ELECTRODEPOSITION ON ALUMINIUM
AND ITS ALLOYS

by

JAMES WILLIAM GOLBY

A thesis submitted for the degree of Doctor of

Philosophy of the University of Aston in Birmingham.

October 1981.

The University of Aston in Birmingham

TITLE Electrodeposition on Aluminium and its Alloys.

AUTHOR James William Golby.

DEGREE Ph.D.

DATE October 1981.

SUMMARY

Aluminium alloys S1C, NS4, HE9, LM25 and the 'difficult' zinc-containing U.S. specification alloy used for automobile bumpers (X-7046), have been successfully electroplated using pretreatments which utilized either conventional immersion, elevated temperature or electrolytic modified alloy zincate (M.A.Z.) deposits. Satisfactory adhesion in excess of 7·5 KN m^{-1} was only achieved on X-7046 using an electrolytic M.A.Z. pretreatment. The limitations of simple zincate solutions were demonstrated.

Growth of deposits was monitored using a weight loss technique and the morphology of the various deposits studied using scanning electron microscopy. The characteristics of a specific alloy and processing sequence selected had a significant influence on the growth and morphology of the M.A.Z. deposit. These all affected subsequent adhesion of electrodeposited nickel. The advantages of double-dip sequences were confirmed.

Superior adhesion was associated with a uniform, thin, fine grained M.A.Z. deposit which exhibited rapid and complete surface coverage of the aluminium alloy. The presence of this preferred type deposit did not guarantee adhesion because a certain degree of etching was essential. For a satisfactory combination of alloy and M.A.Z. pretreatment, there was a specific optimum film weight per unit area which resulted in maximum adhesion. An ideal film weight of 0·06 ± 0·01 mg cm^{-2} was determined for S1C. Different film weights were required for the other alloys due to variations in surface topography caused by pretreatment. S1C was the easiest alloy on which to achieve high bond strength.

Peel adhesion was not directly related to tensile strength of the alloy. The highest adhesion value was obtained on S1C which had the lowest strength of the alloys studied. The characteristics of the failure surfaces after peeling depended on alloy type, adhesion level and pretreatment employed.

Plated aluminium alloys exhibited excellent corrosion resistance when appropriately pretreated. The M.A.Z. layer was not preferentially attacked. There was a threshold value of adhesion below which corrosion performance was poor. Alloy type, pretreatment and coating system influenced corrosion performance. Microporous chromium gave better corrosion protection than decorative chromium.

KEY WORDS : ALUMINIUM
IMMERSION DEPOSITS
ELECTRODEPOSITION
ADHESION
CORROSION

Contents

Contents

Contents

Contents

Contents

List of Tables

List of Tables

List of Tables

List of Figures

List of Figures

List of Figures

List of Figures

List of Figures

List of Figures

List of Figures

List of Figures

List of Figures

List of Figures

CHAPTER ONE

1. LITERATURE REVIEW

1.1. Introduction

Aluminium ores have a forecast life of at least three hundred years and new finds are frequently made. In addition aluminium is the lowest cost non-ferrous metal. Aluminium and its alloys have a number of useful engineering properties, for instance low density, high specific strength, high thermal and electrical conductivities and reasonable corrosion resistance. There is therefore considerable incentive to use aluminium and its alloys in a variety of applications. However the application range of these materials can be further widened by electrodeposition to alter the surface characteristics.

Aluminium was first electroplated by Marino (1) in 1913. Although a number of new techniques have been introduced, the pretreatment operations required for the various alloys of aluminium remain complex. Commercially pure aluminium is relatively easy to electroplate but there is no universal pretreatment for aluminium alloys. The reason for this is the wide variety of surface characteristics of the alloys. For instance, special interest is currently being shown by the automotive industry in high zinc aluminium alloys which have a high specific strength, and are being considered for the manufacture of car bumpers. These specialized alloys are posing many problems to the commercial electroplater.

1.2. Problems with Electroplating on Aluminium

West (2) listed the following difficulties associated with plating aluminium :

1. The presence of a 'troublesome' oxide film.
2. Its amphoteric nature.
3. The position of aluminium in the electrochemical series, Table I, leading to immersion deposits in plating solutions.
4. The wide range of aluminium based alloys which are also often just termed 'Aluminium'.
5. The expansion coefficient of aluminium relative to other metals, Table II, can result under certain conditions in bond rupture between substrate and electrodeposit.
6. On the surface of polished aluminium there is frequently a 'Beilby' layer of flowed or amorphous material possibly incorporating grease or oil impregnated oxide.

Aluminium is an extremely reactive element and has a high affinity for oxygen. It has a rapidly self-healing oxide that offers some protection from corrosion and when electroplated, reduces adhesion between coating and substrate. However using conventional pretreatments, preventing exposure of the oxide free surface to the atmosphere is difficult. Aluminium is amphoteric, and so readily dissolves in most acids and alkalis, and is strongly

TABLE I. ELECTROLYTIC POTENTIALS OF SEVERAL METALS AGAINST PURE ALUMINIUM.

Data from West (2). Based on "Electrode-Potentials of Metals" Turnbull and Davies, Ministry of Aircraft Production R. and M. No. 1901 (6,204) A.R.C. Technical Report H.M.S.O. 1942.

TABLE II. MEAN COEFFICIENT OF LINEAR EXPANSION OF THE COMMON METALS PER °C.

Metal	x 10^{-6}

Data from West (2)

electropositive. Therefore aluminium is attacked in many plating solutions and undesirable immersion deposits are often formed by metallic displacement. Jongkind (3) stated it is necessary to modify the aluminium surface before plating. For instance, this is achieved when the oxide is replaced by an immersion film that provides a suitable base for further electrodeposition.

1.3. Classification of Methods for Plating on Aluminium

There are three distinct operations common to commercial electroplating processes :

1. Cleaning.
2. Surface preparation.
3. Electrodeposition.

Proposed pretreatment processes can be classified broadly as follows :

1. Direct plating.
2. Preparation by anodic or chemical oxidation.
3. Mechanical roughening.
4. Chemical roughening.
5. Use of immersion films.

1.3.1. Direct plating

Zinc,(4-7) copper,(8,9) nickel,(10-13) chromium,(14-16) and tin,(17) have been electroplated directly onto aluminium from specialized baths.

In the U.S. Work (4) reported a direct zinc plating method in 1931. However in the U.K. the most commercially accepted zinc process was the Vogt process developed in 1929 for the plating of holloware. Technical details of the Vogt method were not published until the 1950's (5,6) and a typical processing sequence is shown in Table III. It is claimed to be superior to the immersion technique as a uniform zinc layer is more easily produced on relatively non-homogeneous aluminium alloys. The Vogt process also has numerous disadvantages :

1. Problems can arise with the precurser thin zinc and brass layers.
2. The heat-treatment involves dejigging and so hinders automation.
3. Heat-treatment and nickel finishing increase cost.
4. It is not possible to use a bright nickel deposit onto which chromium can be directly plated.

TABLE III. PROCESSING SEQUENCE FOR NICKEL PLATING ON ALUMINIUM USING THE VOGT DIRECT PLATING PROCESS.

1. Cathodic alkali clean at room temperature using approx. 7V for 4 min.
2. Water rinse.
3. Dip in solution containing equal volumes of concentrated nitric and sulphuric acids at room temperature for 4 s.
4. Water rinse.
5. Cathodic alkali clean at room temperature using approx. 7V for 20 s.
6. Water rinse.
7. Zinc plate at 0·5 A dm^{-2} for 20 s at room temperature in a solution containing :

sodium hydroxide	10·5g/l
zinc chloride	0·5g/l
sodium cyanide	0·5g/l

8. Brass plate at 1·0 A dm^{-2} for 8 s at 30°C in a solution containing :

sodium cyanide	31g/l
copper acetate	13g/l
sodium bisulphite	13g/l
zinc chloride	13g/l
sodium carbonate	9g/l

9. Water rinse.

10. Nickel plate at 1·5 A dm^{-2} in a Watts type solution at 40 °C containing typically :

nickel sulphate	250g/l
magnesium sulphate	100g/l
boric acid	25g/l
sodium chloride	5g/l

11. Water rinse.
12. Heat treat at 230 °C for 30 min. to develop necessary adhesion. (This also serves as an indication of adhesion as formation of blisters reveals poor bonding).
13. After stoving the dull nickel should be finished and reactivated before chromium plating.

Data from Wallbank.(6)

Improvements to the Vogt process were suggested by Ore(7,18) and the B.N.F. modification,(19) which included a zincating stage, dispenses with the heat-treatment.

Schwartz and Newkirk (20) recently reported a method to apply a Cu-Zn alloy, selected using the Hume-Rothery alloy theory,(21) which is crystallographically coherent with the substrate. A biased A.C. voltage was employed whereby oxide removal was aided during the positive cycle, with plating in the negative cycle. This method is not used commercially as it is difficult to scale up.(22)

1.3.2. Preparation by anodic or chemical oxidation

1.3.2.1. Anodic oxidation

There are various commercial techniques involving thickening the oxide layer by anodizing prior to electroplating.(23-29) Electrolytes including phosphoric acid (Eytal process),(30) oxalic acid (Krome-Alume process),(27,31,32) sulphuric-hydrochloric acid, sodium carbonate and others (33-36) are used.

In conventional plating the oxide on aluminium is a disadvantage. However an anodic oxide coating formed under controlled conditions can provide a sound base for electrodeposition. The anodic oxide consists of the 'barrier' and 'porous' layers. Pores in the layer act as keys for the electrodeposit and are preferably large. Pore dimensions depend on electrolyte type and operating conditions.

The commonly used phosphoric acid electrolytes produce the largest pores. The original 1930's method (30) involved anodizing in a 30% phosphoric acid solution, followed by cathodic treatment in an alkaline bath which rendered the anodic coating more receptive to the plated layer. Bunce,(37) Wittrock,(33) Bengston,(38) and others (39,40) suggested process modifications. There may be problems when plating from strongly alkaline solutions if the anodic layer dissolves before being totally covered with electrodeposit.(37) This is solved by applying a copper strike from a pyrophosphate bath before the main plating operation. All phosphoric acid anodizing processes are sensitive to alloy composition, and treatment of above 99·3% purity aluminium is difficult. Different electrolyte concentration, pretreatment and operating conditions are often recommended for each alloy type. The technique is suitable only for a few sand cast and no common die casting alloys. The anodic coating characteristics are influenced by current density and so large and complex shaped components are awkward to process. Additionally, formation of an anodic coating requires a relatively high voltage power source and this increases process cost and complexity. Furthermore when plating to improve electrical conductivity the presence of the dielectric anodic coating is undesirable.(38)

In recent work on electroplating of a copper-silver alloy on to anodized surfaces, of the various electrolytes investigated only phosphoric acid was found satisfactory for the anodic treatment. Using the other electrolytes a further etching stage was required to ensure suitable keying of electrodeposit. (41)

Levinson and Mondolfo (42) reported a procedure where, following anodic oxidation, direction of the current flow is reversed and metal deposition accomplished in the same bath.

1.3.2.2. Chemical oxidation

To avoid the cost of equipment required for anodizing, chemically produced aluminium oxide coatings have been used as a base for electrodeposition, e.g. the M.B.V. process.(43) This technique involves post-plating heat-treatment to develop adhesion and is not commercially important.

1.3.3. Mechanical roughening

Sand blasting was one of the first methods used commercially for preparing aluminium for electroplating. However the surfaces produced are generally too rough and sand blasting may distort thin sheet.(44) Work (45) indicated sub-standard bonding usually results.

A proprietary process,(46) involving removal of the oxide and surface roughening by blasting with a slurry of quartz crystals and water, has been used commercially prior to hard chromium plating. The component is introduced into the plating solution still slurry-covered to prevent reoxidation. Meyer-Rassler (47) was however unable to reproduce the results claimed.

1.3.4. Chemical roughening

Chemical roughening or etching can be used as an alternative to mechanical methods to prepare the surface. Work (45,48) developed methods used commercially in the 1930's based on acid dips containing varying amounts of a metal ion, e.g. nickel, iron or manganese. Using 'high' metal content dips surface roughening is also accompanied by formation of a metallic immersion film. Chemical roughening produces etch pits having correct undercut shape, so that the electrodeposit is keyed to the substrate. Although etching is critical and requires considerable skill it is claimed many alloys can be successfully processed. Most alloys have a recommended procedure because each type usually poses specific problems. A post-plating heat-treatment can improve bond strengths. Chemical roughening has similar disadvantages to mechanical roughening as the etched surfaces may be too rough to be smoothed by typical thicknesses of decorative levelling nickel. Although there are several etching techniques,(44, 49-58) no single method has proved totally successful.

1.3.5. Use of immersion films

Immersion films, used as a pretreatment prior to plating aluminium are deposited by a displacement reaction. For instance chemically active aluminium dipped in a copper sulphate solution tends to establish a potential, relative to the solution, greater than that required to deposit copper. Thus aluminium has displaced copper ions from the solution and aluminium has dissolved from sub-microscopic regions. After a few minutes action essentially ceases when the substrate is covered by a film of copper.

Aluminium has such a high negative potential that when placed in most plating solutions, immersion deposits are formed. Typically these are non-adherent and unlikely to provide a suitable base for further plating. However under favourable conditions satisfactory immersion films can be deposited from various solutions.

Immersion processes for producing adherent metallic films on aluminium must incorporate two essential constituents : a salt of a metal such as zinc which is more noble than aluminium and an aggressive anion capable of removing the oxide layer without dissolving the underlying metal.(59) Heiman (60) found the ability of anions to remove the oxide decreases in the order, OH^-, F^-, SiF_6^{2-}, BF_4^{2-}, PO_4^{3-} and Cl^-. Only hydroxyl and fluoride ions removed the oxide at a suitable rate and OH^- is most widely employed in the zincate process.

The immersion films utilized as pretreatments for electroplating of aluminium and its alloys are broadly grouped into processes based on deposits of :

1. Zinc
2. Tin
3. Others

1.3.5.1. Zinc immersion processes

Zinc pretreatment has proved the most successful process in general.

The most important method of applying a zinc immersion deposit involves using as alkaline zincate solution. This technique is studied in detail in this thesis and is discussed further in later sections.

An acid solution containing fluorides and additional agents was developed in 1942 by Perner.(61) Heiman (60) used acid zinc immersion solutions containing zinc sulphate and hydrofluoric acid, or zinc fluoroborate, at room temperature. Heiman found films formed from these solutions gave equal or better adhesion than comparable zinc deposits produced from solutions of zinc oxide and sodium hydroxide. Currently however the most successful zinc immersion solutions are not fluoride based.

Another method of pretreatment, the 'Alcoa 661 process',(62,63) has been developed which differs significantly from all former techniques. A zincate immersion step is used to remove the aluminium oxide and then coat the work with zinc. The zinc coating is then dissolved in a nickel plating solution followed by nickel electrodeposition on the oxide free aluminium. The dissolution of zinc is monitored by measuring the electrode potential difference and plating started when a pre-determined voltage is reached. This still experimental process has the additional advantage of being cyanide free.

1.3.5.2. Tin immersion processes

Tin immersion deposits and tin strikes deposited electrolytically, have been used for pretreatment of aluminium and its alloys. The use of tin immersion films received little attention until Jongkind,(3) Poll (64) and others reported the use of stannate solutions in the late 1960's. Prior to this, most deposition of tin was as electroplate to serve as the final finish for certain applications.(49,59,65-79) Tin was electrodeposited from solutions based on stannous chloride,(68-73) sodium and potassium stannate,(49,65-67,73-76) and stannous sulphate-fluoride.(60,77-79) Stannate solutions have since been used for both electrolytic and ordinary immersion tin pretreatments.(80-83)

The most important tin immersion preparatory process is the stannate based, proprietary 'Alstan 70' treatment.(3,84-92)

A typical processing sequence using the stannate immersion process is shown in Table IV. The acid dip is crucial as it should produce a uniform oxide layer. The acid dip therefore is often formulated specially for specific aluminium alloys. A major difference between stannate and zincate processes is that the work is not rinsed following the stannate immersion treatment. The function of the stannate dip is to remove the oxide layer and 'activate' or 'condition' the surface and then protect the bare metal as the part is transferred 'live' into the electrolytic bronze bath. Jongkind (3) claims a non-continuous immersion tin film is produced that suggests the bronze layer is plated directly on to aluminium.

TABLE IV. PROCESSING SEQUENCE FOR NICKEL PLATING ON ALUMINIUM USING THE STANNATE IMMERSION PROCESS.

Data from Jongkind.(3)

* Other acid mixes may be used for different alloys.

Plated aluminium, pretreated by the stannate process is claimed to have better corrosion resistance than that which has been zincate pretreated as the zinc film is susceptible to lateral attack.(3) While this criticism may apply to the early simple zincate solutions it is not necessarily true of more recent improved formulations. Furthermore the stannate process appears more sensitive to alloy type.

Beyer (93) described an electrolytic variation of the Alstan process designed to give increased uniformity of response where the conventional process fails to achieve satisfactory performance.

While the zincate process is used widely in the U.K. the stannate process is preferred in the U.S.A.

1.3.5.3. Other immersion processes

Immersion films of nickel,(48) copper,(94-96) iron,(97) silver,(98) cadmium, mercury and lead have found limited use for preparation of aluminium and its alloys for electroplating. However none have achieved commercial success.

1.4. The Zincate Immersion Process

The use of immersion films as a pretreatment was one of the first approaches to electroplating aluminium. At present in the U.K. most electroplating on aluminium and its alloys utilizes a preparatory zinc layer applied from an alkaline zincate type solution. The immersion zincate processes are easily operated, require no extra equipment and need relatively little control apart from regular additions to compensate for operating losses. However they are not completely universally applicable.

1.4.1. History and development of the zincate immersion process

The first alkaline zincate immersion bath was patented in the U.S. by Hewitson (99) in 1927. In the 1930's zinc immersion procedures were used in Germany by Altmannsberger,(100) and Elssner,(101) in Britain by Braund and Sutton,(102) and in Russia by Lainer and Orlova.(103) A modified version of the original solution was patented by Korpium (104) in 1939 and Perner (61) in 1942 and extensive work has since continued.

The original and simplest zincate solution comprised zinc oxide (100g/l) dissolved in excess sodium hydroxide (525g/l). The alkaline sodium hydroxide dissolves the surface oxide followed by slight dissolution of the exposed aluminium and deposition of a 0·8 - 4·0 μm thick zinc film.(97) The oxide is prevented from re-forming by the zinc film which provides a suitable base for further electrodeposition.(106) This is referred to as the simple zincate immersion process and Table V illustrates a typical processing sequence.

However the zincate process was not widely used until considerably later when work was reported by Bengston,(38) Meyer, (106-107) Ehrhardt and Guthrie,(108) Bullough and Gardam,(109) Heiman,(60) Keller and Zelley (110-112) and Bailey.(113) More recently,

TABLE V. PROCESSING SEQUENCE FOR NICKEL PLATING ON ALUMINIUM USING THE SIMPLE ZINCATE IMMERSION PROCESS.

Data taken from Such and Wyszynski.(105)

* Other acid mixes may be used for various alloys of aluminium.

Note. The use of a double zincate dip is often advantageous. This necessitates the repetition of stages 4 to 7 employing possibly shorter immersion times.

contributions were made by Saubestre and Morico,(114) and significant research undertaken by Such and Wyszynski.(105,115,116)

Investigations have increased the effectiveness and versatility of the zincate process, by modifying zincate solution formulation and adapting pretreatment prior to zincating to yield a superior type deposit.

1.4.1.1. Variations of the zincate solution

There were beneficial effects when small additions of copper (104,117,118) and others (105,118,119) were added to the standard simple zincate (S.Z.) solution. Complexing agents, typically cyanide (117,118,120) and tartrate,(119) were used to retain these metals in solution.

Chloride,(119) nitrate (112) and sulphate (38) ions have also resulted in a limited improvement. An improved modified alloy zincate (M.A.Z.) type solution is used at present.

1.4.1.2. The double-zincate immersion technique

An important development to the zincate process was the 'double-dip' technique devised by Korpium.(104) This is used for most aluminium alloys apart from commercial purity material where inhomogeneity can result in a considerable variation of activity over the surface during zincating. This results in the formation of a non-uniform immersion deposit that when over-plated may produce a coating prone to blistering.(3) This problem is overcome using a double-zincate immersion whereby the first zincate deposit is stripped in 50% nitric acid (102,109,114,121) and a further zinc film deposited by re-zincating. It is believed the first zincate dip selectively reacts with the most active regions. Removing this film exposes a surface of more uniform activity upon which, during re-zincating, a finer grained and thinner deposit forms.(122)

1.4.1.3. The ultrasonic zincate immersion technique

This further processing modification was first described by Forbes and Ricks.(123) Ultrasonic agitation of a S.Z. solution, and subsequent plating solutions has been used in the electroplating of aluminium bus bars.(123,124) Initially the zincate solution is operated as an electrolytic cleaner. The ultrasonic vibrations prevent dislodged contaminants from re-depositing during cleaning and also remove any non-adherent zinc that is subsequently formed. Although this technique is claimed to produce a superior type deposit, it is not widely used.

1.4.2. Theory of the zincate immersion process

1.4.2.1. Mechanism of immersion film deposition from zincate solution

Bullough and Gardam (109) stated that in S.Z. solution at room temperature, the following chemical reaction occurs :

$$3Na_2ZnO_2 + 2Al + 2H_2O \longrightarrow 2NaAlO_2 + 3Zn + 4NaOH$$

However in the absence of zinc the reaction is :

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

This was considered an electrochemical reaction because hydrogen can be produced at different locations from where the aluminium dissolves and may be represented as follows :

$$Al + 3(OH)^- \longrightarrow Al(OH)_3 + 3e^- \longrightarrow (AlO_2)^- + H_2O + H^+ + 3e^-$$
$$\longrightarrow (AlO_2)^- + H_2O + \tfrac{1}{2}H_2 + 2e^-$$

The discharge of hydrogen, which may disrupt the zinc film, only occurs if the surface is of sufficiently low over voltage. They claimed that ideally a monomolecular layer of zinc should form. However this behaviour was not observed on typical heterogeneous alloys which contain surface imperfections, e.g. microconstituents, grain boundaries and flowed layers. Thus local differences in potential are established and it was believed the zinc film deposited by such electrolytic action was unsatisfactory.

