. This displacement reaction will occur more readily at these areas, probably because of the more rapid diffusion of copper through the thinner diffusion layer and the greater activity of the aluminium at the peaks, which participate in the displacement reaction. As there is a higher corrosion current density in the vicinity of each deposited copper particle, compared with the rest of the surface, localised dissolution of the aluminium will take place at the ridges. The effect of this dissolution on the $\{100\}$ and $\{110\}$ planes is shown schematically in Fig. 5.1.

It can be seen that there will be a decrease in the scale of the submicro dissolution figures, together with a smoothing of the asperities, both of which are observed by electron microscopy and specular reflectivity results.

The explanation of the different polishing patterns on different grain orientations is not complete at the present time. However, it is probably associated with the relative dissolution rates along each crystallographic plane.

The localised dissolution, discussed above, will produce undercutting of the deposit and further deposition will occur on other asperities. Each deposit will enlarge during polishing, as the amount of copper on the aluminium surface increases and metal is preferentially deposited at cathodic sites. At the same time, the spacing of the surface structure is reduced,

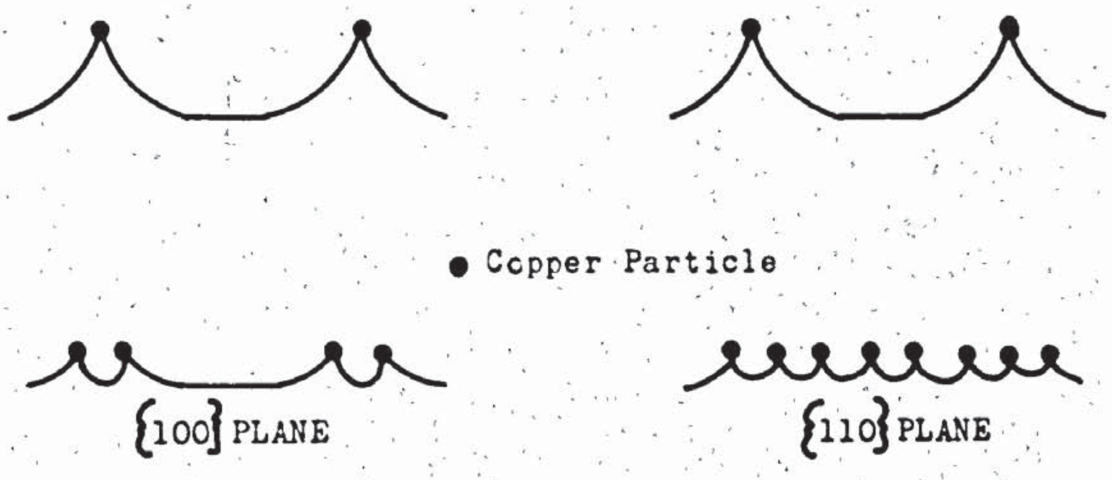


Fig. 5.1. Schematic Cross Sectional View of the Effect of Deposited Copper on the Dissolution of Different Grains of Aluminium.

by the dissolution at the asperities. A stage is reached when the size of the deposited copper particles approach the dimensions of each surface feature, whereupon the copper particles on neighbouring asperities will touch and agglomerate. Electron microscopy examination indicates that this occurs when the copper particles and the surface features are about 0.4 µm. in size.

This agglomeration prevents any further decrease in the scale of the dissolution figures and a deterioration of the surface quality occurs if polishing is continued.

The results obtained during this investigation now permit further discussion on the mechanism by which brightening, that is, the absence of structural etching, is produced during chemical polishing. Experimental work on the mechanism of brightening has been confined to electropolishing, and has produced two different theories, the acceptor theory of Edwards(10) and the solid film theory of Hoar and Mowat(9).

Electrode potential determinations carried out during this investigation indicate that a compact solid film is present on the aluminium surface during polishing. Potential measurements also indicate that the original oxide film on the metal surface is removed in the initial stage of polishing, during which the aluminium is etched. As polishing continues a compact solid film is formed which coincides with the polishing of the surface. After the optimum polishing time is exceeded and the surface coarsens, potential measurements indicate a decrease in the soundness of the compact film. It is also significant that the specimens polished in the solution containing no copper, which are not brightened satisfactorily, do not show an appreciable potential rise during polishing.

The observations of the polishing behaviour of pretreated aluminium specimens favour the compact solid film theory of brightening. This was particularly evident with the electropolished then chemically polished specimens. With these samples there was little initial etching of the surface during chemical polishing. This was in contrast to the other specimens used in this investigation, all of which formed an equiaxed etched cell network of much lower specular reflectivity than the starting material, during the initial stage of chemical polishing.