More recently Straumanis and Brakss,(125) Streicher (126) and Petrocelli (127) confirmed that the dissolution of aluminium in alkaline solution is electrochemical in character.

Wernick and Pinner (122) listed the basic reactions in zincate solution under normal conditions as :

Anodic : $Al + 3OH^- \longrightarrow Al(OH)_3 + 3e^-$

$Al(OH)_3 \longrightarrow (AlO_2)^- + H_2O + H^+$

Cathodic : $H^+ + e^- \longrightarrow H \longrightarrow \frac{1}{2}H_2 \uparrow$

They indicated there may be hydrogen evolution at cathodic areas, though at the high overpotential of zinc this is usually unimportant. Dirkse (128) had indicated the zincate ion in strongly alkaline solution was probably in the form, $Zn(OH)_4^{2-}$, and therefore deposition of zinc could be expressed as :

Cathodic : $Zn(OH)_4^{2-} \longrightarrow Zn^{2+} + 4OH^-$

$Zn^{2+} + 2e^- \longrightarrow Zn$

However the reactions that occur in a zincate solution containing additives are more complex. For example, when ferric chloride and sodium potassium tartrate are present it is stated that nine aluminium atoms pass into solution for every zinc atom deposited.(129,130)

1.4.2.2. Formation of the zincate immersion film

The initial formation characteristics of the immersion deposit are important because the adhesion between the zinc and aluminium surface will influence the adhesion of any subsequent electrodeposit.

Bullough and Gardam (109) suggested adhesion between the zinc film and aluminium was affected by the degree of epitaxy between deposit and substrate. Although no experimental evidence was reported, they quoted orientations of zinc which could be expected on the aluminium principal planes exposed by etching.

Lashmore (130,131) found that the dissolution of aluminium in zincate solution is a sensitive function of the crystallographic orientation of the substrate. Zinc deposited from zincate solutions, with or without additives present, initially formed thin semi-continuous films epitaxial with the 99·999% aluminium substrate. Further growth continued in the form of larger separate crystallites which maintained the epitaxial relationship. The zinc epitaxial relationships were summarized as follows :

$$\mathrm{Zn} : (0001)\ \langle 10\bar{1}0\rangle\ //\ \mathrm{Al} : (100)\ \langle 010\rangle,$$
$$\mathrm{Zn} : (0001)\ \langle 11\bar{2}0\rangle\ //\ \mathrm{Al} : (1\bar{1}0)\ \langle 111\rangle,$$
$$\mathrm{Zn} : (0001)\ \langle 11\bar{2}0\rangle\ //\ \mathrm{Al} : (111)\ \langle 1\bar{1}0\rangle.$$

The adhesion of zinc to aluminium was thought to be aided by the low energy epitaxial boundaries between the zinc and the aluminium. Zincate films grew in a similar way on aluminium alloys. The highly deformed surface usually present on polished or machined components, was found to interfere with epitaxial phenomena.

1.4.3. Developments in zincate solution formulation

Since the first highly viscous S.Z. solution consisting of ZnO (100g/l) and NaOH (525g/l) was patented, many workers (109, 110,115,132) have investigated the influence of solution composition.

Keller and Zelley (110) found increasing the sodium hydroxide content of S.Z. solution decreased the initial rate of film deposition, Fig. 1.

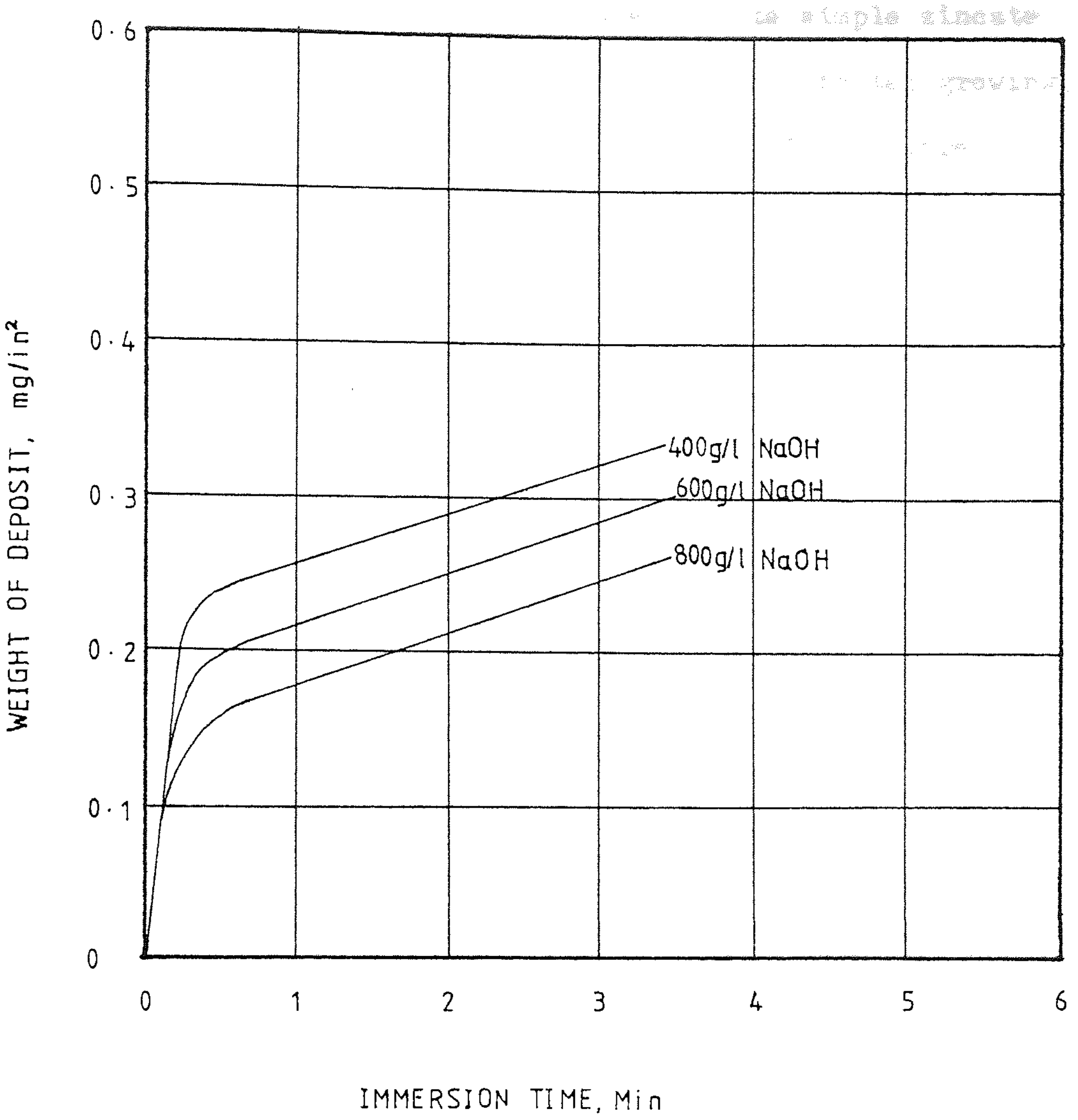


Fig 1. The effect of sodium hydroxide content of concentrated simple zincate (C.S.Z.) solution on the weight of zinc immersion deposit formed on commercial aluminium (2S) sheet at 21°C. (After Keller and Zelley).(110)

0·1 mg/in^2 = 0·0155 mg/cm^2

For composition of the alloy see Table IX.

Investigations (110,113-115) indicated dilute simple zincate (D.S.Z.) solutions yielded deposits which were faster growing, coarser and less compact and continuous than from a more concentrated type solution.

Bailey (113) studied the characteristics of films deposited from various S.Z. baths. From a D.S.Z. solution containing ZnO (5g/l) and NaOH (45g/l), thicker, larger grained deposits with a 'tree-like' structure believed to be single crystals were obtained. Finer grained, more compact deposits were produced using a concentrated simple zincate (C.S.Z.) solution containing ZnO (100g/l) and NaOH (500g/l). Bailey calculated the crystal size from the D.S.Z. solution to be theoretically one hundred times that from the C.S.Z. solution. Bailey attempted to correlate electrodeposit adhesion with S.Z. solution composition and concluded that the concentrations for optimum adhesion were : ZnO (40-50g/l) and NaOH (400-450g/l). Under conditions associated with good adhesion the S.Z. deposit was always covered with a thin film of zinc hydroxide.

Other studies have also indicated there is a lower limit to S.Z. solution concentration below which adhesion is usually poor.(105,115,116)

Such and Wyszynski (105) found that film growth from C.S.Z. solution was more dense and uniform than the random and irregular growth produced using D.S.Z. solution. Using either type of solution they obtained a rapid rate of film growth which resulted in excessively thick deposits. Film growth proceeded by nucleation at a limited number of sites and filamental zinc crystals were formed. The bonding of an electroplated coating to this type of film would be poor, due to the relatively few adhesion sites and inherent mechanical weakness of the dendritic crystals.

Numerous modifications have been made to the basic S.Z. solution to aid formation of a more satisfactory, fine grained uniform and adherent type deposit.

Braund and Sutton (102) found small additions of sodium stannate to the S.Z. solution produced improved deposits with the added benefit that there was no hydrogen evolution. This discovery resulted in the development of the stannate immersion solution described previously.

Bullough and Gardam (109) found the tartrate ion, added as sodium potassium tartrate to a D.S.Z. solution containing ZnO (5g/l) and NaOH (10g/l), prevented precipitation of zinc hydroxide and resulted in a superior deposit on certain alloys.

Korpium (104) found that the addition of copper, as potassium copper cyanide, and sodium sulphite to a C.S.Z. solution containing ZnO (80g/l) and NaOH (400g/l), improved the adhesion of various electrodeposits on zincated aluminium.

West (2) indicated that copper ions in the zincate solution reduced the rate of zinc deposition and made the process more controllable.

The Alumon process (133) utilizes additions of copper to the zincate solution to control film formation.

Zelley (112,134) claimed the three modified zincate solutions shown in Table VI gave superior results. Small amounts of ferric chloride in conjunction with the tartrate ion improved deposit adhesion. Sodium nitrate present in the dilute solutions limited film weight. Solutions 2 and 3 were recommended for plating complex shaped components, where rinsing and 'drag-out' would pose problems. Solution 3 was a compromise between dilute and concentrated formulations to give the large zinc reserve needed for high volume production with only slightly increased drag-out.

Wyszynski (115) stated that the two major modifications required to improve the S.Z. type solution were :

1. The solution should be complexed to prevent rapid film growth.
2. Film growth should be arrested at a certain thickness to prevent subsequent mechanically weak, filamental growth.

For commercial acceptability this modified zincate solution should also satisfy the following requirements :

1. It must produce good adherent zinc deposits on any aluminium alloy.

2. While the deposit produced must be thin, coverage must be complete, i.e. vertical growth discouraged and rapid nucleation encouraged.
3. The solution should be dilute to minimize drag-out and carry-over problems and enable more rapid penetration of blind holes and crevices.
4. The processing cycle, including pretreatments and after-treatments, must be as short as possible.
5. Solution composition and processing cycle must be compatible with the main plating cycle so the dangers of cross-contamination are minimized.
6. The process should be simple and the working parameters objective rather than subjective, the evaluation of the results of the treatment being based on independent test methods.
7. The presence of metals inserted or attached to the aluminium should not influence adhesion and the inserts should themselves be adherently plated.
8. The solution efficiency should be predictable by analysis and solution composition correctable after analysis.
9. The solution must be economical, and both chemically and physically stable during operation and during storage.

TABLE VI. MODIFIED ZINCATE SOLUTIONS PROPOSED BY ZELLEY.

Solution composition

Data from Zelley.(112,134)

Such and Wyszynski (105) found the presence of nickel in the zincate solution beneficial in promoting adhesion of nickel plated directly on to the zinc immersion film. Additions of copper to the modified solution were also found useful for zincating certain alloys. However excess quantities of copper in solution caused unsatisfactory adhesion. Metal additions were maintained within a range of concentration and the ratios between the metals kept within certain limits.(105)

Metal additions are usually retained in solution using complexing agents such as cyanide (117,118,120) and tartrate.(119)

Cyanide anion concentration has been shown to affect electrodeposit adhesion.(105)

Bengston (38) obtained improvements when zinc oxide was partially or totally replaced by zinc sulphate. A typical solution containing zinc sulphate comprised of zinc sulphate (354g/l) and sodium hydroxide (525g/l). Copper,(104,117,118) nickel,(105,118) iron,(119) tin or lead may be added to act as activators plus chelating and/or complexing agents.

The benefits of the sulphate ion were confirmed by Such and Wyszynski.(105) However they obtained equally good results by partially or totally replacing the sulphate with chloride or nitrate as also indicated by Zelley.(112,119,134)

The work of Such and Wyszynski resulted in the formulation of the proprietary modified alloy zincate (M.A.Z.) solution called 'Bondal'.(135) This contains :

Nickel sulphate ($NiSO_4.6H_2O$)	30g/l
Zinc sulphate ($ZnSO_4.7H_2O$)	40g/l
Sodium hydroxide	106g/l
Potassium cyanide	10g/l
Potassium hydrogen tartrate ($KHC_4H_4O_6$)	40g/l
Copper sulphate ($CuSO_4.5H_2O$)	5g/l
Ferric chloride ($FeCl_3.6H_2O$)	2g/l

This complexed, dilute zincate based solution yields a superior zinc-alloy film comprising approximately 86% zinc, 8% copper and 6% nickel.(105,115) However the nickel content of the film increases with time. It is believed the growing surface of the deposit is gradually poisoned with nickel and that this eventually arrests film growth.(105,115) Further grain refinement is achieved by adding a small amount of ferric chloride which inhibits growth of acicular crystals from the uniform, fine grained crystal matrix. Improved levels of adhesion were obtained using the M.A.Z. rather than S.Z. type solution, Table VII. A typical processing sequence using M.A.Z. solution is shown in Table VIII.

First introduced in 1961, in the U.K. the Bondal process has become the most commercially important technique for plating a range of aluminium products with a variety of electrodeposits.

TABLE VII. COMPARISON OF ADHESION OF DULL NICKEL ELECTRODEPOSIT TO ALUMINIUM BUS BAR STOCK AFTER VARIOUS ZINCATE PRETREATMENTS.

Solution composition	Reference	Adhesion

Data from Wyszynski.(115)

1 lb/in = 0·175 KN/m

TABLE VIII. PROCESSING SEQUENCE FOR NICKEL PLATING ON ALUMINIUM USING THE MODIFIED ALLOY ZINCATE IMMERSION PROCESS.

Data from Such and Wyszynski.(105)

* Other acid mixes may be used for various alloys of aluminium.

Note. Use of a double dip is often advantageous. This necessitates the repetition of stages 4 to 7 employing possibly shorter immersion times.

1.4.4. Factors affecting the characteristics of the zincate immersion film

Apart from zincate solution formulation, the growth and properties of the immersion deposit are also influenced by the precise conditions of pretreatment, alloy type and zincate solution temperature.

1.4.4.1. Influence of pretreatment

Thorough cleaning and suitable etching and conditioning of the aluminium is required prior to satisfactory zincating. Specific pretreatment effectiveness depends on alloy type and condition.

Bullough and Gardam (109) reported that film growth from S.Z. solutions was affected by etching and pretreatment.

Keller and Zelley (110) illustrated that the specific cleaning and etching operations prior to immersion in a C.S.Z. solution affected the weight of film deposited, Fig, 2.

Zelley (112) indicated that pretreatment influenced the potential difference between aluminium and zinc in solution, and therefore affected the nature of zinc deposited.

Furthermore the major development in zincate pretreatment, the double-dip technique, was adopted because it produced improved film characteristics.

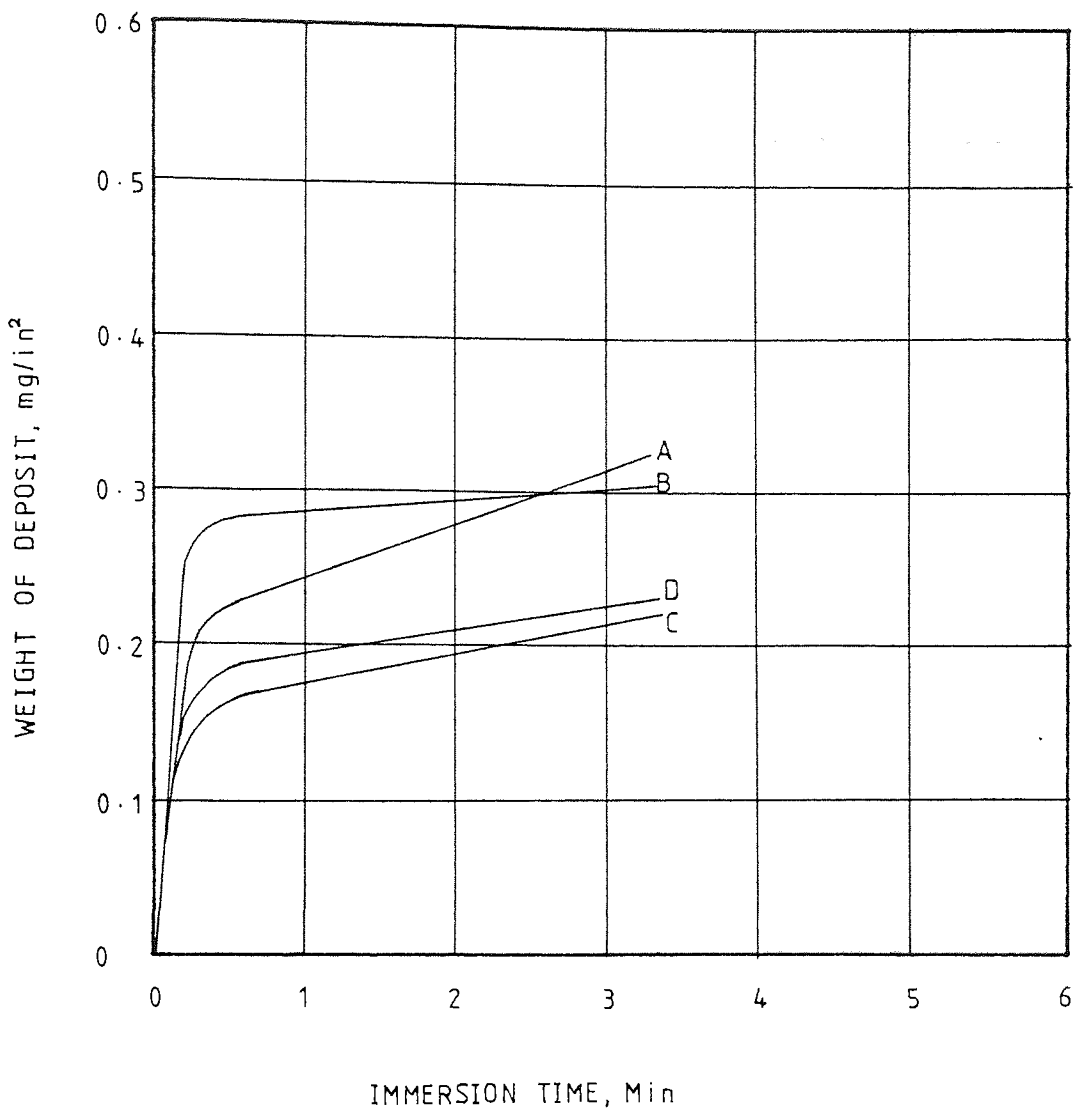


Fig 2. The effect of different pretreatments on the weight of zinc immersion deposit from concentrated simple zincate (C.S.Z.) solution on commercial aluminium (2S) sheet.

A: carbonate-phosphate cleaner plus zincate dip;

B: as A but cleaning followed by 25% sulphuric acid etch;

C: as A but double zincate dip; D: phosphoric-nitric acid chemical polishing solution (Alcoa R5 bright dip) plus zincate dip. (After Keller and Zelley).(110)

0·1 mg/in² = 0·0155 mg/cm²

For composition of the alloy see Table IX.

1.4.4.2. Influence of alloy type

The alloying elements in aluminium alloys may be present :

1. In solid solution in the aluminium.
2. As microparticles of the elements.
3. As particles of intermetallic compounds with aluminium or other alloying elements.

Each alloy may have a characteristic response to a particular pretreatment and furthermore the surface of a specific alloy may not respond uniformly to pretreatment.

Many studies (38,110,113,132,136) have found that alloy composition affected S.Z. film thickness.

Keller and Zelley,(111) observed that the rate of film deposition from a C.S.Z. solution often varied on different alloys, Fig.3. They believed this was the result of inherent differences in the solution potential characteristics of the alloys, Table IX.

Such and Wyszynski (105) indicated adhesion of electrodeposited nickel to alloys pretreated using an M.A.Z. solution was influenced by alloy composition and heat-treatment, Table X. M.A.Z. deposit characteristics were affected by alloy microstructure and surface behaviour. For specific alloys electrodeposit adhesion was reduced at areas rich in certain alloying constituents because of incomplete film development.

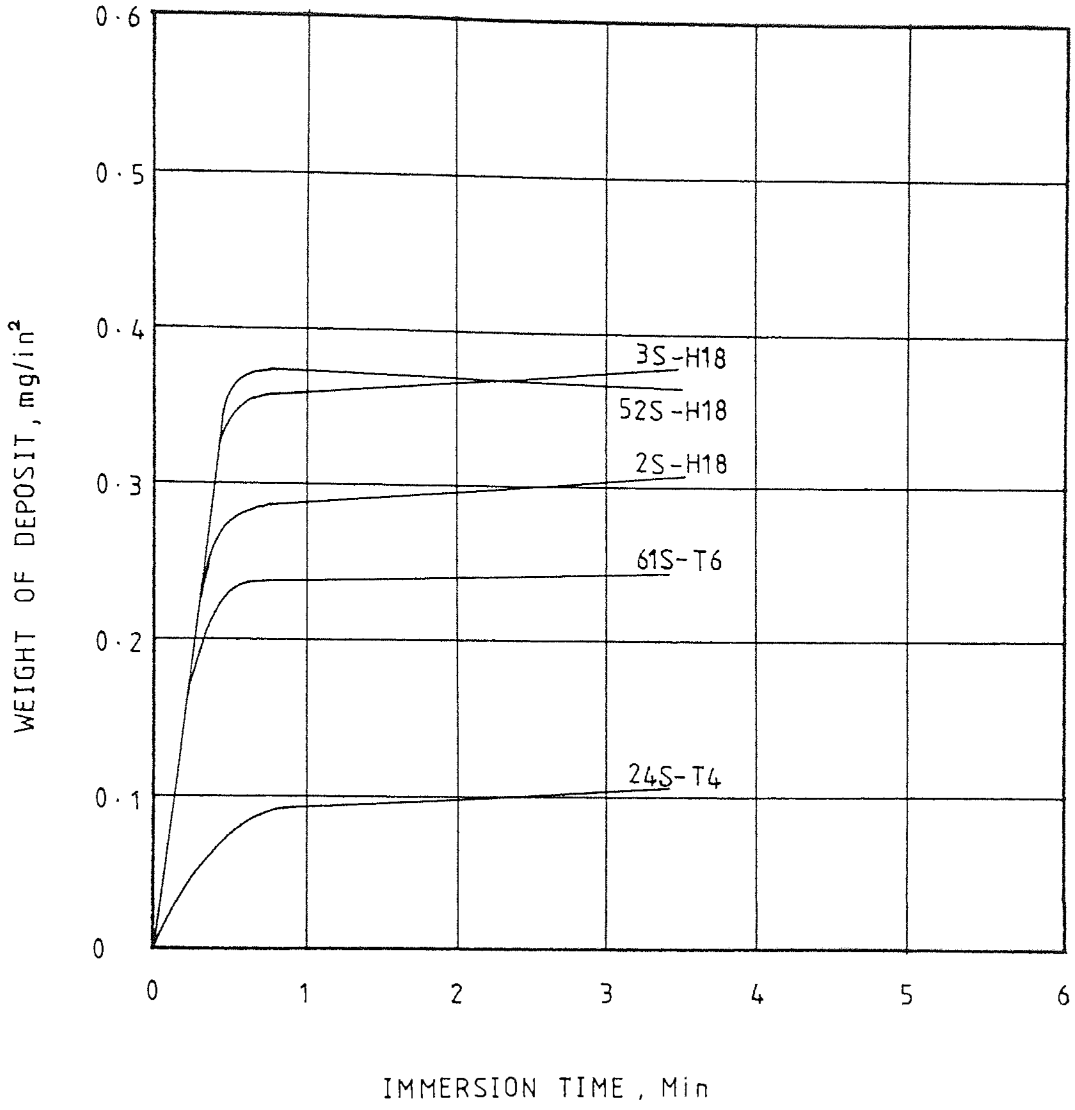


Fig 3. The weight of zinc immersion deposit from concentrated simple zincate (C.S.Z.) solution obtained on different wrought alloys using the same pretreatment. (After Keller and Zelley).(110)

0·1 mg/in² = 0·0155 mg/cm²

For composition of the alloys see Table IX.

TABLE IX. SOLUTION POTENTIALS OF SOME ALUMINIUM ALLOYS AND OTHER METALS IN NORMAL SODIUM CHLORIDE SOLUTION CONTAINING 0·3% HYDROGEN PEROXIDE.

Alloy or metal	Composition %	Solution potential V

The aluminium alloys numbered according to BS:1470 are given in brackets.

Data from Keller and Zelley.(111)

TABLE X. ADHESION OF DULL NICKEL ELECTRODEPOSIT TO VARIOUS ALUMINIUM ALLOYS AFTER PRETREATMENT USING THE MODIFIED ALLOY ZINCATE IMMERSION PROCESS.

Alloy type	Main alloying elements %			Peel
	Copper	Magnesium	Silicon	lb/in

The LM alloys are numbered according to B.S:1490, the S1B alloy according to B.S:1470 and the HE alloy according to B.S:1476 (single values are maxima for impurities).

M = As cast. W = Solution heat-treated.

WP = Solution and precipitation heat-treated.

Data from Such and Wyszynski.(105)

1 lb/in = 0·175 KN/m

1.4.4.3. Influence of zincate solution temperature

Keller and Zelley (110) illustrated the initial rate of deposition from a C.S.Z. solution was increased by raising the solution temperature, Fig.4. Higher temperatures, promote the formation of generally undesirable thick deposits.

Using a similar solution at room temperature Bailey (113) obtained good adhesion with a 1-3 min immersion but although at 85°C adhesion was good after 1 min, it was poor after 3 min. At -6°C a 20 min immersion was required.

With a M.A.Z. solution Such and Wyszynski (105) observed film weight increased with temperature and that behaviour was complex and dependent upon alloy type, Fig.5.

Therefore it is crucial that the zincate solution is operated within the recommended temperature range. A proprietary solution such as Bondal (135) is formulated for room temperature operation where close control over film weight is possible.

1.4.5. Procedures used for plating on aluminium and its alloys using the zincate immersion process

Typical processing sequences for plating aluminium using the S.Z. and M.A.Z. immersion processes are shown in Tables V and VIII respectively. Before zincating it is important that cleaning and etching pretreatments accomplish the following :

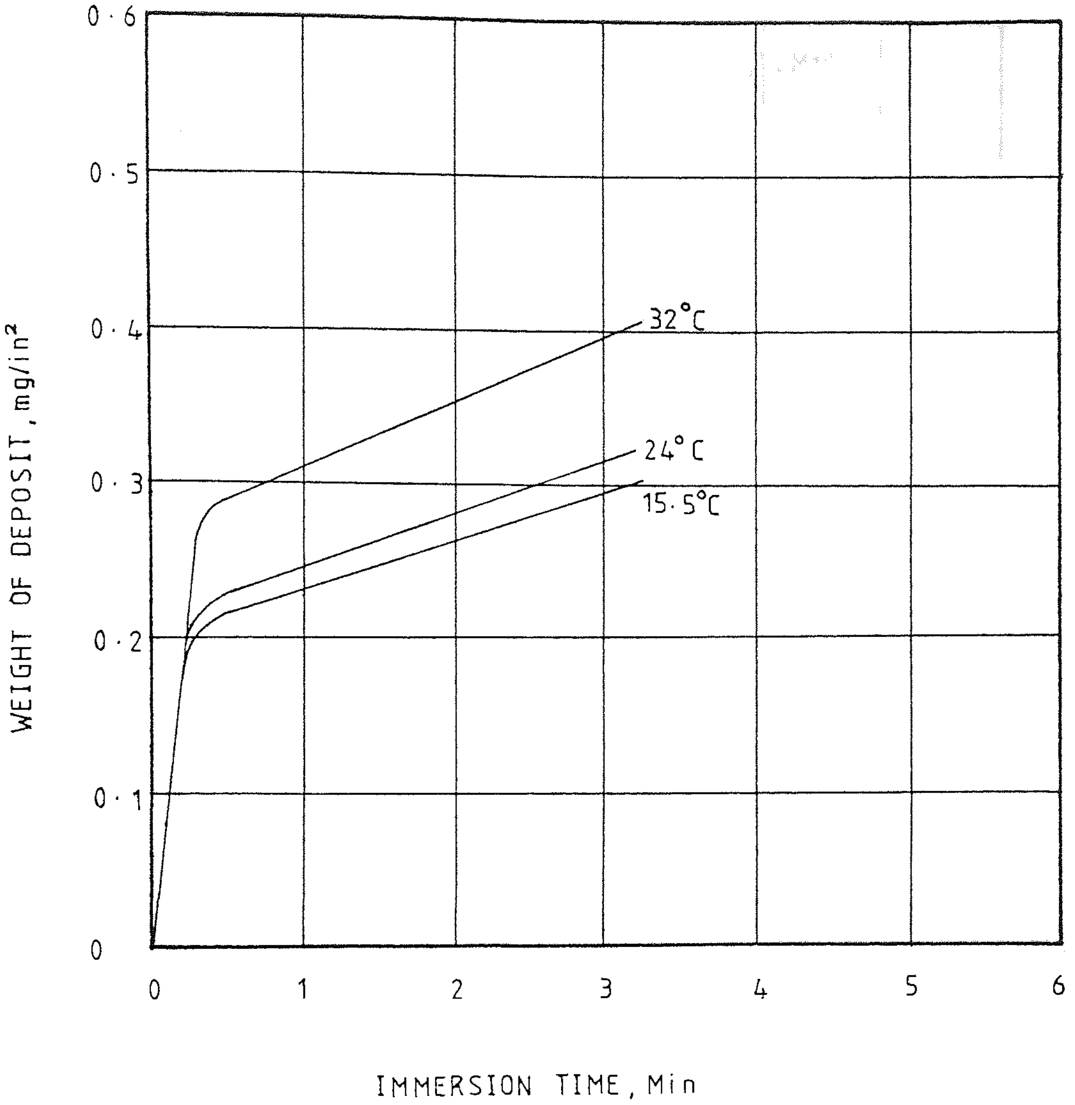


Fig 4. The effect of temperature of concentrated simple zincate (C.S.Z.) solution on the weight of zinc immersion deposit on commercial aluminium (2S) sheet. (After Keller and Zelley).$^{(110)}$

0·1 mg/in^2 = 0·0155 mg/cm^2

For composition of the alloy see Table IX.

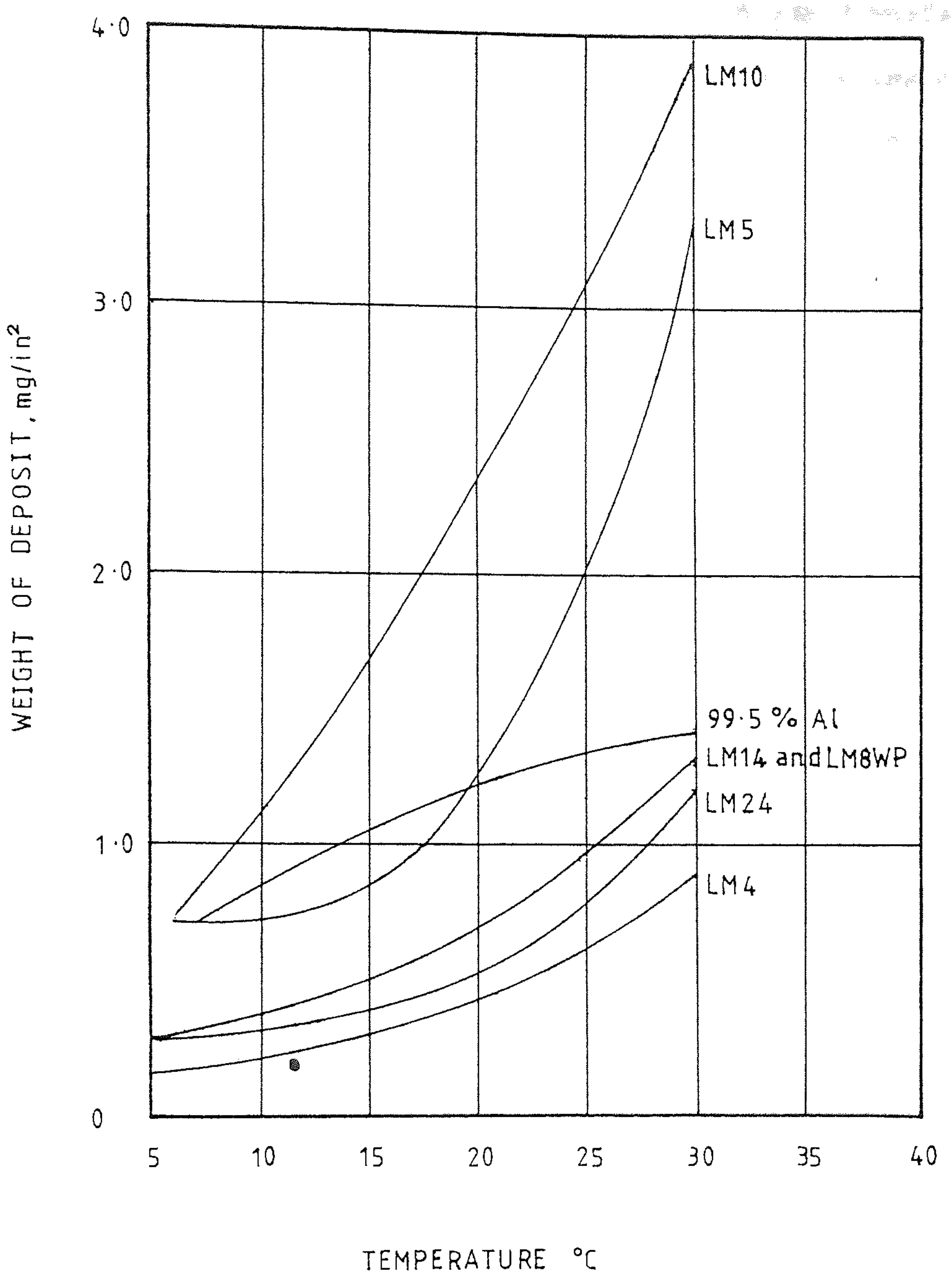


Fig 5. The effect of temperature of modified alloy zincate (M.A.Z.) solution on the weight of zinc immersion deposit obtained on different alloys using a 1 minute dip.

(After Such and Wyszynski).(105)

1·0 mg/in² = 0·155 mg/cm²

For composition of the alloys see Table X.

1. Remove dirt, oil, grease and other surface contamination, e.g. smut formed during cleaning.
2. Replace the natural oxide by a thinner more uniform type.
3. Remove any surface microconstituents that may interfere with formation of a continuous uniform immersion film or react with subsequent plating solutions.
4. Render the remaining bulk surface in a suitable condition to permit growth of a satisfactory immersion film.

To achieve these requirements with aluminium alloys many pretreatment operations have been proposed. However it is generally accepted the use of the double-dip technique is essential for most alloys.

1.4.5.1. Cleaning solutions

Many cleaners have been recommended. Work (48) used a cleaner containing sodium carbonate (22·5g/l) and sodium bicarbonate (45g/l) at 93°C.

Keller and Zelley (110) used an alkaline dip of sodium carbonate (23g/l) and trisodium phosphate (23g/l) operated from 60°C-80°C.

There are a variety of proprietary alkaline cleaners which may be used at room temperature or above, either as soak or electrolytic cleaners.

1.4.5.2. Acid etchants

Many acid etches have been used, depending on alloy type, and microconstituents to be removed.

For wrought alloys a 10% hydrofluoric - 10% nitric acid solution used at temperatures up to 40 °C has been recommended. This was claimed to give a crystal plane revealing etch rather than the random pitting obtained with sodium hydroxide and hydrochloric acid.(109)

A 50% nitric acid dip at room temperature may be sufficient for some wrought alloys,(97,105,138,139) while Bengston (38) used a chromic-sulphuric acid mixture at 65 °C.

A 15% sulphuric acid solution at 90 °C has been used for many wrought and cast alloys.(105,138,139)

A 75% nitric -25% hydrofluoric acid solution has been suggested for high-silicon casting alloys.(38,105,138,139)

Wyszynski (140) stated that although no universally acceptable etch has been developed, the nearest compromise is based on 30% nitric acid, 3% sodium hydrogen bifluoride and 1% ferric chloride.

Other etchants including 3% sodium bifluoride, 1% hydrofluoric acid, 30% nitric acid and 33% sulphuric - 5% chromic acid have also been used.

1.4.5.3. Zincate solutions

While reports confirm that pretreatment should result in the formation of a uniform and thin zincate deposit, in practice various composition zincate solutions are used to produce the ideal deposit. In the U.K. the M.A.Z. solution (135) is most widely used commercially. However in the U.S. processing routes utilizing the S.Z. type solution, with and without additives, are still recommended. (97,138,139)

1.4.5.4. Plating on the zincate immersion film

Nickel, tin, gold, hard chromium and others can be directly electrodeposited on to the M.A.Z. deposit. Methods normally suitable for plating on to zinc are adopted. To avoid dissolution of the immersion film the work is loaded 'live' into the plating bath. When electroplating from a strongly acid or alkaline solution, especially when hot, a thin strike from a less aggressive solution is applied first.

However a protective copper or brass strike is always electroplated over the S.Z. type film before final plating.

1.5. Electroplated Aluminium

1.5.1. Applications

Electroplated aluminium alloys pretreated using the zincate technique are used in three main areas :

1. Decorative and corrosion protection.
2. Electrical.
3. Engineering.

1.5.1.1. Decorative and corrosion resistant finishes

For indoor or light outdoor exposure decorative coatings are applied to cast, extruded and stamped aluminium articles.(116)

Aluminium components are also plated to improve corrosion resistance and appearance, e.g. automobile bumpers.(141)

1.5.1.1.1. Corrosion performance

As indicated by the electrochemical series, aluminium is anodic to the metals most commonly deposited over it. The problem of protecting aluminium may be further aggravated by the presence of a zinc interply between the aluminium and more noble electrodeposits. Therefore the corrosion performance of plated aluminium, especially when zincate pretreated, has been viewed with some scepticism and often criticised. Investigations (111,142,143) indicate that the relatively thick films deposited from S.Z. solutions are prone to lateral corrosion and this undercutting results in blistering of the electroplate.

Keller and Zelley (111,112) observed improved corrosion results with thinner zinc deposits obtained using the double-dip technique. A S.Z. bath with additives also yielded superior thin zinc films containing traces of iron.

The thicker the zinc interply and the lower its adhesion to the substrate, the easier penetration by corrosive electrolyte and more voluminous its corrosion products. Zinc and aluminium readily form hydroxides and hydrated oxides, with a corresponding large volume increase. Therefore a thin adherent film will restrict lateral spread of corrosion and subsequent blistering.

Workers in the U.S. reported the proprietary Alstan 70 (84) pretreatment produced superior corrosion performance to the standard S.Z. process.(3,84,144) However the M.A.Z. process produces improved zinc-alloy deposits which provide a plating underlayer, not prone to rapid lateral attack, and therefore improved corrosion performance.(105,115) A recent A.S.T.M. comparison (145) revealed little difference in corrosion performance of plated aluminium pretreated by the M.A.Z. and stannate processes. Both gave appreciably better results than the standard S.Z. method.

Studies (105,115) have shown the corrosion resistance of aluminium plated using the M.A.Z. process is dependant upon thickness and nature of coating system, the alloy type being of relatively minor significance. With a copper undercoat being unnecessary, the superior corrosion resistance of the duplex nickel and microcracked chromium systems were confirmed. These were recommended for severe conditions, capable of meeting the requirements of B.S.1224 : 1970.(146) For normal indoor service however, the bright nickel - decorative chromium system was satisfactory.

1.5.1.2. Electrical finishes

Aluminium alloys are being used increasingly by the electrical and electronics industries. Aluminium has excellent electrical conductivity but the oxide layer results in a high contact resistance and poor solderability. Plating with copper, nickel, tin or cadmium improves solderability and gold and silver finishes increase surface conductivity.(97,122) Examples include, bus bars, silicon chip bases, connectors, terminals and contact plates.(140)

1.5.1.3. Engineering finishes

The surfaces of aluminium alloys have been modified by electroplating for numerous engineering purposes.(105,116) Aluminium-silicon pistons and cylinder blocks are hard chromium or hard iron-tin plated to improve wear resistance.(147) Wear resistance is also increased by deposition of a coating incorporating either hard particles or a soft phase which acts as a solid lubricant for bearings (148) and anti-friction applications.

Other aluminium components are plated to perform under conditions of thermal shock, fatigue and impact loading.

1.5.2. Assessment of performance

The two most important methods of investigating the performance of the electroplated coating on aluminium are adhesion and corrosion testing.

1.5.2.1. Adhesion tests

The adhesion between coating and base metal is an important measure of the quality of a plated article. Though many methods have been suggested an ideal adhesion test has not yet been developed because of its demanding requirements.(149-151) Furthermore the results obtained from the various tests cannot be directly compared.

1.5.2.1.1. Qualitative adhesion tests

Numerous qualitative tests each with specific limitations are listed in A.S.T.M. B.S.71-72 (152) and include tests involving bending, burnishing, peeling, sawing, filing and thermal cycling. Some of these tests have the advantage that they can be performed on production components rather than special test pieces, but they rely on visual interpretation and non-standardized manual application. Though most have been used to assess the bond strength and performance of plated aluminium (60,105,109,113) the most successful is the temperature cycling test.(140)

1.5.2.1.2. Quantitative adhesion tests

Quantitative adhesion tests such as the Ollard method and variants, (153-156) have been used to test plated aluminium,(60,113,157) and Bullough and Gardam (109) used a modification of the Hothersall and Leadbeater method.(158)

Such and Wyszynski (105,115) evaluated adhesion of dull nickel electrodeposits to aluminium alloys using a peel test based on a method proposed by Jaquet (159) and improved by Wittrock and Swanson.(141) This test involves using a spring balance to measure the force required to steadily peel perpendicularly the plating from the surface. The test is simple, but the coating must be strong enough to withstand the continuous peeling operation.