This can be explained by assuming that the presence of a compact solid film from the electropolishing process, allows metal dissolution during chemical polishing immediately, with no etching. It has been shown that the rate of metal dissolution of the electropolished aluminium during chemical polishing is the same as that for the other specimens which are etched initially. Potential measurements also indicate that the electropolished surface is covered with a compact film throughout the chemical polishing cycle. It is apparent therefore, that the electropolished specimens are able to retain a bright surface, together with appreciable metal dissolution, during chemical polishing, by the immediate presence of a compact film, as proposed by Hoar and Mowat(9) to explain brightening during electropolishing.

It could be argued that the initial smoothness of the electropolished specimens results in a lack of etching during the initial stage of polishing. However, this is unlikely in view of the fact that most of the other specimens used in the investigation had very smooth starting surfaces, particularly the electropolished and anodised specimens, and these were all initially etched during chemical polishing.

With the other pretreated specimens, the effect of increasing the thickness of the original oxide film appears to be merely to delay the initial etching of the metal. The polishing time required to produce etching varies with the soundness of the original oxide film, but in each case the equiaxed cell network is formed in the usual manner. Polishing then takes place in the same way as the untreated specimens, by a smoothing of the etched cell pattern and its replacement by a finer polished structure.

It is observed that during the etching stage appreciable submicro smoothing occurs after an initial roughening of the surface. As it has been shown that no solid film is present on the surface at this time, it is probable that it is the action of acceptor ions, in this case PO_4^{3-}, which restrict the depth of etching. At the start of the polishing treatment the acceptor has access to practically all parts of the surface, so there is no restriction on the development of anodic dissolution and the initial etch pits produced are quite deep. As polishing proceeds, the access of acceptor to the depths of the etch pits is impeded, which delays their development, and the dissolution takes place at other areas on the surface which have a smaller initial potential difference. The deepening of the etch pits is thus replaced by their lateral growth, to produce the cell network. When the cell network is complete, the localised dissolution of the aluminium around the deposited copper ensures a further smoothing of the surface to reduce the difference in height between the ridge boundaries and the cell centres.

Once the etched structure has been established, it is proposed that brightening of the surface is maintained by the presence of a solid film, which acts in a similar manner to that proposed by Hoar and Mowat(9) to explain brightening during electropolishing. Thus it is assumed that brightening is produced by the formation of a compact solid film that permits metal cations to pass into and through it, and finally to leave the film/solution interface at the same rate as they enter it from the metal. This dictates random removal of cations on account of the random arrival of film cation vacancies at the metal/film interface.

The solid film is probably formed by the combined action of the corrosion current density supplied by the deposited copper and the oxidising nature of the nitric acid present in the chemical polishing solutions. The relative importance of these two factors is not clear. Brace and Kape(43) have stated that a certain amount of nitric acid is necessary in a chemical polishing solution for brightening to take place. They concluded that below the optimum nitric acid content, etching occurs, probably because insufficient oxygen ions reach the surface to maintain a stable passive film. Above the optimum content, the film breaks down due to changes in local pH values or to other reactions at the metal/electrolyte interface.

The results of this investigation show that approximately $2\text{-}5.5 \times 10^{-6}$ gm./sq.cm. of deposited copper is necessary on the surface of a specimen for brightening to take place. Below this optimum amount, etching takes place as the galvanic corrosion cells are probably insufficient to produce a stable film. Above the optimum amount, coarsening of the surface occurs as large agglomerated particles of copper build up on the surface and produce high current densities in localised areas.

It was also observed that specimens chemically polished in the solution containing no copper additions had a greater rate of metal removal than those polished in the solutions containing 0.25 and 0.5 gm. of copper per litre. The above results indicate that the presence of the copper in these solutions is to promote the formation of a solid film on the metal surface and reduce the rate of metal dissolution. This is contrary to the increase in the rate of metal removal to be expected in solutions containing copper, due to the presence of galvanic corrosion cells, if no solid films were present.

It is therefore apparent that both nitric acid and copper (or perhaps some other heavy metal addition) are necessary constituents of chemical polishing solutions for brightening to take place.