1.5.2.2. Corrosion tests

Various accelerated and outdoor corrosion tests are specified for the assessment of nickel and chromium electroplated coatings on aluminium. These are listed in B.S.1224 : 1970.(146) The exact correlation between accelerated and actual service tests has not been determined.

CHAPTER TWO

2. EXPERIMENTAL PROCEDURE

2.1. Materials Used

The plating characteristics of a number of commercial aluminium alloys which are commonly plated were studied. The plating process used was the zincate immersion technique. Information on the alloys involved in the test programme is given in Table XI. The as-cast LM25 was also used in the heat-treated condition. Heat-treatment was as B.S:1490 and details are given in Table XII.

2.1.1. Material preparation

The wrought alloys, S1C, NS4 and HE9 were supplied as extruded and rolled strip which was guillotined as required.

Samples of wrought X-7046, a U.S. specification bumper stock alloy were cut from extruded bumper sections.

The casting alloy LM25 was obtained as primary ingot from which slabs of the required dimensions were chill cast.

Specimens were prepared for the various tests by machining.

2.2. Surface Examination

The alloy surfaces were examined at various stages in the test programme using : scanning electron microscopy, optical microscopy

TABLE XI. COMPOSITION, CONDITION AND MECHANICAL PROPERTIES OF THE ALUMINIUM ALLOYS.

Alloy	Material designation								Min. U.T.S. N.mm^{-2}	Min. elong. %
Type	Condition	I.S.O.	Main alloying additions %							
			Al	Si	Fe	Mn	Mg	Zn		
S1C Non-heat treatable wrought.	M	Al(99%) remainder impurities mainly Fe, Si.	Rem.	0·5	0·7	0·1	-	0·1	70	11
NS4 Non-heat treatable wrought.	M	AlMg	"	0·5	0·5	0·5	1·7 2·4	-	160	7
X-7046 Heat-treatable wrought.	?	AlZnMg	"	0·2	0·4	0·05 0·30	1·0 1·6	6·6 7·6	?	?
HE9 Heat-treatable wrought.	TF	AlMgSi	"	0·3 0·7	0·4	0·1	0·4 0·9	0·2	150	6
LM25 Heat-treatable casting.	M	AlSiMg	"	6·5 7·5	0·5	0·3	0·2 0·45	0·1	160	3

* Unless otherwise stated all limits are maxima.

M = As manufactured, e.g. as cast, as extruded and rolled, etc.

TF = Solution and precipitation heat-treated.

? = Test panels were cut from extruded bumper section and it was assumed that the alloy had already been heat-treated.

TABLE XII. HEAT-TREATMENT AND MECHANICAL PROPERTIES OF LM25 ALUMINIUM-SILICON ALLOY.

Heat-treatment	Thermal treatments applied	Condition	Min. U.T.S. Nmm^{-2}	Min. elong. %
-	-	M	160	3
Precipitation treated	Heat at 165°C for 9·5 hrs. Air cool	TE	190	2
Solution treated	Heat at 535°C for 12 hrs. Hot water quench Heat at 250°C for 4 hrs. Air cool	TB7	230	5
Solution and precipitation treated, (fully heat-treated).	Heat at 535°C for 12 hrs. Hot water quench Heat at 165°C for 9·5 hrs. Air cool	TF	280	2

and electron probe micro-analysis (E.P.M.A.). A scanning electron microscope (S.E.M.) fitted with a qualitative 'Kevex' energy-dispersive X-ray micro-analysis attachment was also used to identify elements present on the surface.

2.3. Zincate Immersion Processing Sequences

2.3.1. Standard pretreatment sequences

2.3.1.1. Sequence I

1. Acetone degrease if required.
2. Cathodic alkali clean (Load-Live) at 60°C for 2 min.
3. Water rinse.
4. Cathodic alkali clean (Load-Live) at room temperature for 2 min.
5. Water rinse.
6. Dip in 50% nitric acid for 1 min.
7. Running water rinse.
8. Dip in one of either of the following zincate solutions :
    - (i) Modified alloy zincate (M.A.Z.) solution.(135)
    - (ii) Dilute simple zincate (D.S.Z.) solution containing ZnO (10g/l), NaOH (120g/l).
    - (iii) Concentrated simple zincate (C.S.Z.) solution containing ZnO (100g/l), NaOH (500g/l).

    Standard condition : room temperature, e.g. SEQ I RT.

    Immersion time variable, i.e. 10 s - 6 min.
9. Running water rinse.

    Electroplating as required.

2.3.1.2. Sequence II

As sequence I except 1 min. 50% nitric acid dip replaced by a 1 min. 5% hydrofluoric - 50% nitric acid dip.

2.3.1.3. Sequence III

The 'double-dip' equivalent of sequence I. As SEQ I except that stages 6 to 8 were repeated.

With the standard pretreatment, for both the first and second dips the zincate solution was used at room temperature. For example, SEQ III $\substack{\text{RT, 2 min.}\\ \text{RT, 2 min.}}$, indicates that both dips were of 2 minutes duration.

2.3.1.4. Sequence IV

The 'double-dip' equivalent of sequence II. As SEQ II except that stages 6 to 8 were repeated.

2.3.2. Variations of the standard pretreatment sequences employed

Initially the M.A.Z. solution was operated as a conventional immersion solution at room temperature. However to improve adhesion on certain alloys it was also operated a) at various temperatures other than and generally above room temperature, and b) electrolytically at room temperature using a range of current densities.

2.3.2.1. Pretreatment incorporating use of heated M.A.Z. solution

Pretreatment involving immersion in M.A.Z. solution at a temperature other than room temperature, e.g. 50 °C, in conjunction with sequence I will be indicated : SEQ I 50 °C.

In the case of the double-dip equivalent of SEQ I 50 °C, this could involve a first film deposited from M.A.Z. solution either at room temperature or 50 °C. These would be specified by SEQ III $\genfrac{}{}{0pt}{}{\mathrm{RT}}{50\,^{\circ}\mathrm{C}}$ and SEQ III $\genfrac{}{}{0pt}{}{50\,^{\circ}\mathrm{C}}{50\,^{\circ}\mathrm{C}}$, respectively.

2.3.2.2. Pretreatment incorporating use of M.A.Z. solution operated electrolytically

For pretreatments involving an electrolytic immersion stage in room temperature M.A.Z. solution a similar pretreatment reference code was adopted, e.g. SEQ III $\genfrac{}{}{0pt}{}{\mathrm{RT,}\,2\ \mathrm{min.}}{0{\cdot}5\ \mathrm{A\ dm}^{-2}\quad 1\ \mathrm{min.}}$ refers to a sequence III pretreatment using a 2 minute conventional immersion first film and a second, final film applied electrolytically using a current density of $0{\cdot}5\ \mathrm{A\ dm}^{-2}$ for 1 minute.

2.4. The Effect of Pretreatment Prior to Final Zincate Immersion

The S.E.M. was used to investigate the surface response of the alloys to the different pretreatments, prior to final zincating. Specimens were polished with 1 μm diamond paste, pretreated, vacuum coated with carbon and gold-palladium and examined using the S.E.M. The surfaces were also analysed using the Kevex attachment previously described.

2.5. Determination of Zincate Solution Viscosity

Zincate solution viscosity was measured with a Ubbelöhde suspended level viscometer supported vertically in a 20°C water bath. The viscosity of the three zincate solutions was measured relative to water.

2.6. Study of Zincate Film Morphology

The morphology and growth characteristics of the zincate deposits were investigated using the S.E.M. The Kevex attachment fitted to the S.E.M. was also utilized. Specimens for S.E.M. examination were prepared as described in section 2.4. The influence of pretreatment, zincate solution composition and mode of operation, and duration of immersion were monitored.

2.7. Determination of Zincate Film Weight

Zincate film weight was measured using a weight-loss technique. For each alloy type a set of six carefully machined test panels 9·0cm × 4·0cm × 0·5cm were prepared. The panels were 240 grit finished and processed according to a specific pretreatment route, with each panel receiving a final zincate dip of differing duration. By accurately weighing each zincated panel, of known total surface area, before and after stripping the zinc film in a 50% nitric acid solution the weight of the film was determined.

2.8. Quantitative Analysis of Zincate Film Composition

Film composition was determined using an atomic absorbtion spectrophotometer (A.A.S.). Alloy specimens of known total surface area were 240 grit finished, pretreated, zincated and accurately weighed. The zincate film was then stripped in a known volume of 50% nitric acid which was then analysed using the A.A.S.

2.9. Potential Measurements

The variation of surface potential with time during zincate film build-up was measured by reference to a 0·1 M KCl calomel electrode and continuously monitored with a fast response chart recorder. The calomel electrode was connected to the positive terminal of the recorder. Aluminium alloy specimens were 240 grit finished and pretreated as required prior to immersion in a thermostatically controlled M.A.Z. solution.

Potential-time results were also used to compare the relative nobility of a number of metals and aluminium alloys when immersed in either room temperature sodium chloride (53g/l) - hydrogen peroxide (4g/l) or M.A.Z. solution. Measurements were made with respect to the 0·1 M calomel electrode. A non-standard pretreatment was used which involved polishing to 240 grit finish, degreasing in acetone and dipping in 50% nitric acid for about 4 s.

2.10. Electrodeposition

Standard size machined test panels 9·0cm × 4·0cm × 0·5cm were 240 grit finished and plated using proprietary solutions and standard conditions. Solutions and operating conditions are listed in Table XIII. For comparison all coatings were plated directly on to the zincate film. While this is standard practice when using a M.A.Z. deposit, a thin copper or brass strike is normally applied over a S.Z. type deposit before final plating. Zincated panels were always loaded 'live' into the plating solution to avoid dissolution of the immersion film.

2.10.1. Plating for adhesion testing

A 250 μm Watts nickel deposit was used to support the peeling load involved when good adhesion had been achieved.

2.10.2. Plating for corrosion testing

Electroplating was performed in accordance with B.S.1224 : 1970,(146) service condition 3 being selected. The three coating systems selected for this study were as follows :

1. Decorative Chromium

40 μm bright nickel.

0·25 μm decorative chromium.

TABLE XIII. OPERATING CONDITIONS OF THE PLATING SOLUTIONS

Plating solution	Current density A dm^{-2}	Ph	Temperature °C	Agitation
Watts nickel	4	4·0	60	Air
Bright nickel	4	4·5	55	Air
Nickel seal* (containing inert particles)	4	3·5	55	Air blowing downwards to keep particles in suspension
Bright decorative chromium	10	< 1·0	35	None

* Proprietary product, Oxy Metal Finishing (Europe).

2. Thin Microporous Chromium

30 µm bright nickel.

1 µm nickel seal*(deposit containing inert particles).

0·25 µm decorative chromium.

3. Thick Microporous Chromium

30 µm bright nickel.

1 µm nickel seal*(deposit containing inert particles).

0·50 µm decorative chromium.

Microporous chromium deposits were obtained using the following procedure. After application of the bright nickel layer a special nickel layer of about 1 µm was deposited from a solution containing silica particles, approximately 0·02 µm diameter. The inert particles were kept in suspension by vigourous air agitation and co-deposited with the nickel. A chromium layer was then deposited using a conventional decorative chromium plating solution. Deposition of the chromium was prevented at the silica particles which resulted in a microdiscontinuous chromium top coat.

When applying the multi-layer coating systems thorough rinsing between each stage was imperative to prevent contamination of the solutions by carry-over.

After electroplating panels were washed, dried and stored in a dry atmosphere until ready for corrosion testing.

2.11. Post-plating Heat-treatment

One method of plating on aluminium, the Vogt process,(5,6) involves a post-plating heat-treatment of 230°C for 30 minutes. This causes interdiffusion and improves adhesion while also serving as a test of deposit quality, which blisters if adhesion is unsatisfactory.

Post-plating heat-treatment is undesirable in commercial plating as it is not a readily automated operation and involves the use of extra equipment. However because product requirements may occasionally justify extra expense it was decided to assess its value as a means of increasing adhesion. A number of M.A.Z. pretreated, Watts nickel plated specimens were heat treated in air at 230°C for either 0·5, 1·0 or 1·5 hours prior to adhesion testing.

2.12. Adhesion Testing

2.12.1. Peel adhesion testing

The panels for adhesion testing were plated with Watts nickel and stored for 10 days before slitting and testing.

Peel adhesion was measured using an 'Instron' tensile testing machine fitted with the peel test attachment shown in Fig 6, bolted to the bottom cross-head. Specimens were screwed to the moveable trolley of the peel testing attachment. The trolley moved in such a way as to ensure the angle of the peeling strip was maintained perpendicular to the specimen surface. The width of the peeled deposit, standardized at 2·54cm, was achieved by milling two parallel slits through the coating into the substrate, Fig 7. A tab of deposit was then lifted from the substrate using pliers, an operation made easier by not zincating one end of the panel. The fluctuations of the adhesive force monitored by the Instron load cell were displayed on a chart recorder. The chart speed and rate of peel were standardized at 5cm min^{-1}. The average peel adhesion per panel side was determined by measuring the area under the peel curve using a planimeter. This gave a measure of the work expended in detaching the plating from the substrate. A typical panel following peel testing is shown in Fig 8.

2.12.2. Examination of peel adhesion tested panels

After peel testing, samples of failure surfaces on the alloy substrate and back of the peeled foil were cut from the test panels. Samples were vacuum coated with carbon and gold-palladium alloy and examined using the S.E.M. The Kevex attachment fitted to the S.E.M. was also used to qualitatively assess the amount of substrate detached.

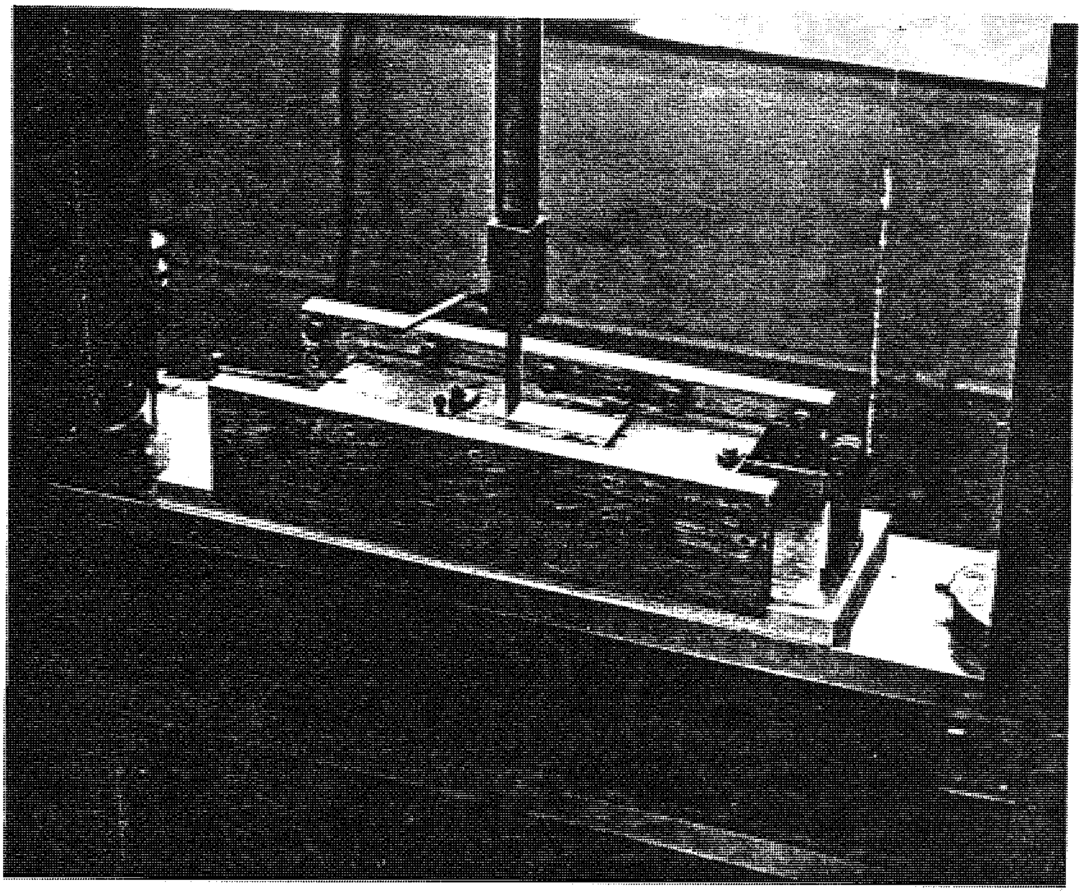


Fig.6. Peel adhesion test attachment used on 'Instron' tensile testing machine.

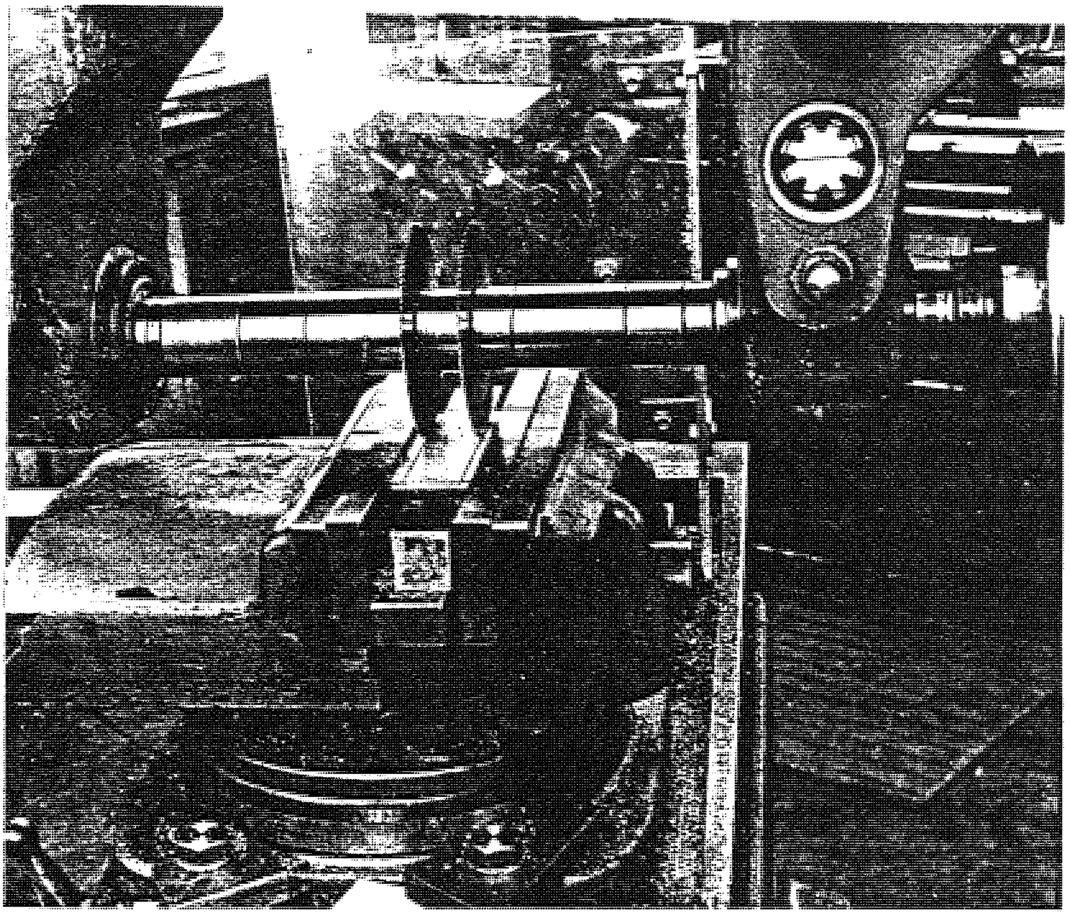


Fig. 7. Milling machine attachment used for slitting panels for peel adhesion testing.

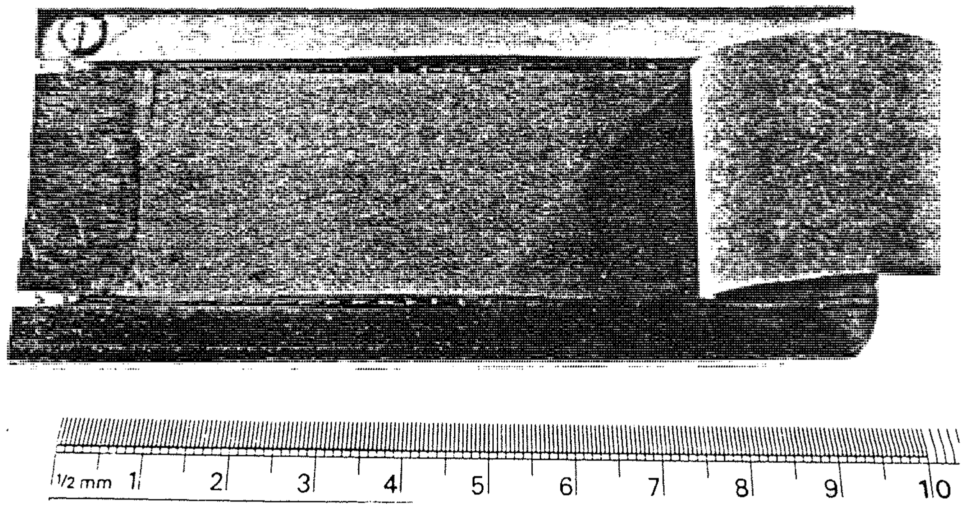


Fig.8. A typical test panel following peel adhesion testing.

2.13. Corrosion Testing

A programme of accelerated corrosion testing using the C.A.S.S. test was undertaken. This was performed in accordance with B.S.1224 : 1970,(146) appendix H. According to this specification, to meet the requirements of the 'severe' service condition : 3, after 16 hours C.A.S.S. testing the corrosion rating should be at least 8. Hence a C.A.S.S. cycle time of 16 hours was used. Corrosion rating was carried out after each cycle which is equivalent to approximately one year of service outdoors. As discussed in section 1.5.1.1.1., the corrosion performance of zincate pretreated plated aluminium has been criticised. Therefore all panels were exposed to a total of 5 C.A.S.S. cycles. Hence the results of this severe test would indicate the corrosion resistance of the plated aluminium alloys under extreme conditions.

2.13.1. Assessment of corrosion behaviour

All corroded panels were visually assessed using the A.S.T.M. specification B537 - 70 (160) rating method. This is based on comparing the corroded test panel with standard photographs. Corrosion products were removed prior to rating by careful swabbing in warm water.

2.13.2. Examination of corrosion tested panels

Apart from visual assessment, corrosion sites on the corroded panels were studied using optical and scanning electron microscopy.

The Kevex attachment fitted to the S.E.M. was used to identify elements present in the corrosion products that had exuded out of corrosion pits. Metallographically prepared cross-sections were also examined to observe if preferential attack of the zincate layer had occurred. Dennis and Fuggle (161) described the use of the S.E.M. for the investigation of the morphology of corrosion pits in decorative nickel and chromium coatings. A similar procedure was adopted; sections were cut from the panels, vacuum coated with carbon and gold-palladium alloy and examined using the S.E.M.

CHAPTER THREE

3. RESULTS

3.1. Effect of the Standard Pretreatments Prior to Final M.A.Z. Immersion

S.E.M. examination revealed that the surface of each alloy responded differently when subjected to an identical pretreatment and behaved in a different manner when the acid etch was the only stage in the pretreatment to be altered, Figs 9 and 10. The 5% HF etch (sequence II) consistently caused more severe surface attack than when the 50% HNO_3 etch (sequence I) was used, Fig 9. With sequence I, the pitting was due to the electrolytic alkaline cleaning rather than the 50% HNO_3 acid dip. The larger etch pits resulted from preferential attack of the microconstituents and precipitates, some of which partially remained around the edges or bottom of the etch pits as shown by Kevex examination.

The double-dip pretreatments, sequences III and IV, had a more severe effect than the conventional single dip sequences, the effect being more exaggerated than just a doubling of the etch time, Fig 10. During the formation of the first zinc immersion film, which in this case was deposited for 2 min from room temperature M.A.Z. solution, dissolution of the aluminium surface occurs.

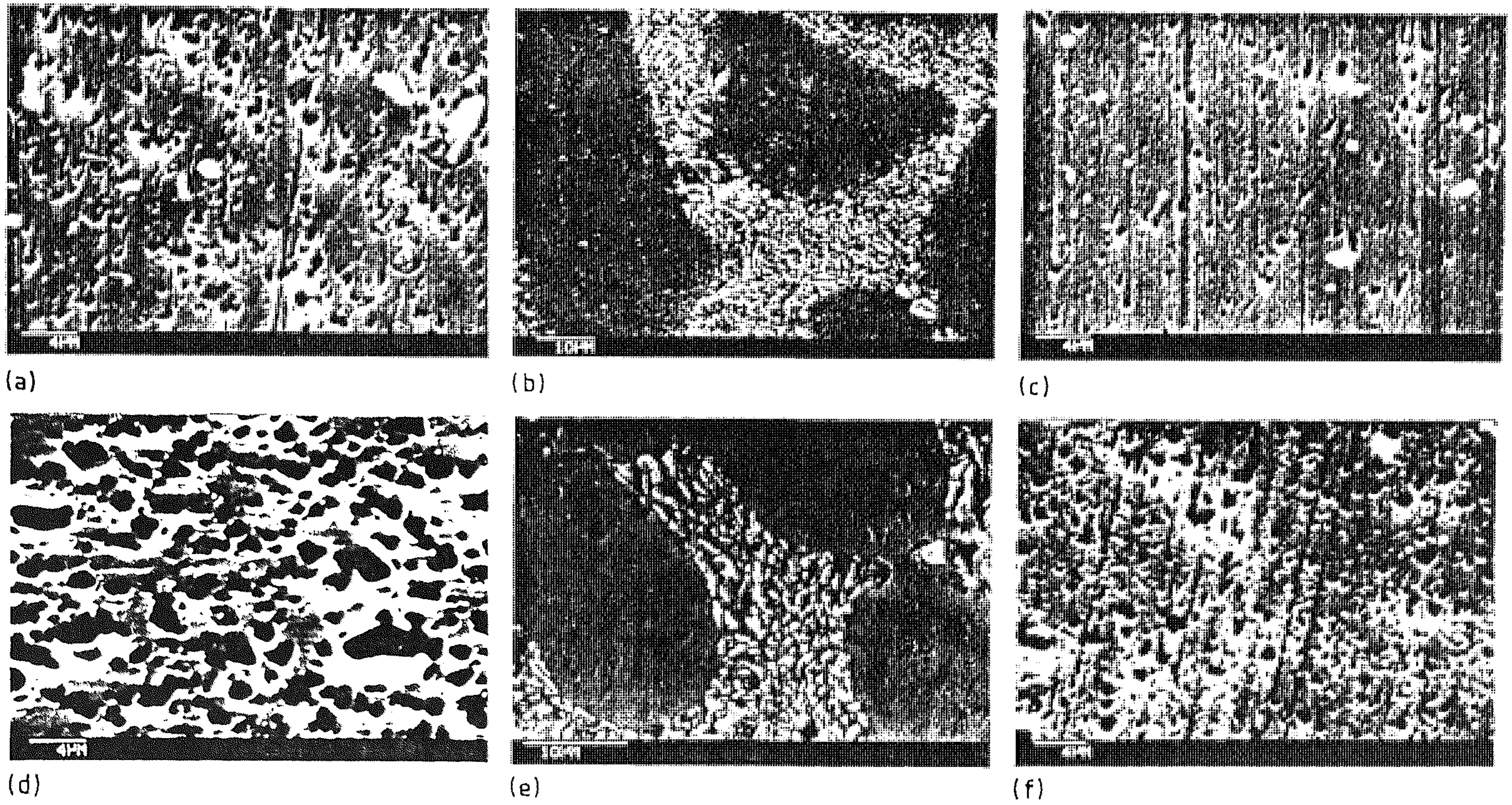


Fig.9. Scanning electron micrographs of alloy surfaces after the acid dip stage in sequences I and II : (a) S1C, sequence I; (b) LM25, sequence I; (c) HE9, sequence I; (d) S1C, sequence II; (e) LM25, sequence II; (f) HE9, sequence II.

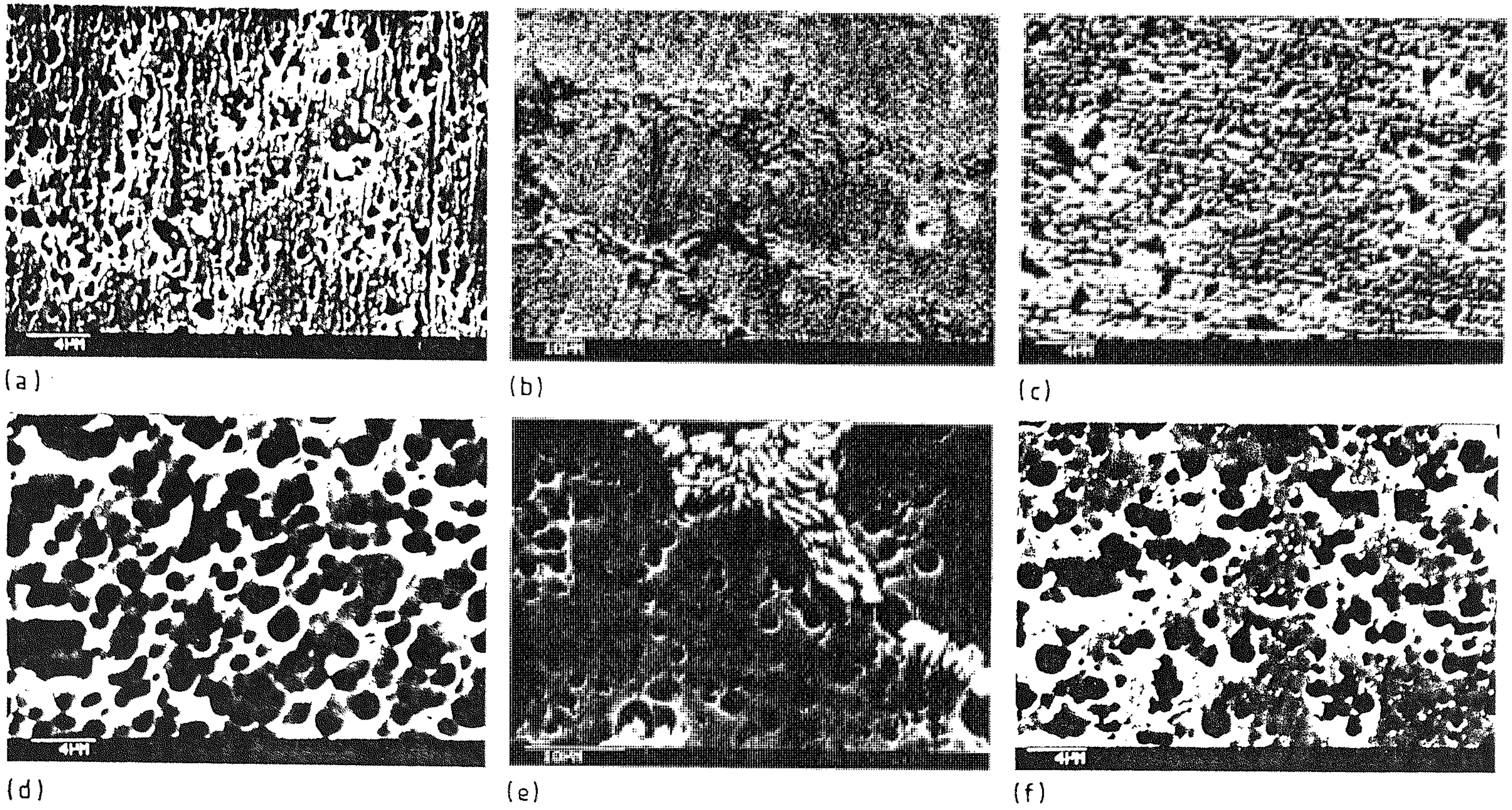


Fig.10. Scanning electron micrographs of alloy surfaces after the second acid dip stage in sequences III and IV : (a) S1C, sequence III; (b) LM25, sequence III; (c) HE9, sequence III; (d) S1C, sequence IV; (e) LM25, sequence IV; (f) HE9, sequence IV.

3.2. Modified Alloy Zincate (M.A.Z.) Solution Operated at Room Temperature

3.2.1. Morphology of M.A.Z. films

The S.E.M. was used to study the influence of the surface condition of the alloys prior to M.A.Z. immersion on the morphology of films formed with various immersion times. The morphology of M.A.Z. films on S1C, pretreated using sequence II, is shown in Fig 11. It consisted of numerous rounded growths. There was preferential growth around etch pits after a 5 s immersion, Fig 11a. After 30 s the number of growth sites had increased and more surface was covered with the film, some of which was becoming continuous, Fig 11b. The growths appear to be of uniform size, which would support Wyszynski's suggestion (115) that when using a M.A.Z. type solution a film-growth-arresting mechanism takes place once a critical size is reached. Even after 2 min immersion the surface was not always completely covered but the preferential growth around etch pits became less obvious.

When pretreatment failed to remove surface layers damaged excessively by mechanical polishing, there was preferential nucleation of the film along scratch lines. This is illustrated in Fig 12, which shows an M.A.Z. deposit after 30 s immersion on LM25 pretreated using sequence I.

The influence of specific pretreatment sequence and differences in microstructure of the alloys on the surface response and morphology of immersion films is highlighted in Fig 13. Film

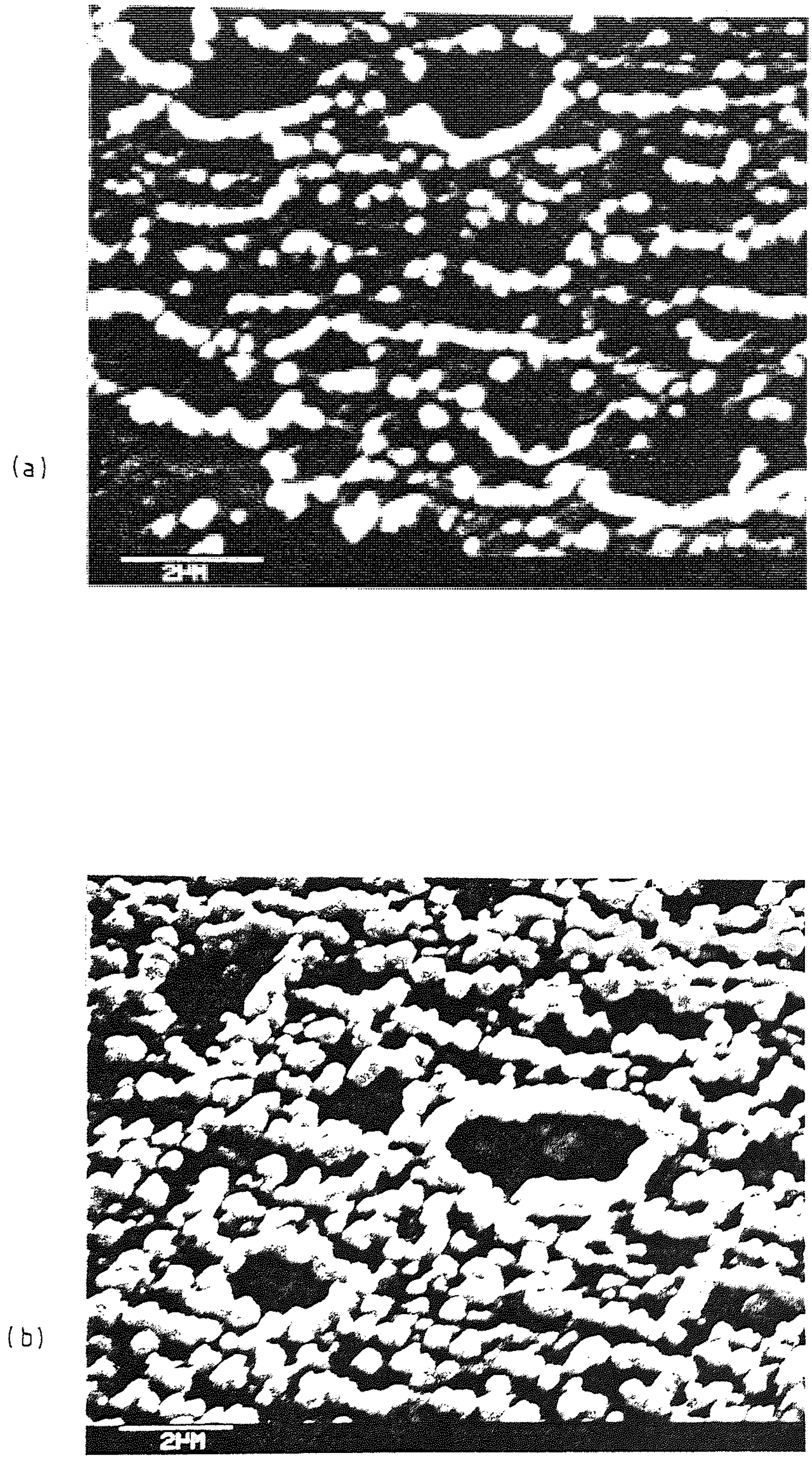


Fig.11. Scanning electron micrographs of the surface of alloy S1C after pretreatment using sequence II and: (a) 5 s immersion in room temperature M.A.Z. solution; (b) 30 s immersion in room temperature M.A.Z. solution. Preferential film growth around etch pits.

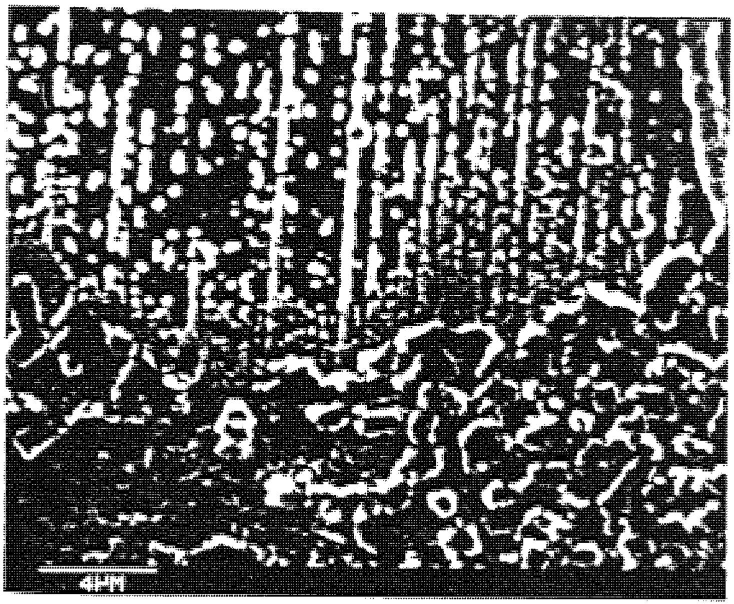


Fig.12. Scanning electron micrograph of the surface of alloy LM25 after pretreatment using sequence I and 30 s immersion in room temperature M.A.Z. solution. Preferential film film growth along scratch lines.

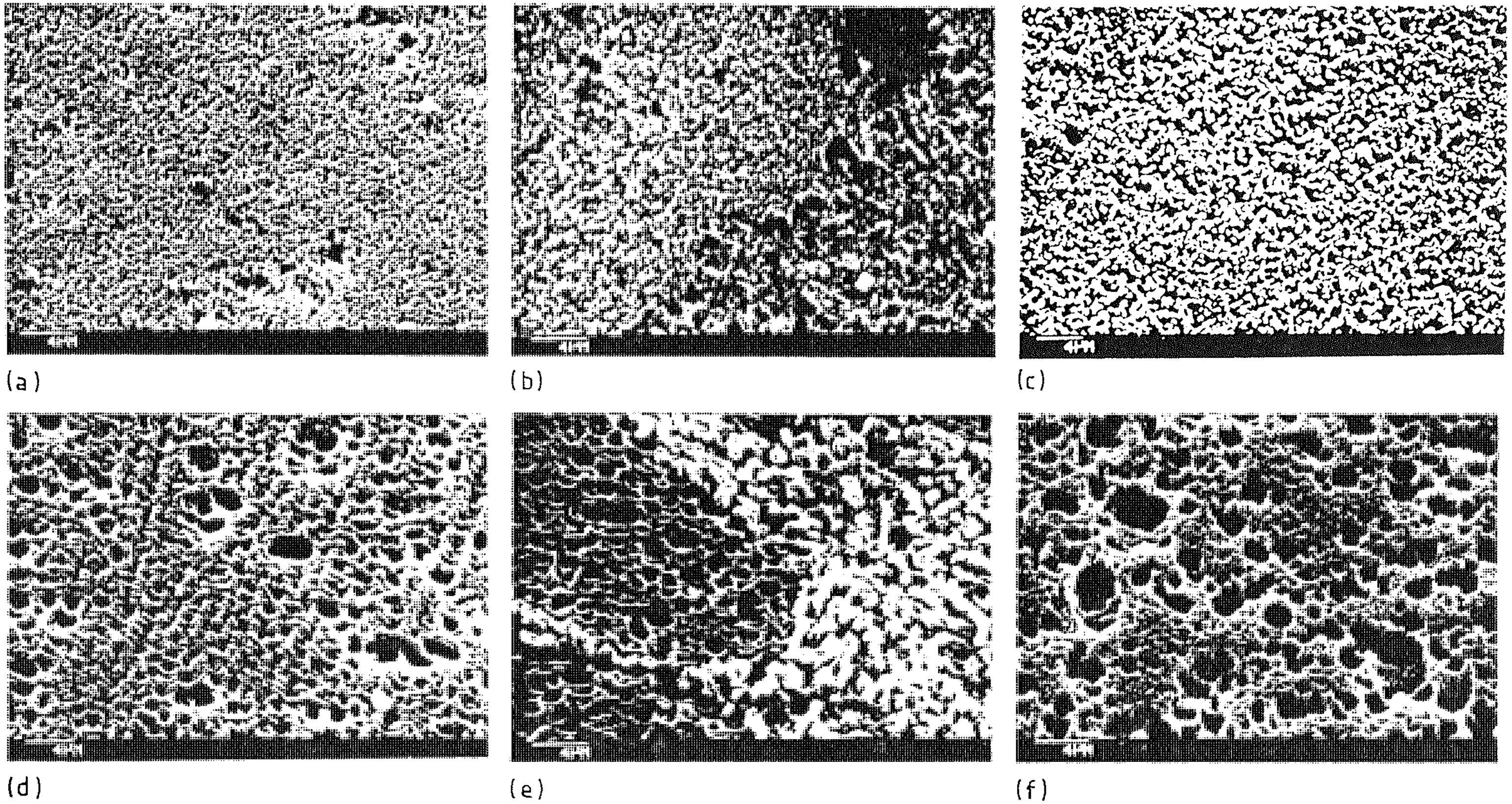


Fig.13. Scanning electron micrographs of alloy surfaces after pretreatment using sequences I and IV and 1 min immersion in room temperature M.A.Z. solution: (a) S1C, sequence I; (b) LM25, sequence I; (c) HE9, sequence I; (d) S1C, sequence IV; (e) LM25, sequence IV; (f) HE9, sequence IV.

growth on LM25 after 1 min immersion is illustrated in Figs 13b and 13e for pretreatment sequences I and IV respectively. Fig 13b shows that the film nucleated on the casting alloy preferentially around platelets of eutectic silicon. There was only limited growth on the silicon plates. Scattered growth centres can be assumed to have developed at regions where 'matrix aluminium', smeared on the silicon plates during polishing, had not been removed during pretreatment. On the outer regions of the dendrites, growth centres were finer and surface coverage more complete. This suggests that in moving away from areas of silicon platelets there is a change in the nucleation and growth characteristics of the film. E.P.M.A. indicated that the percentage of silicon present in solid solution in the dendrites was lowest at their centres and reached a maximum at the silicon platelet boundary. Comparing Figs 13e and 13b illustrates that the use of different pretreatment sequences can result in significant variations in response. In both cases the film grows on the dendritic regions and around the eutectic silicon. However the HF - containing etch together with the double-dip effect, sequence IV, caused considerably more attack of the silicon platelets and reduced them to more prominent rounded humps, than sequence I.