Conclusions

The conclusions may be enumerated:

1. An extensive study of the properties of aluminium surfaces chemically polished in a phosphoric, sulphuric and nitric acid solution, not previously recorded 'in extenso', has been carried out and explanations suggested for the observed phenomena.
2. There is a clear relationship between the surface structure of the aluminium and thus its surface quality, and the amount

of copper deposited on the surface during polishing. Bright surfaces are only produced when the amount of deposited copper is within a certain range, approximately 2 - 5.5×10^{-6} gm./sq.cm. Super-pure aluminium polished in a solution containing no copper is not brightened satisfactorily for this reason.

3. The deposited copper is in the form of discrete particles which increase in size as polishing takes place. The particles are 0.1 - 0.2 µm. in size shortly after immersion and increase to 5 - 10 µm. during coarsening of the surface.

The copper is deposited on the submicro asperities of the surface during polishing. This promotes a localised dissolution at the asperities, which results in a decrease in the scale of the surface structure and a brighter, smoother surface is produced.

When the copper particles are of dimensions similar to the surface structure (about 0.4 µm.), agglomeration occurs, which prevents any further decrease in the scale of the surface structure.

4. The short chemical polishing cycle observed when aluminium is polished in solutions containing high copper contents is due to the rapid deposition of copper that occurs in these solutions. Aluminium chemically polished in solutions of low copper contents show a slow rate of deposition of copper and therefore have a relatively long polishing cycle.

5. During the initial stage of chemical polishing the aluminium is etched and has a much lower specular reflectivity

than the starting material. The surface structure of the aluminium during the etching stage consists of an equiaxed cell network, each cell being approximately 0.5 - 1 µm. across. This structure is produced by the merging of spherical etch pits, nucleated at defects in the original oxide film.

It is suggested that during chemical polishing the initial etching of the surface is controlled by an "acceptor" mechanism, which results in the lateral growth of the etch pits to form a cell network, rather than their increase in depth.

6. It has been shown that a compact solid film exists on the aluminium surface during the polishing stage of the process. It is suggested that brightening of the surface, which occurs after the initial etch structure is established, is maintained by the presence of a compact solid film which promotes uniform dissolution of the aluminium. The formation of the solid film is assisted by the corrosion current density supplied by the copper present in the polishing solution.

7. Deterioration of the surface quality of the aluminium occurs when long polishing times are employed. This deterioration occurs rapidly when the metal is polished in solutions containing large quantities of copper and more gradually in the solutions containing smaller quantities of copper. The deterioration is caused by the build up of large agglomerated particles of deposited copper on the surface. The high

localised current densities set up by these particles, result in rapid metal dissolution in adjacent areas.

8. Surface treatments of the aluminium prior to chemical polishing, modify the behaviour of the metal during polishing. This effect is only pronounced until the original oxide is removed and the etched cell pattern produced. After which, polishing takes place in the usual manner with the same relationship between surface structure, surface quality and amount of deposited copper.

Recommendations for Further Work

1. Further investigations are required to provide a complete explanation of the surface structures that exist on the surface of chemically polished aluminium. As the polished structures exhibit a unique orientation dependence, it would be valuable to use the techniques in this investigation to study the behaviour of single crystals of aluminium during polishing. The heavy metal deposited on the surface has been shown to modify the surface structure, therefore, another possible approach would be to carry out a study of the current distribution in the area of a galvanic couple.

2. It would be valuable to use aluminium at different stages of chemical polishing to determine the effect of the polished structure on the properties of a subsequent anodic oxide film.

The anodic film often replicates the pretreatment patterns, and it is claimed that pores are nucleated at protuberances of the original surface structure. Therefore, it is likely that the properties of anodic films such as structure, porosity, impedance and reflectivity will be effected by the morphology of the surface structure before anodising.

3. Another investigation, which may have significant commercial application, would be to extend the study of heavy metal additions. It is possible that some heavy metal other than copper may give an improved brightening effect, as there is little information to support the use of copper in preference to other metals. It would also be interesting to include aluminium alloys in this investigation, particularly those with a super-purity base containing individual additions. The results from this would provide much needed information on the effect of the heavy metals residing in the surface of the bulk aluminium during polishing.