Fig 13 highlights some of the benefits to be gained by using a double-dip rather than a single dip procedure, e.g. finer grained more coherent films. However it also demonstrates the consequences of 'over-etching', i.e. severe weakening of the subsurface layers of the alloy.

S.E.M. examination revealed that, (i) on alloy X-7046 totally unsatisfactory, slow growing, coarse grained films which exhibited poor coverage were obtained with all four sequences, (ii) sequences I and II gave coarse grained films on all alloys, (iii) sequence IV gave fine grained deposits but excessive pitting with all alloys, (iv) on the wrought material sequence III gave fine grained, featureless deposits, Fig 14, of much lower thickness than those produced using sequences I, II and IV and without the excessive attack associated with sequence IV. (v) although sequence III resulted in the thinnest and most fine grained deposits on the casting alloy LM25, these were not as satisfactory as those observed on the wrought alloys. Due to the inhomogeneity of LM25, it exhibited the greatest tendency for non-uniform etching and subsequent coarse non-uniform film growth.

Kevex examination indicated that the M.A.Z. deposits contained mostly zinc, alloyed with the following elements in order of concentration: copper, nickel and iron. Furthermore the concentration of copper and nickel increased slightly with time, the greatest change occurring during the first two minutes of immersion.

The alloys bearing M.A.Z. films were similar in appearance, being various shades of dull grey depending on the pretreatment sequence used. However as illustrated, S.E.M. examination at high magnification revealed the appearance of the immersion films on the various alloys often differed quite dramatically.

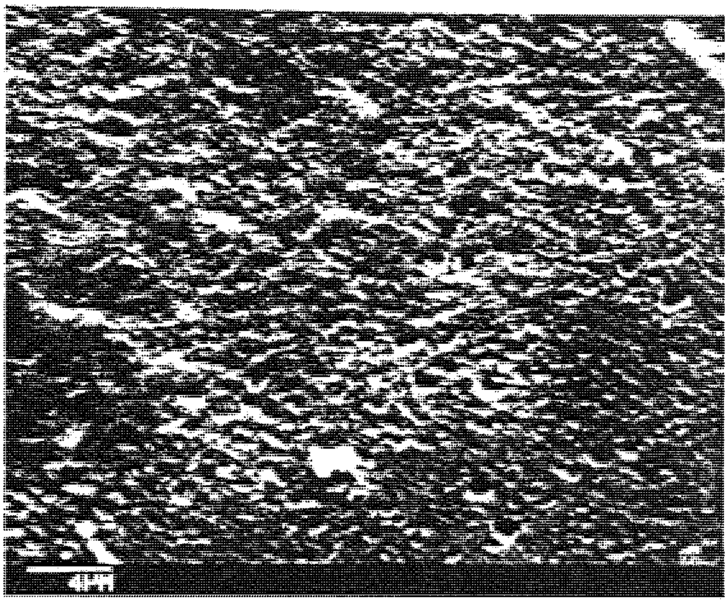


Fig.14. Scanning electron micrograph of the surface of alloy S1C after pretreatment using sequence III and 2 min immersion in room temperature M.A.Z. solution. A fine grained, featureless deposit.

3.2.2. Determination of M.A.Z. film weight

Figs 15 to 17 show the change in film weight with immersion time in M.A.Z. solution for the various alloys. All the curves have a similar characteristic shape in that there is a high initial growth rate followed by an extended period where the film weight increases more slowly and essentially linearly with time.

It can be seen that with no pretreatment, Fig 15, the high initial growth rate continued for longer on the alloys that had been pretreated, Figs 16 and 17.

In all cases film growth was greatest on LM25 and least on X-7046. This is illustrated in Fig 16, for the alloys pretreated using sequence I.

Film weight was affected by pretreatment. Fig 17 shows the influence of pretreatment on film weight for alloys S1C and LM25 pretreated using sequences I to IV. The variation in film weight due to altering pretreatment was most pronounced for alloy LM25.

The use of the double-dip pretreatment, sequence III, resulted in the thinnest, slowest growing films on all alloys except X-7046. Film growth on X-7046 was always slow and least affected by changes in pretreatment.

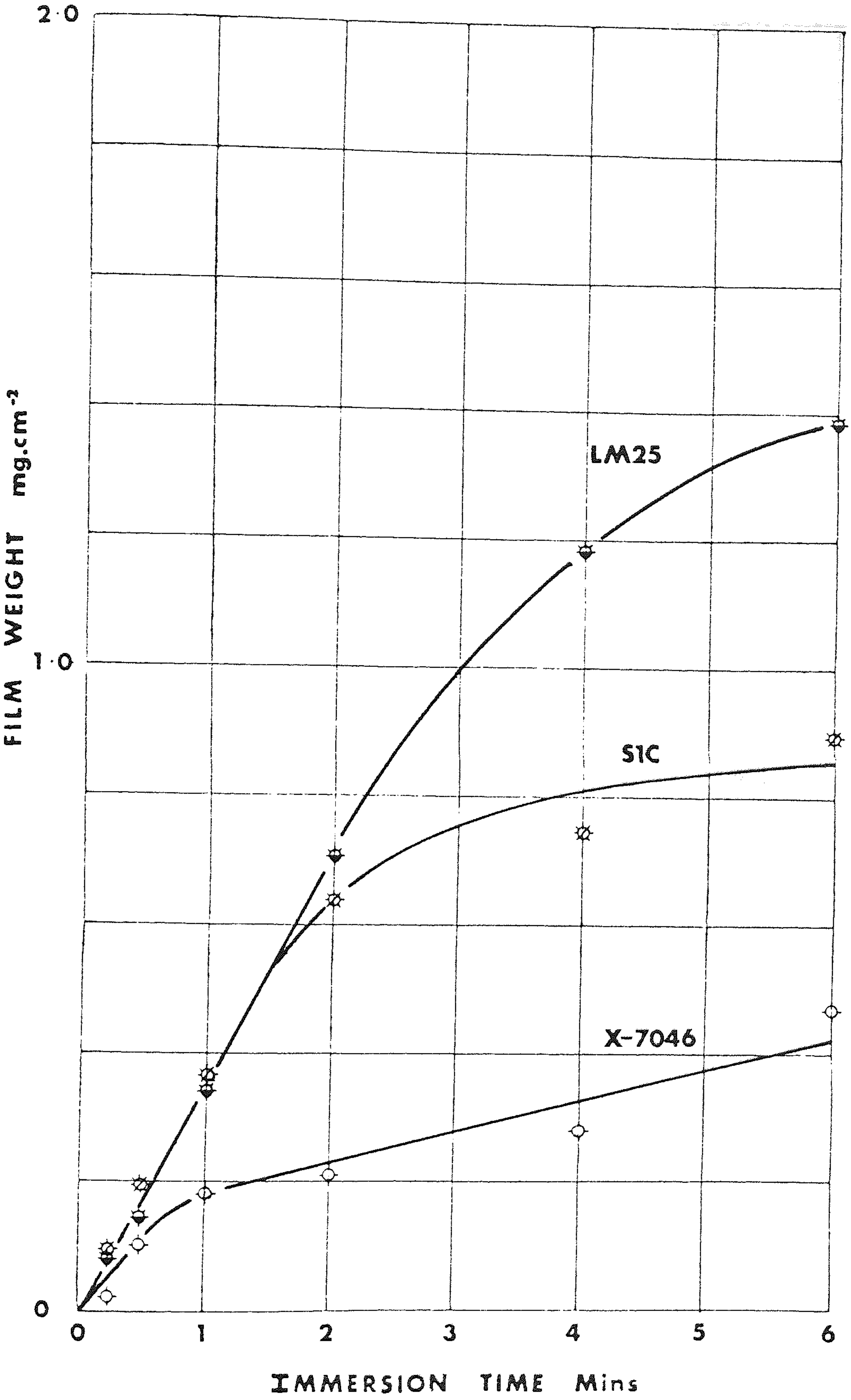


Fig.15. Relationship between film weight and immersion time in room temperature M.A.Z. solution for various aluminium alloys after no pretreatment.

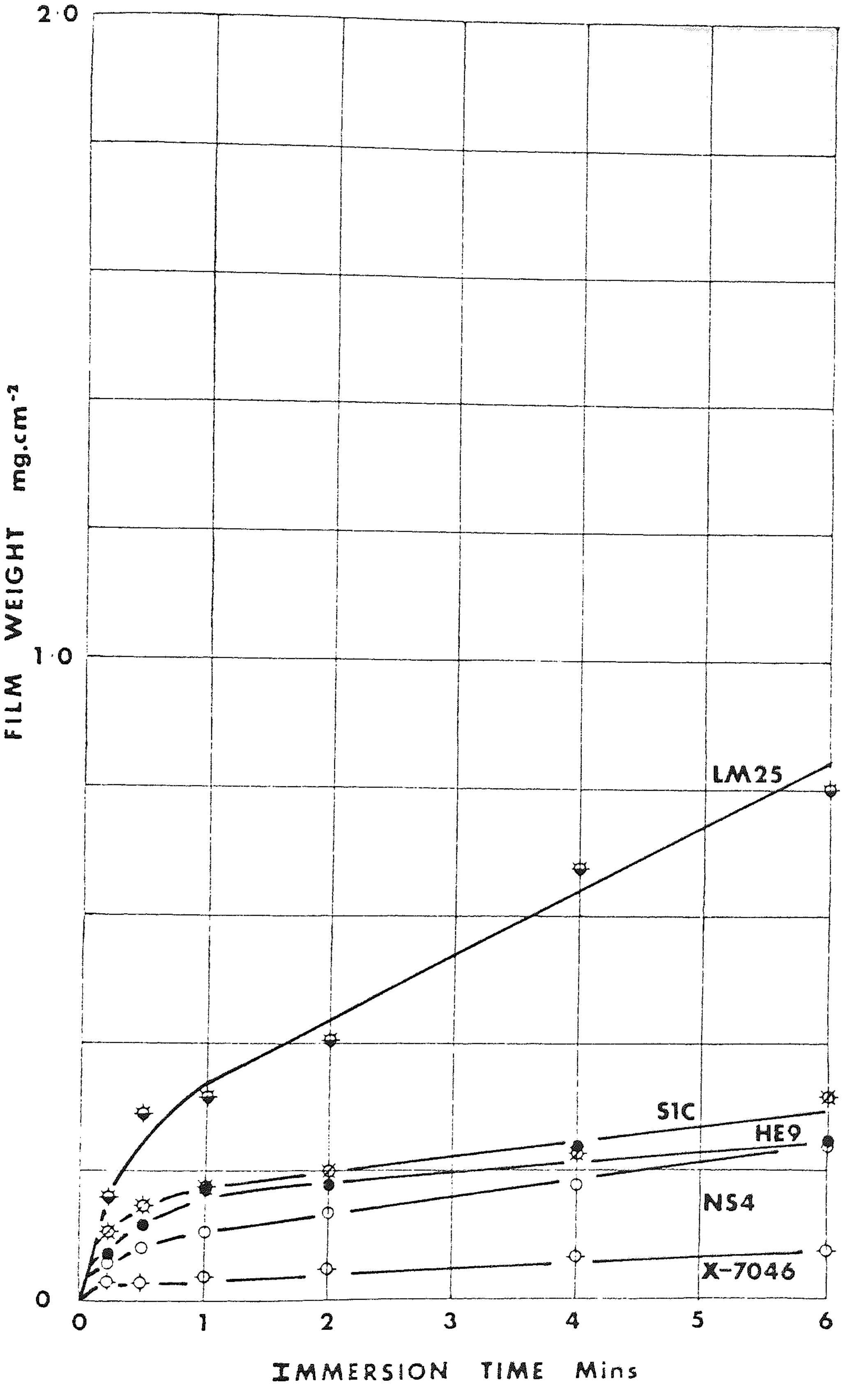


Fig.16. Relationship between film weight and immersion time in room temperature M.A.Z. solution for various aluminium alloys after pretreatment using sequence I.

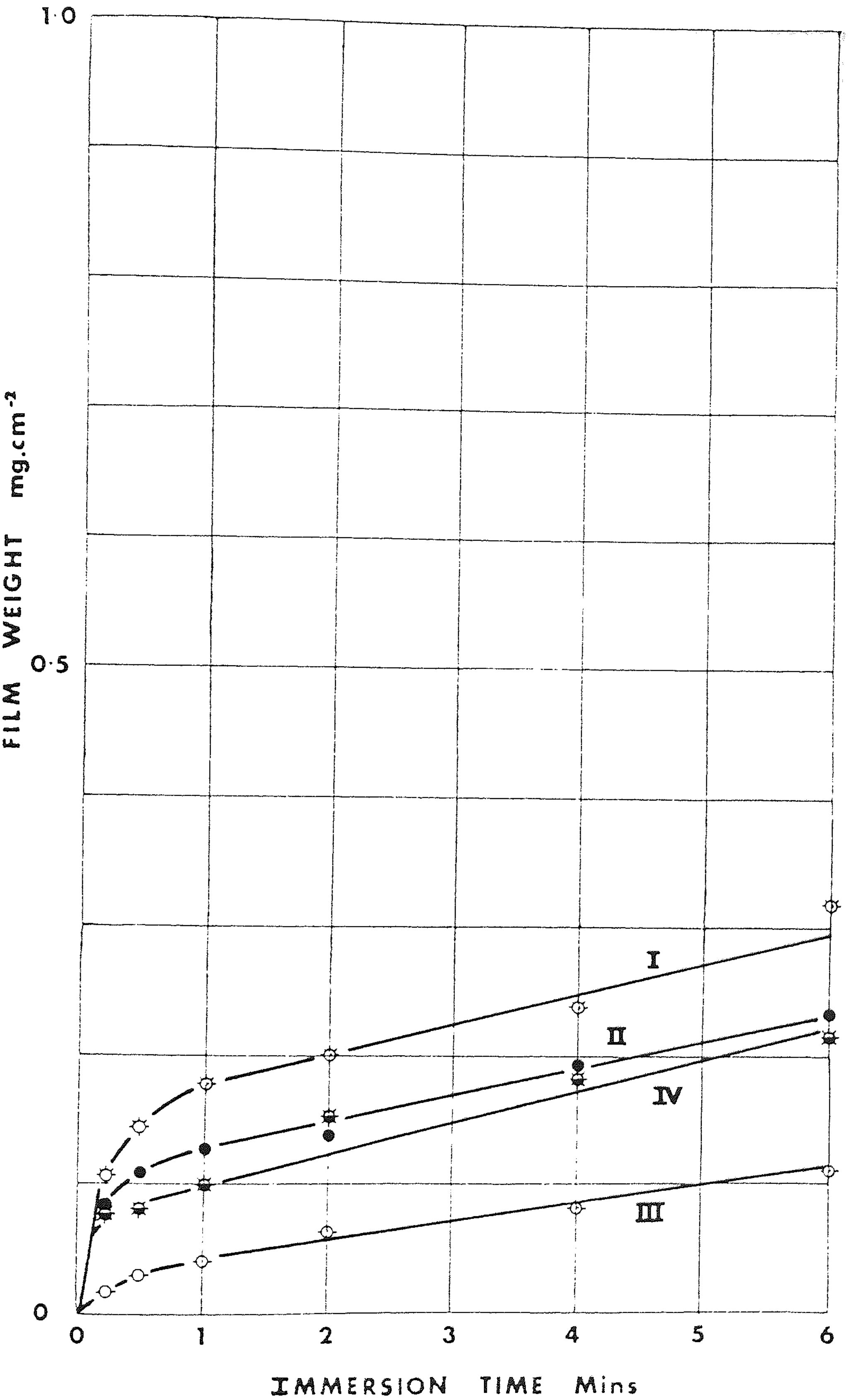


Fig.17a. Relationship between film weight and immersion time in room temperature M.A.Z. solution for alloy S1C after pretreatment using sequences I to IV.

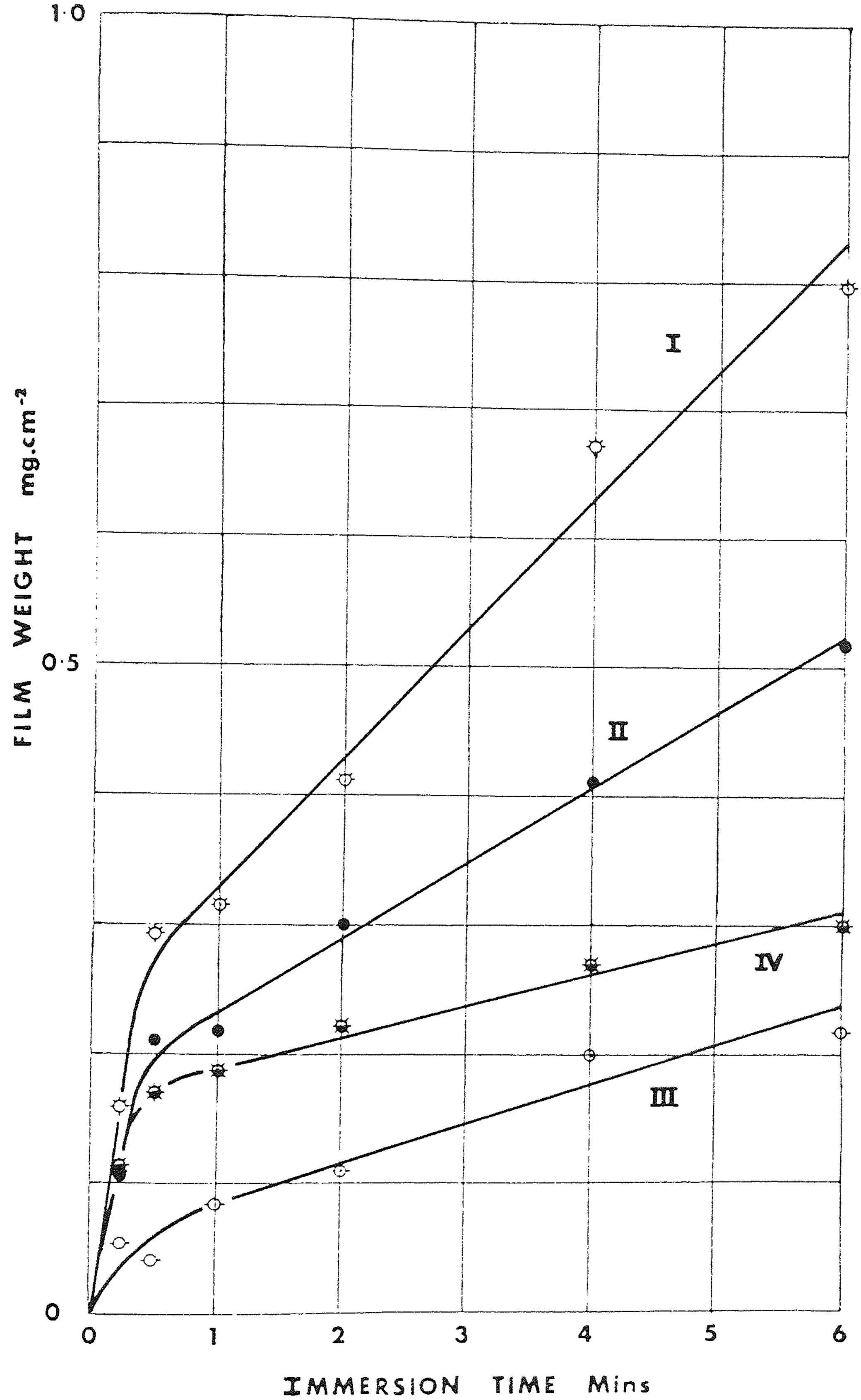


Fig.17b. Relationship between film weight and immersion time in room temperature M.A.Z. solution for alloy LM25 after pretreatment using sequences I to IV.

TABLE XIV. FILM WEIGHT ON THE ALUMINIUM ALLOYS AFTER VARIOUS STANDARD PRETREATMENT SEQUENCES AND 2 MINUTES IMMERSION IN ROOM TEMPERATURE M.A.Z. SOLUTION.

Alloy type	Average film weight mg/cm² Processing sequence I	II	III	IV
S1C	0·200	0·138	0·062	0·153
NS4	0·134	0·134	0·075	0·201
X-7046	0·045	0·032	0·056	0·068
HE9	0·178	0·101	0·048	0·107
LM25	0·414	0·303	0·109	0·221

The main peel adhesion testing programme, section 3.2.4., involved processing the alloys using the standard pretreatment sequences I to IV with a 2 min immersion in M.A.Z. solution. Table XIV indicates the corresponding weight of M.A.Z. deposit per unit area on the alloys prior to electroplating. Each value represents the average of three results. Film weight depended upon alloy type and pretreatment used.

3.2.3. Potential measurements

The change in potential with time during the build up of the M.A.Z. deposit was monitored. The potential-time curves for the various pretreatments and different alloys were then compared with the appropriate details of film morphology and growth rate, discussed previously, to interpret the relationships that existed between the results. Fig 18 indicates the potential-time curves recorded for S1C after pretreatment using sequences I and III and shows the effect of different immersion film growth modes on the shape of the curves. The immersion film produced on S1C, pretreated using sequence I, exhibited a fast growing but coarse grained deposit with poor surface coverage, whilst using sequence III resulted in slower but significantly more uniform coverage. It was therefore thought that the shape of the potential-time curves will be determined by the growth characteristics of the immersion deposit, namely film growth rate, uniformity of coverage, film composition and nature of the substrate upon which the film was developing. This is shown in the S1C sequence I curve, where the relatively poor coverage rate resulted in base

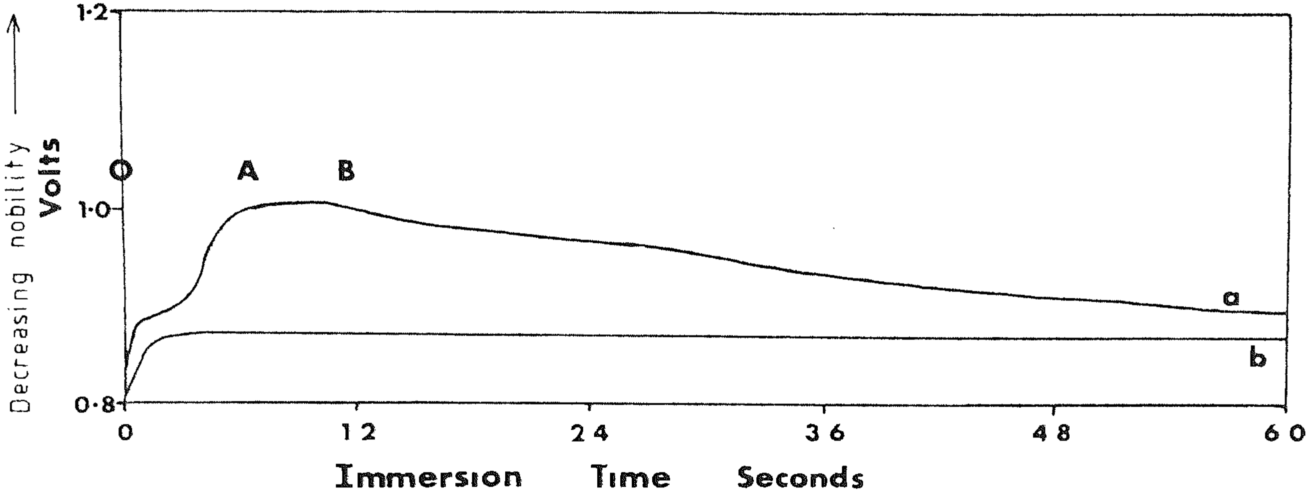


Fig.18. Change in potential on immersion in room temperature M.A.Z. solution (vs 0·1 M KCl calomel electrode) for alloy S1C : (a) after pretreatment using sequence I; (b) after pretreatment using sequence III.

aluminium alloy being exposed to the M.A.Z. solution long after initial immersion.

In the case of S1C sequence I,(Fig 18, curve a), from 0 to A oxide dissolution and exposure of the alloy surface occurs and has the dominant effect. The alloy surface devoid of oxide is more base. Neither oxide removal, effected by the caustic nature of the immersion solution, nor the total coverage of the surface with zinc rich immersion deposits is instantaneous all over the surface. Between A and B the influence of immersion film growth and oxide removal upon the overall potential are in balance. From B onwards the build-up of the zinc film, which has an ennobling effect, begins to have the dominant influence. Once total surface coverage has been achieved the curve takes on a much flatter appearance. At this point either film growth has stopped or the aluminium alloy surface is covered completely with a growing immersion film of constant composition.

In contrast, the S1C sequence III,(Fig 18, curve b), represents a situation where the aluminium surface, which is more uniform and less reactive by virtue of the double-dip treatments, is covered rapidly and uniformly by a thin film. Thus its influence on the overall potential value is reduced quickly, although the film still continues to grow slowly.

Hence it appears that the rate of change of surface potential with time is determined more by the rate of surface coverage by the film than by its overall rate of growth in terms of film weight per unit area.

Each alloy had a potential-time curve determined by its response to a specific pretreatment sequence and the growth characteristics of the subsequent M.A.Z. film. Fig 19 illustrates potential-time curves for S1C, LM25 and X-7046 processed according to sequence I. The first two alloys exhibit coarse, fast growing films. After a certain immersion time, when total surface coverage is almost complete these curves tend to approach the equilibrium potential line for X-7046, sequence I, which by comparison relates to a coarse but slow growing film. All the sequence I films exhibited poor coverage rate. X-7046 alloy shows only a slight change in potential, for although the growth is slow and coarse, giving poor coverage, the base aluminium regions still exposed to the M.A.Z. solution contain a relatively high percentage of zinc. It is known that small amounts of alloying additions can have a significant effect on surface properties. By reference to Table XV, the solution potential characteristics of aluminium are seen to be changed significantly by the addition of only one percent zinc. In the case of X-7046, which contains more than six percent zinc, the influence of any exposed regions of this alloy will be to move the overall potential towards that of zinc, rather than towards that of aluminium which would be the case for exposed regions on an S1C surface. The potential-time curves for LM25 and S1C immersed in M.A.Z. solutions will eventually tend towards the potential line for pure zinc immersed in the same solution, once the base aluminium alloy has been covered by immersion film. For LM25, where silicon will be exposed due to poor coverage, the time to reach equilibrium will be much longer as shown in Fig 20. To obtain these results the specimens were only degreased

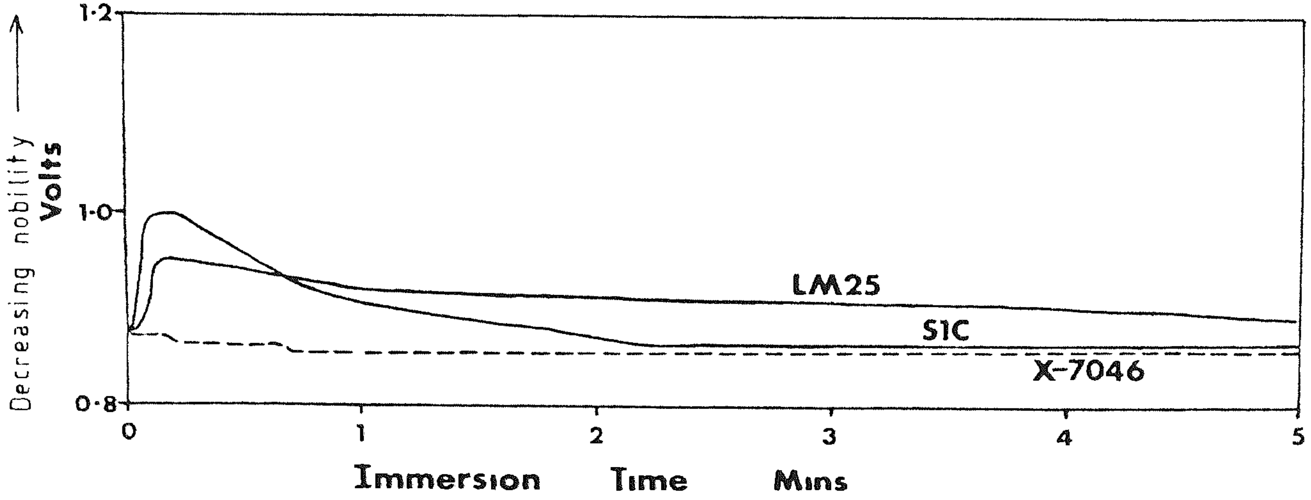


Fig.19. Change in potential on immersion in room temperature M.A.Z. solution (vs 0·1 M KCl calomel electrode) for various aluminium alloys after pretreatment using sequence I.

TABLE XV. POTENTIAL OF ALUMINIUM SOLID SOLUTIONS AND MICROCONSTITUENTS IMMERSED IN A SOLUTION CONTAINING 53g/1 NaCl AND 4g/1 H_2O_2.

Solid solution or microconstituent	Potential V

This table applies to measurement of solution potential in 53g/1 NaCl, 4g/1 H_2O_2 solution versus a 0·1 M calomel electrode. Data largely taken from Varley.(162)

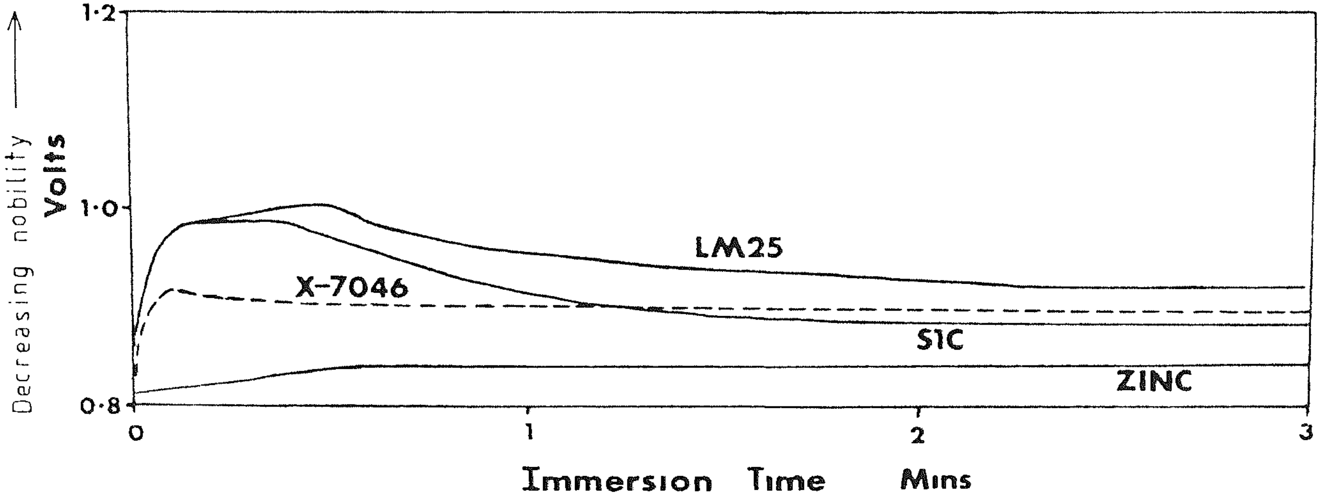


Fig.20. Change in potential on immersion in room temperature M.A.Z. solution (vs 0·1 M KCl calomel electrode) for various aluminium alloys and zinc after a non-standard pretreatment described in the text.

in acetone and dipped in 50% nitric acid for a few seconds prior to immersion in M.A.Z. solution. This resulted in thick loose films on LM25 with little tendency for coverage of any silicon platelets. Their influence in the overall potential is never overridden completely, as illustrated in Fig 20, with the equilibrium potential at a less noble level than for X-7046. Since the typical immersion deposit contains only about 84% zinc, the potentials of a thick uniform immersion deposit and pure zinc will always differ. Fig 20 shows that X-7046, on immersion in M.A.Z solution for a few seconds and hence oxide free, had a potential nearer to that of pure zinc than S1C or LM25. However, after about seventy-five seconds the potential of S1C with a very thick immersion film, by virtue of no real pretreatment, reached a value closer to that of pure zinc than did the X-7046. LM25 would probably never achieve this, due to the influence of the silicon regions on the surface and the spongy porous nature of the immersion deposit formed.

A misconception of earlier literature has been to quote solution potential values for aluminium alloys immersed in sodium chloride solution. This is not relevant to reactions taking place in M.A.Z. solution where the oxide film is quickly removed. Aluminium is more noble than zinc when protected by oxide, whereas without it the reverse is true. Additional work was undertaken to compare the potential-time values obtained on the three aluminium alloys with various other metals immersed in both sodium chloride and M.A.Z. solutions. Relevant information is summarised in Table XVI. Reference to this simple table shows that any conclusions

TABLE XVI. RELATIVE NOBILITY OF SOME METALS AND ALUMINIUM ALLOYS IN SODIUM CHLORIDE/HYDROGEN PEROXIDE SOLUTION AND M.A.Z. SOLUTION.

	Metal or alloy immersed in solutions at room temperature.	
	53g/l NaCl + 4g/l H_2O_2	M.A.Z. solution
↑ Increasing nobility	Copper	Iron
	Iron, lead	Copper
	Tin	Lead
	LM25	Tin
	S1C	Zinc
	X-7046	X-7046*
	Zinc	S1C*
		LM25*
	Natural oxide remains on Al alloys	Natural oxide removed rapidly from Al alloys

All metals were degreased in acetone and then dipped in 50% nitric acid for about 4 seconds. Results were obtained by measuring the potential of immersed specimens with respect to a 0·1 M calomel electrode.

* Maximum values obtained after removal of oxide but before the formation of a significant amount of immersion zinc film.

concerning surface potential, in sodium chloride solution, are irrelevant to behaviour in M.A.Z. solution. For example, the values obtained in M.A.Z. solution indicated that after the removal of oxide from LM25 aluminium alloy it had the most reactive surface. This confirmed practical observations and was attributed to the greater driving force between the surface and zinc ions present in the M.A.Z. solution. The alloy structure consisted of aluminium rich dendrites and eutectic silicon platelets and so resulted in heavier deposits. These extreme surface microstructural variations are believed to be the reason why the normal sequence III pretreatment, which provided thin fine grained deposits on wrought alloys such as S1C, NS4 and HE9 which are more homogeneous, failed to do so on LM25. The combination of etching out of microconstituents during cleaning and the preferential dissolution of surface constituents during growth of the first film in the double-dip technique can achieve a less reactive surface, since it becomes more electrochemically uniform and allows growth of a much finer grained immersion film to take place. The silicon platelets present in LM25 are not so easily removed and result in the formation of active cells which maintain the potential difference responsible for film growth. The films formed on LM25 when pretreated by sequence III were still quite coarse and thick.

3.2.4. Peel adhesion

For the adhesion testing programme the alloys were processed using the standard pretreatment sequences I to IV and electroplated with Watts nickel. A 2 min immersion in M.A.Z.

solution was used for both single and double-dip pretreatments. Peel adhesion results are given in Table XVII where each value represents the mean of eight results. Although an earlier study by Wittrock (33) found that adhesion of 5·0 KN m^{-1} was adequate, in this investigation a target of 7·5 KN m^{-1} was selected.

Except for X-7046 there was no problem in covering the surfaces of the alloys with and M.A.Z. deposit. However the presence of a film did not always guarantee good adhesion. This is highlighted by comparing the results in Table XVII with the films shown in Fig 13. Even in the case of adhesion of $< 0·7$ KN m^{-1}, e.g. HE9 and LM25 sequence I, a substantial M.A.Z. deposit was produced.

Table XVII shows the importance the pretreatment sequence had in determining adhesion. Of the four sequences considered, the double-dip, sequence III, consistently yielded the best adhesion results. It was also the least sensitive to immersion time. For instance, with S1C pretreated using sequence III a final M.A.Z. immersion of between 1 min and 4 min would ensure adhesion values in excess of 14 KN m^{-1}. With the other alloys, a final immersion time of 120 ± 30 s had no detrimental effect on adhesion when using this sequence.

Although in a number of instances sequence I resulted in adhesion exceeding 20 KN m^{-1} on S1C, such values were not reproduced consistently.

None of the four standard pretreatments produced adhesion of the electroplate to X-7046. This alloy was susceptible to attack by the plating solution when insufficiently protected by immersion deposit.

TABLE XVII. ADHESION OF WATTS NICKEL ELECTRODEPOSITS TO THE ALUMINIUM ALLOYS AFTER VARIOUS STANDARD PRETREATMENT SEQUENCES AND 2 MINUTES IMMERSION IN ROOM TEMPERATURE M.A.Z. SOLUTION.

Alloy type	Mean($\bar{X}$) peel adhesion value KN/m			
	Processing sequence			
	I	II	III	IV
S1C	12·1 (11·9)	17·0 (8·0)	23·6 (4·2)	12·1 (3·5)
NS4	6·2 (3·5)	7·4 (3·2)	11·5 (1·3)	5·8 (3·5)
X-7046	0	0	0	0
HE9	< 0·7	1·6 (0·7)	13·1 (2·8)	4·0 (1·2)
LM25	< 0·7	< 0·7	10·4 (1·1)	1·2 (0·2)

(Standard deviations given in brackets).

3.2.4.1. The influence of post-plating heat-treatment on peel adhesion

Table XVII indicates that the highest levels of adhesion were not necessarily recorded on the higher strength alloys. For example, the minimum tensile strength of HE9 is more than twice that of S1C. However the maximum mean adhesion values recorded on HE9 and S1C were 13·1 KN m^{-1} and 23·6 KN m^{-1} respectively, achieved using sequence III. Post-plating heat-treatment is used in the Vogt method (5,6) to improve electroplate adhesion. Therefore to assess its usefulness and specifically to improve the electroplate adhesion on HE9 with respect to S1C, heat-treatment following plating was used. Therefore S1C and HE9 panels were pretreated using sequence III with 2 min M.A.Z. dips, and Watts nickel plated. After plating, some of the panels were placed into a furnace preheated to 230°C for times in the range 0·5 h to 1·5 h. Excessive heat-treatment was avoided to prevent formation of an intermetallic layer which would reduce adhesion. The results of peel adhesion tests are given in Table XVIII, where each value represents the mean of six results. These results illustrate that although always lower than on S1C, post-plating heat-treatment performed for sufficient time significantly increases electroplate adhesion to HE9. No such corresponding improvement was monitored for S1C.

In addition, after heat-treatment all the plated panels were blister-free. This is also indicative of 'good quality plating'. (122)

TABLE XVIII. EFFECT OF POST-PLATING HEAT-TREATMENT AT 230 °C ON ADHESION OF WATTS NICKEL ELECTRODEPOSITS TO ALUMINIUM ALLOYS S1C AND HE9 PRETREATED USING SEQUENCE III AND 2 MINUTES IMMERSION IN ROOM TEMPERATURE M.A.Z. SOLUTION.

	Mean ($\bar{X}$) peel adhesion value KN/m			
Alloy type	Duration of 230 °C heat-treatment h			
	0	0·5	1·0	1·5
S1C	24·5 (7·6)	24·2 (6·4)	26·8 (8·8)	26·3 (8·0)
HE9	13·8 (3·2)	12·3 (3·2)	12·6 (1·3)	18·8 (2·9)

(Standard deviations given in brackets).

3.2.4.2. Appearance of failure surfaces after peel adhesion testing

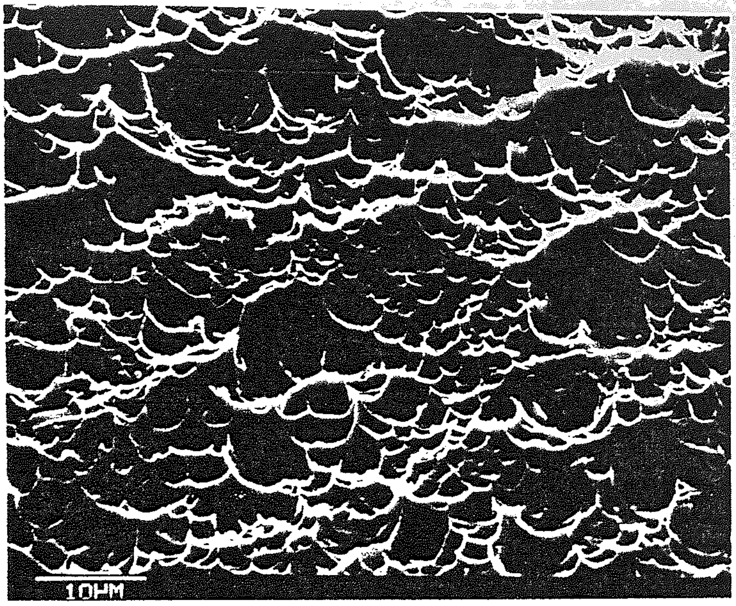
Depending on adhesion, differing amounts of substrate were detached on the back of the peeled foil. Furthermore there were differences, not due to variations in adhesion, in the failure surfaces of LM25 compared to those of S1C, NS4 and HE9.

A number of failure surfaces of various alloys given different pretreatments, and having different levels of adhesion, were examined on the S.E.M. The object was to illustrate variations in failure due to the influence of pretreatment, the nature of subsequent M.A.Z. deposits and the inherent mechanical properties of the alloy substrates.

The failure surfaces of S1C pretreated using sequence IV, which had adhesion value of 13·9 KN m^{-1}, and the back of the foil peeled from it are shown in Fig 21. Failure occurred partially at the S1C-electroplate interface and partially by ductile cup-and-cone fracture within the aluminium substrate although the adhesion was good.

Fig 22 illustrates the appearance of LM25 pretreated using sequence III to give and adhesion value of 9·3 KN m^{-1}. LM25 has a greater mechanical strength than S1C and it is less ductile. Thus when plated to give relatively good adhesion, the failure surfaces of LM25 exhibit the characteristics of a more brittle material. Silicon plates in the eutectic regions of the surface also influence the maximum adhesion levels attainable. The electroplate

(a)



(b)

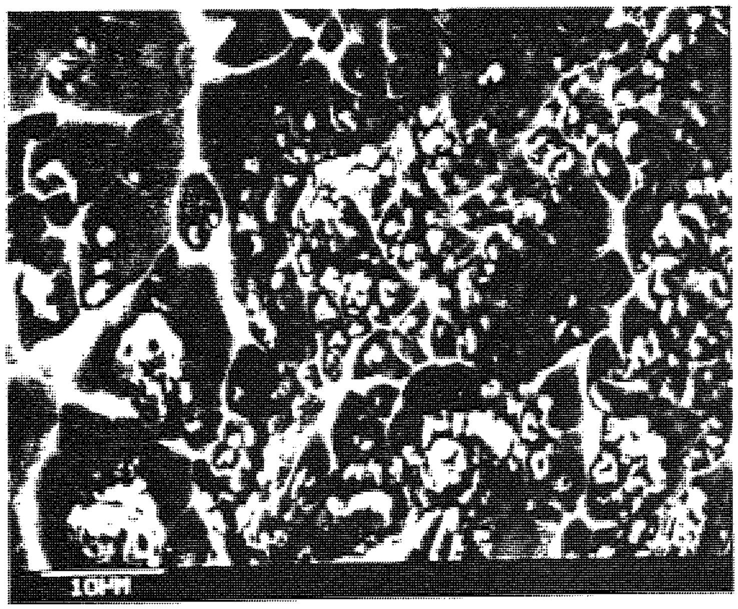


Fig.21. Scanning electron micrographs of the failure surfaces after peel adhesion testing of alloy S1C pretreated using sequence IV (2 min immersion in room temperature M.A.Z. solution) :
(a) the alloy surface after peeling off the nickel foil;
(b) the back of the peeled nickel foil.
The peel adhesion was 13·9 KN m^{-1}.