REFERENCES

1. S. Wernick and R. Pinner. "The Surface Treatment of Aluminium", Robert Draper, 1964.
2. A.W. Brace. Proc. Amer. Electroplaters Soc., 46, 211 (1959).
3. R. Pinner. Electroplating and Metal Finishing, 6, 401 (1953).
4. P.A. Jacquet. Met. Reviews, 1, 157 (1956).
5. A. Vernet. Ger. Pat. 804,054; 814,984.
6. W.K. Bates and C.D. Coppard. Metal Finishing Journal, 4, 5, (1958).
7. Vereinigte Aluminium Werke. Brit. Pat. 673,776; 893,876.
8. J. Edwards. J. Electrochem. Soc., 100, 223C (1953).
9. T.P. Hoar and J.A.S. Mowat. J. Electrodepositors' Tech. Soc., 26, 7 (1950).
10. J. Edwards. J. Electrochem. Soc., 100, 189C (1953).
11. F. Keller, M.S. Hunter and D.L. Robinson. J. Electrochem. Soc., 100, 411 (1953).
12. T.A. Renshaw. J. Electrochem. Soc., 108, 185 (1961).
13. D.J. Arrowsmith and E.A. Culpan. Unpublished work.
14. M.G. Hollo. 1st International Congress on Metallic Corrosion, p.45, London, 1961.
15. H. Bichsel. Metal Treatment and Drop Forging, 27, 409 (1960).
16. P.A. Jacquet. T. Electrochem. Soc., 69, 629 (1936).
17. J.M. Hughes and E.A. Coomes. Phys. Rev., 55, 1138 (1939)
18. J. Liger. Bull. Soc. Chim. France, 11, 568 (1944).

19. K. Huber. Z. Electrochem., 55, 165 (1951)

20. P.A. Jacquet. Compt. Rend., 202, 402 (1936).

21. W.C. Elmore. J. App. Phys., 10, 724 (1939).

22. W.C. Elmore. J. App. Phys., 11, 797 (1940).

23. A. de. Sy and H. Haemers. Ass. Ing. Liege Congress, Sec. Met., Sous-Sec. Met. Phys., p. 185 (1947).

24. H.F. Walton. J. Electrochem Soc., 97, 219 (1950).

25. M. Halfway. Experientia, 7, 175 (1951).

26. U.R. Evans. T. Electrochem Soc., 69, 652 (1936).

27. C. Wagner. J. Electrochem Soc., 101, 225 (1954).

28. J.F. Nicholas and W.J. McG.Tegart. J. Electrochem Soc., 102, 93C (1955).

29. T.P. Hoar and T.W. Farthing. Nature, 169, 324 (1952).

30. J.A. Allen. Trans. Faraday Soc., 48, 273 (1952).

31. M. Cole. Ph.D. Thesis, Univ. Cambridge (1954).

32. M. Cole and T.P. Hoar. C.I.T.C.E. VIII, p. 158, Butterworths, 1956.

33. E.C. Williams and M.A. Barratt. J. Electrochem. Soc., 103, 363 (1956).

34. E. Darmois, I. Epelboin and D. Amine. Compt. Rend., 231, 1222 (1950).

35. E. Darmois and D. Amine. Compt. Rend., 237, 501 (1953).

36. E. Darmois and I. Epelboin. Bull. Soc. Fr. Elec., 5, 679 (1955).

37. W.A. Marshall. J. Electrodep. Tech. Soc., 28, 27 (1951-52).

38. A. Hickling, W.A. Marshall and E.R. Buckle. J. Electrodep. Tech. Soc., 28, 47 (1951-52).

39. E.S. Hedges. "Protective Films on Metals", p. 122, Chapman and Hall, 1937.

40. A. Hickling and A.J. Rostron. Trans. Inst. Met. Finishing, 32, 229 (1955).

41. R. Pinner. Electroplating and Metal Finishing, 7, 127 (1954).

42. A.W. Brace. Aluminium Development Association, Technical Memo No. 212, 1955.

43. A.W. Brace and J.M. Kape. Aluminium Development Association Conference on Anodising p. 167, Nottingham, 1961.

44. H. Fischer and L. Koch. Metall, 6, 305 (1952).

45. B.A. Scott. Aluminium Development Association Conference on Anodising, p. 201, Nottingham, 1961.

46. A.W. Brace and T.S. de Gromoboy. Trans. Inst. Met. Finishing, 33, 177 (1956).

47. W.R. Meyer and S.H. Brown. Proc. Amer. Electroplaters' Soc., 36, 163 (1946).

48. Light Metals, 15, 348 (1954).

49. Brit. Pat. 687,774; 958,499; 1,145,881.

50. R.C. Porter and S.E. Hadden. J. App. Chem., Lond., 3, 385 (1953).

51. H.P. Goddard. "Corrosion of Light Metals", p. 24, Wiley, 1967.

52. M.J. Frazer and R.D. Langstaff. Brit. Corros. J., 2, 11 (1967).

53. R. Pinner. Aluminium Development Association Conference on Anodising, p. 203, Nottingham, 1961.

54. G.L. Bucknell and G.A. Geach. Nature, 164, 231 (1949).

55. A.F. Brown. Nature, 163, 961 (1949).

56. J. Nutting and V.E. Cosslett. "Metallurgical Applications of the Electron Microscope", p.57, Inst. of Metals, 1950.

57. G.L. Bucknell, G.A. Geach and N.C. Welsh. Research, 5, 289 (1952).

58. P. Bussy. Rev. Met., 50, 629 (1953).

59. N.C. Welsh. J. Inst. Met., 85, 129 (1956-7).

60. M.G. Hollo. Acta Met., 8, 265 (1960).

61. M.S. Hunter and D.L. Robinson. Trans. Amer. Inst. Min. Met. Eng., 197, 717 (1953).

62. P.B. Hirsch. Progress in Metal Physics, 6, 236 (1956).

63. E.W. Perryman. J. Inst. Met. 85, 567 (1956-7).

64. N.C. Welsh. J. Inst. Met. 85, 567 (1956-7).

65. R. Phillips and N.C. Welsh. Phil. Mag., 3, 801 (1958).

66. H. Bichsel. Metal Treatment and Drop Forging, 27, 319 (1960).

67. F.B. Cuff and N. J. Grant. J. Inst. Met. 87, 248 (1959).

68. L. Young. Acta Met., 5, 711 (1957).

69. D.H. Napier and J.V. Westwood. Metal Ind., 76, 123 (1950).

70. A. Hone and E.C. Pearson. Metal Progress, 53, 363 (1948).

71. W.J. McG.Tegart and R.G. Vines. Trans. Aust. Inst. Metals, 5, 107 (1952).

72. W.J. McG.Tegart. "The Electrolytic and Chemical Polishing of Metals", Pergamon Press, 1959.

73. U.R. Evans and H.A. Miley. Nature, 139, 283 (1937).

74. S.C. Britton. Brit. Corros. J., 1, 317 (1966).

75. T.P. Hoar, D.C. Mears and G.P. Rothwell. Corrosion Science, 5, 279 (1965).

76. "Anodic Oxidation of Aluminium and its Alloys". p. 47, Aluminium Development Association, Information Bulletin 14, 1961.

77. G. Hass. J. Optical Soc. America, 39, 532 (1949).

78. J.W.A. Scholte and W.Ch. Van Geel. Phillips Research Repts., 8, 47 (1953).

79. M.A. Barrett and A.B. Winterbottom. 1st International Congress on Metallic Corrosion, p.657, 1961.

80. Albright and Wilson Ltd., Metal Finishing Division Data Sheet, 1967.

81. J.B. Mohler. "Finishing of Aluminium", p. 51, Reinhold Publ. Corp., 1963.

82. J.D. Edwards. Proc. Amer. Soc. Test. Mat., 40, 959 (1940)

83. J.E. Lewis and R.C. Plumb. Int. J. App. Radiation and Isotopes, 1, 33 (1956).

84. G.E. Gardam. Metal Finishing, 49, 61 (1951).

85. B.A. Scott. J. Sci. Instruments, 37, 435 (1961); Aluminium Development Association Conference on Anodising, p. 55, Nottingham, 1961.

86. C.S. Barrett. "Structure of Metals", p. 192, McGraw-Hill, 1952.

87. C.S. Barrett and L.H. Levenson. Trans. A.I.M.E., 137, 76 (1940).

88. H.M. Tomlinson. Phil. Mag., 3, 867 (1958).

89. E. Johnson. "Organic Reagents for Metals", Vol. I, Hopkin and Williams, 1955.

90. U.R. Evans. "The Corrosion and Oxidation of Metals", p. 899, Arnold, 1960.

91. M.J. Pryor. Kaiser Aluminium and Chemical Corporation, Interim Project Report No. MSPR 57-44, 1957.

92. R. Lattey and H. Neunzig. Metalloberflache, <u>9</u>, 97 (1955).

93. T.P. Hoar. Corrosion Science, <u>7</u>, 341 (1967).

94. C. Edelenau and J.G. Gibson. 1st International Congress on Metallic Corrosion, p. 73, London, 1961.

95. E.M. Zarecki. Zhur. Priklad. Khim. <u>24</u>, 477 (1951).

96. H. Reather. Metaux et Corrosion, <u>25</u>, (1950).

97. R.B. Mears and R.H. Brown. Ind. Eng. Chem., <u>33</u>, 1001 (1941).

98. M.J. Dignam. J. Electrochem Soc., <u>109</u>, 192 (1962).

99. D.A. Vermilyea. Acta Met., <u>2</u>, 476 (1954).

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