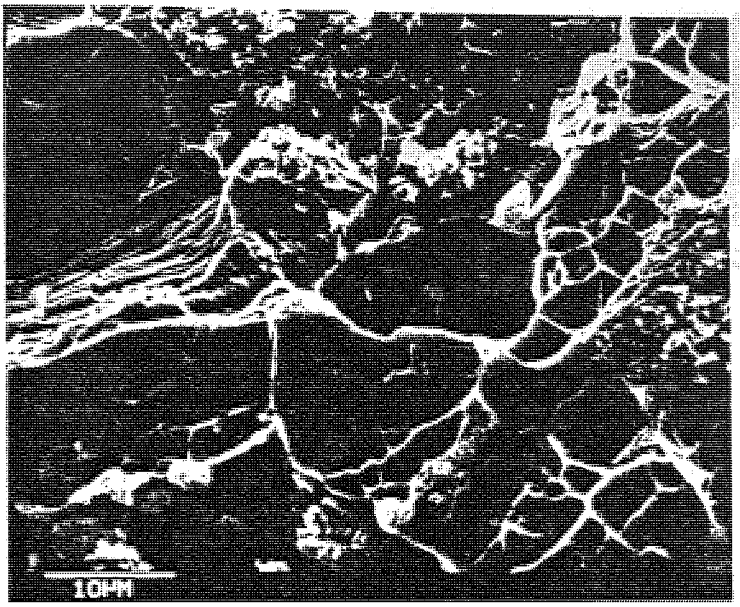


Fig.22. Scanning electron micrograph of the surface of alloy LM25 pretreated using sequence III (2 min immersion in room temperature M.A.Z. solution), after peeling off the nickel foil. The peel adhesion was 9·3 KN m^{-1}.

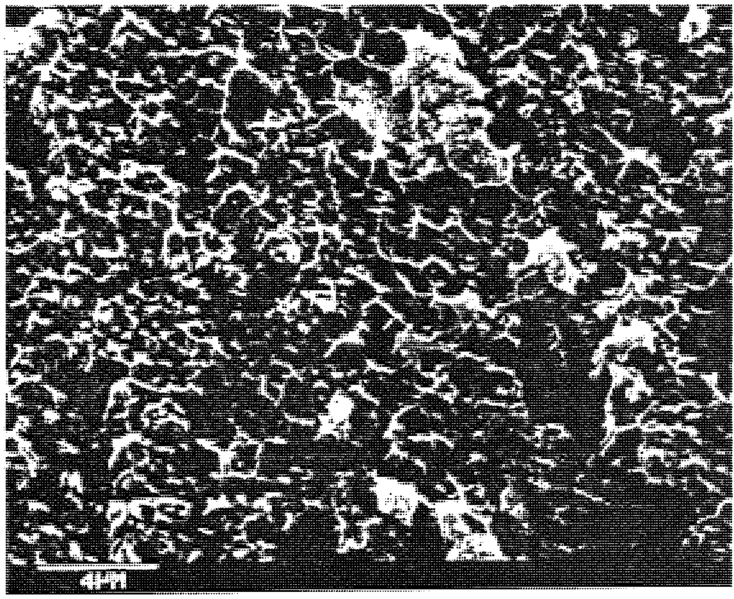
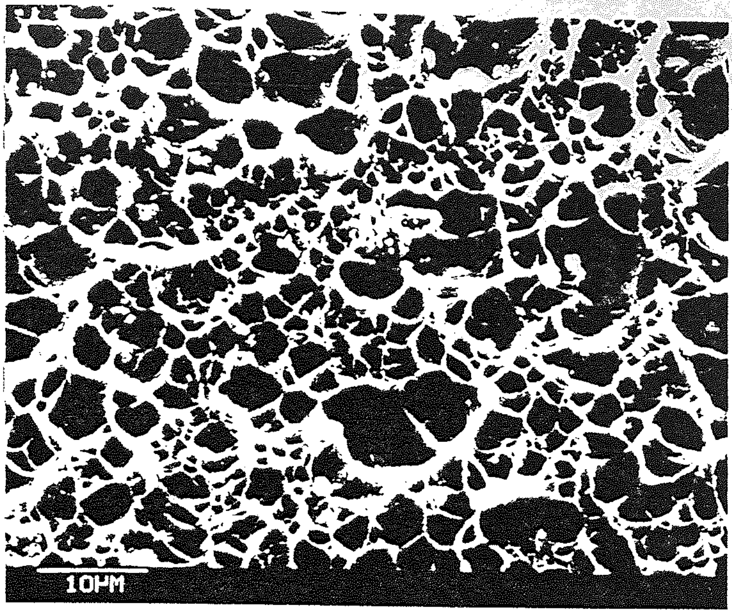


Fig.23. Scanning electron micrograph of the surface of alloy HE9 pretreated using sequence I (2 min immersion in room temperature M.A.Z. solution), after peeling off the nickel foil. The peel adhesion was less than 0·7 KN m^{-1}.

(a)



(b)

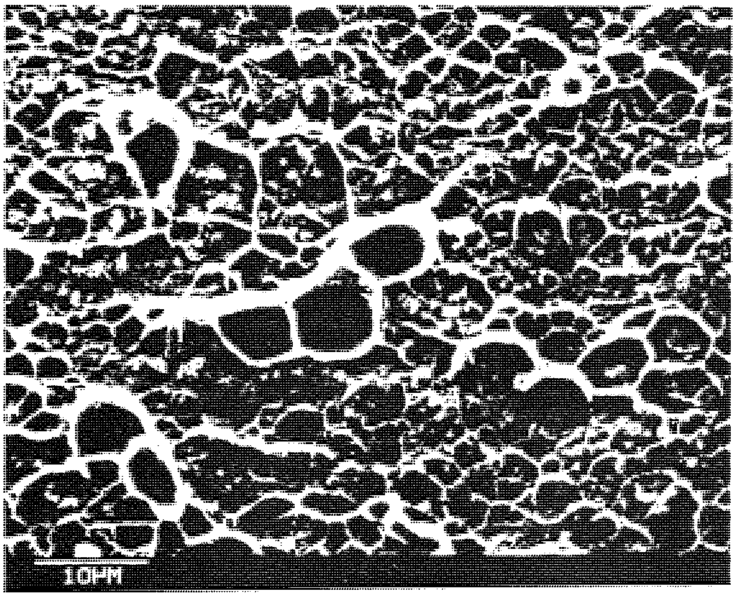


Fig.24. Scanning electron micrographs of the failure surfaces of alloy HE9 pretreated using sequence III (2 min immersion in room temperature M.A.Z. solution) and heat-treated at 230 °C for 1·5 h following plating, after peel adhesion testing : (a) the alloy surface after peeling off the nickel foil; (b) the back of the peeled nickel foil.
The peel adhesion was 20·9 KN m^{-1}.

is less likely to bond as well in such regions and the silicon plates could fail by cleavage.

Fig 23 shows the failure surface of HE9 pretreated using sequence I, which exhibited minimal adhesion. Even in this case a slight amount of failure took place within the alloy substrate.

The failure surfaces of HE9 and S1C pretreated using sequence III, plated and heat-treated at 230°C for different times, were examined. All the failure surfaces of S1C were identical, rupture occurring entirely within the substrate giving very high adhesion values in excess of 24 KN m^{-1}. For HE9, the increase in adhesion due to heat-treatment corresponded to a transition from failure partially within, to entirely within the substrate. S1C and HE9 both exhibited ductile cup-and-cone type failure. The failure surfaces of HE9 pretreated using sequence III, heat-treated at 230°C for 1·5 h following plating and which exhibited excellent adhesion of 20·9 KN m^{-1} are shown in Fig 24. Failure was totally within the substrate, a relatively thick layer of which was detached on the peeled electrodeposit.

3.2.5. The effect of heat-treatment of LM25

The LM25 used for this and all subsequent work came from a different batch to that used in earlier studies.

The heat-treatments and the effect on the properties of LM25 are described in Table XII.

The only effect any of the heat-treatments had on the microstructure was that following solution treatment, the prominent needles of eutectic silicon were more rounded and smaller.

Response to pretreatment, zincate deposit morphology, film growth rate and adhesion were studied using techniques outlined previously.

Effects of pretreatment and M.A.Z. film characteristics were influenced by heat-treated condition. This is illustrated by Figs 25 and 26 which show M.A.Z. deposits on LM25, as-cast and fully heat-treated, respectively. The films produced by a 1 min M.A.Z. immersion following pretreatment sequences I and III are shown in Figs 25a and 26a, and Figs 25b and 26b, respectively. The fully heat-treated LM25 responded more uniformly to pretreatment. Subsequent immersion deposits were more uniform, thinner, finer grained and exhibited superior coverage compared with those on similarly pretreated as-cast LM25. For example the M.A.Z. film which formed on as-cast LM25 pretreated using sequence I, Fig 25a, nucleated preferentially along silicon plate boundaries and polishing lines and gave non-uniform coverage. Figs 25 and 26 also emphasise the improvement in film characteristics produced by using the double-dip pretreatment, sequence III.

However peel adhesion results and the appearance of M.A.Z. deposits on the 'new' as-cast LM25 material indicated that it was not identical in behaviour to the original batch of material. For example, the mean adhesion values achieved on new and original LM25, pretreated using sequence III and 2 min M.A.Z. dips were,

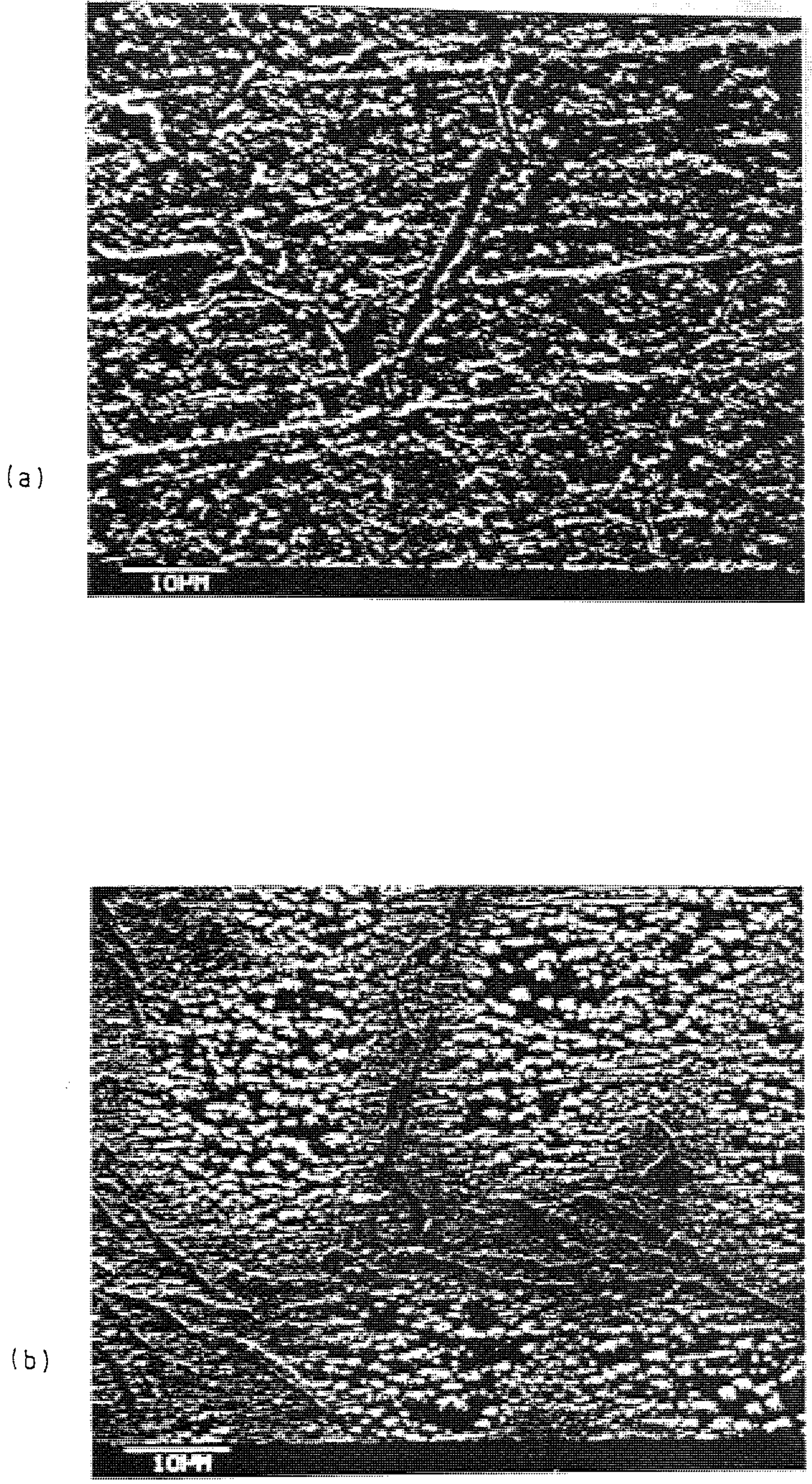


Fig.25. Scanning electron micrographs of the surface of alloy LM25 (as-cast) after pretreatment using :
(a) sequence I, 1 min immersion in room temperature M.A.Z. solution;
(b) sequence III, 1 min immersion in room temperature M.A.Z. solution.

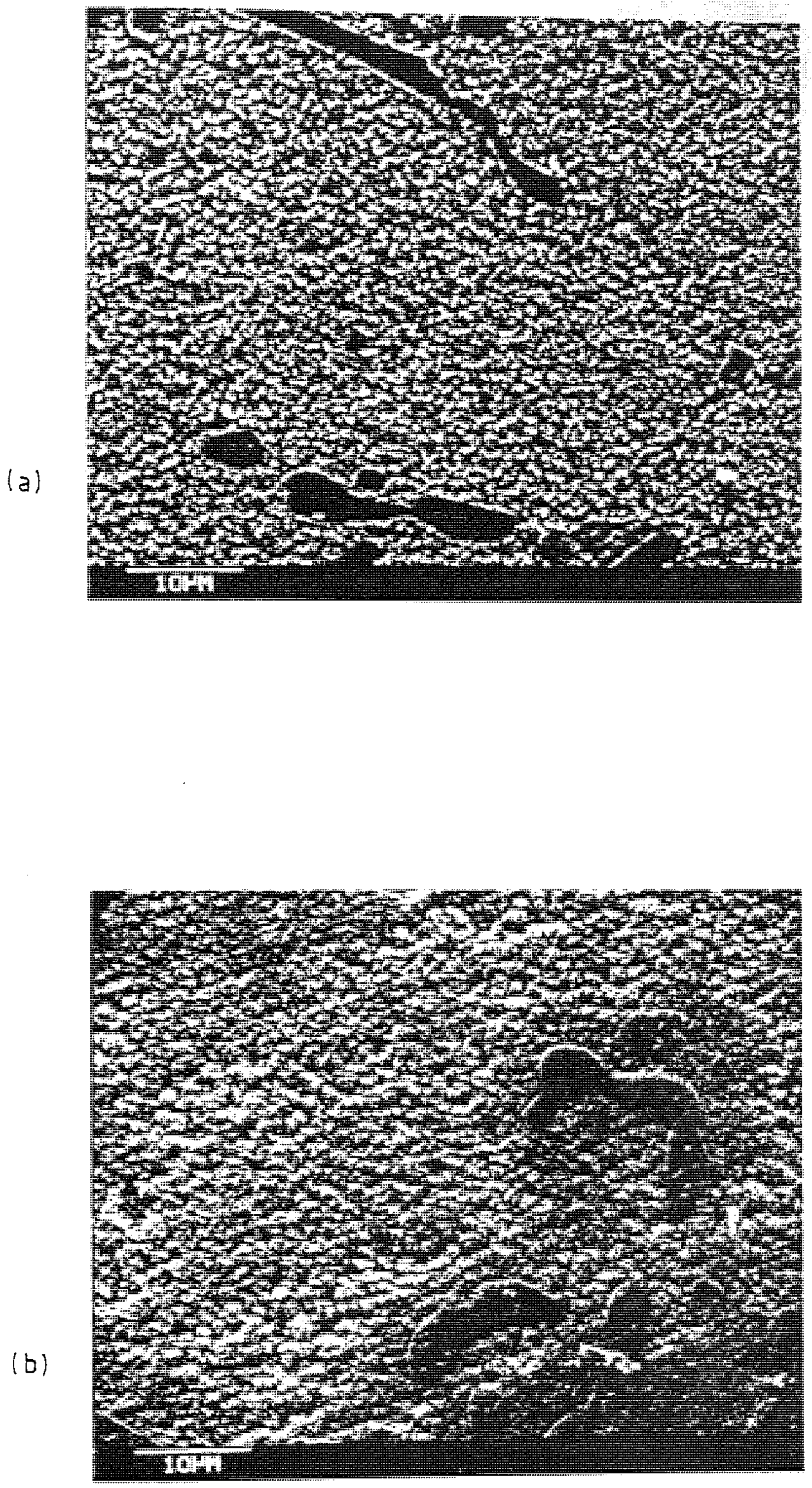


Fig.26. Scanning electron micrographs of the surface of alloy LM25 (fully heat-treated) after pretreatment using : (a) sequence I, 1 min immersion in room temperature M.A.Z. solution; (b) sequence III, 1 min immersion in room temperature M.A.Z. solution.

TABLE XIX. FILM WEIGHT ON HEAT-TREATED ALUMINIUM ALLOY LM25 AFTER VARIOUS STANDARD PRETREATMENT SEQUENCES AND 2 MINUTES IMMERSION IN ROOM TEMPERATURE M.A.Z. SOLUTION.

Alloy type : LM25		Average film weight mg/cm^2	
Heat-treatment	Condition	Processing sequence	
		I	III
-	M	0·357	0·119
Precipitation treated	TE	0·306	0·110
Solution treated	TB7	0·224	0·085
Solution and precipitation treated (Fully heat-treated)	TF	0·273	0·106

TABLE XX. ADHESION OF WATTS NICKEL ELECTRODEPOSITS TO HEAT-TREATED ALUMINIUM ALLOY LM25 PRETREATED USING SEQUENCE III AND 2 MINUTES IMMERSION IN ROOM TEMPERATURE M.A.Z. SOLUTION.

Alloy type : LM25 Heat-treatment	Condition	Mean ($\bar{X}$) peel adhesion value KN/m
-	M	4·4 (1·2)
Precipitation treated	TE	6·0 (1·4)
Solution treated	TB7	10·0 (0·7)
Solution and precipitation treated (Fully heat-treated)	TF	8·9 (2·5)

(Standard deviations given in brackets).

$4{\cdot}4$ KN m^{-1} and $10{\cdot}4$ KN m^{-1}, respectively. Therefore the effects of heat-treatment reported, only apply to the new LM25 material.

The rate of M.A.Z. film growth was affected by heat-treated condition and pretreatment sequence, Table XIX. For a specific sequence and immersion time, the thinnest deposits were obtained on solution heat-treated LM25 while the thickest occurred on the as-cast material. It can also be seen that the double-dip, sequence III, caused a significant reduction in film weight irrespective of heat-treated condition.

The effect of heat-treatment on peel adhesion is shown in Table XX, where each value represents the mean of six results. All panels were pretreated using sequence III with 2 min M.A.Z. dips and then Watts nickel plated. The lowest mean peel adhesion value was obtained on as-cast LM25, e.g. $4{\cdot}4$ KN m^{-1}, while the highest was achieved on the solution heat-treated material, e.g. $10{\cdot}0$ KN m^{-1}.

3.2.6. Corrosion tests

The alloys used in this study were S1C, HE9 and LM25. These were processed using the standard pretreatment sequences I to IV. A 2 min immersion in M.A.Z. solution was used for both single and double-dip pretreatments. The three coating systems applied are described in section 2.10.2. Plated panels were C.A.S.S. tested for 5 cycles and corrosion rated according to the A.S.T.M. method (160) after each 16 h cycle. Two panels of each type were tested and the corresponding rating values averaged.

3.2.6.1. Assessment of corrosion behaviour

Figs 27, 28 and 29 show the graphs of A.S.T.M. rating against number of C.A.S.S. cycles for the decorative, thin microporous and thick microporous coating systems, respectively, applied to the three alloys. These graphs broadly indicate the following :

1. For all the alloys and coating systems, sequence I was always associated with the worst corrosion performance.
2. The microporous chromium systems gave better corrosion protection than the decorative chromium system.
3. For any specific pretreatment sequence or coating system, the best corrosion behaviour was exhibited by S1C.
4. Plated LM25 exhibited the lowest resistance to corrosion for all pretreatment sequences and coating systems.
5. The double-dip pretreatments, sequences III and IV, resulted in a significant improvement in corrosion performance.

According to B.S. 1224 : 1970, to meet the requirements of service condition 3, the rating after 1 C.A.S.S. cycle must be 8 or above. This was achieved with all the alloys and coating systems when using both sequences III and IV. However, this was not always the case with the single dip pretreatments ; the corrosion

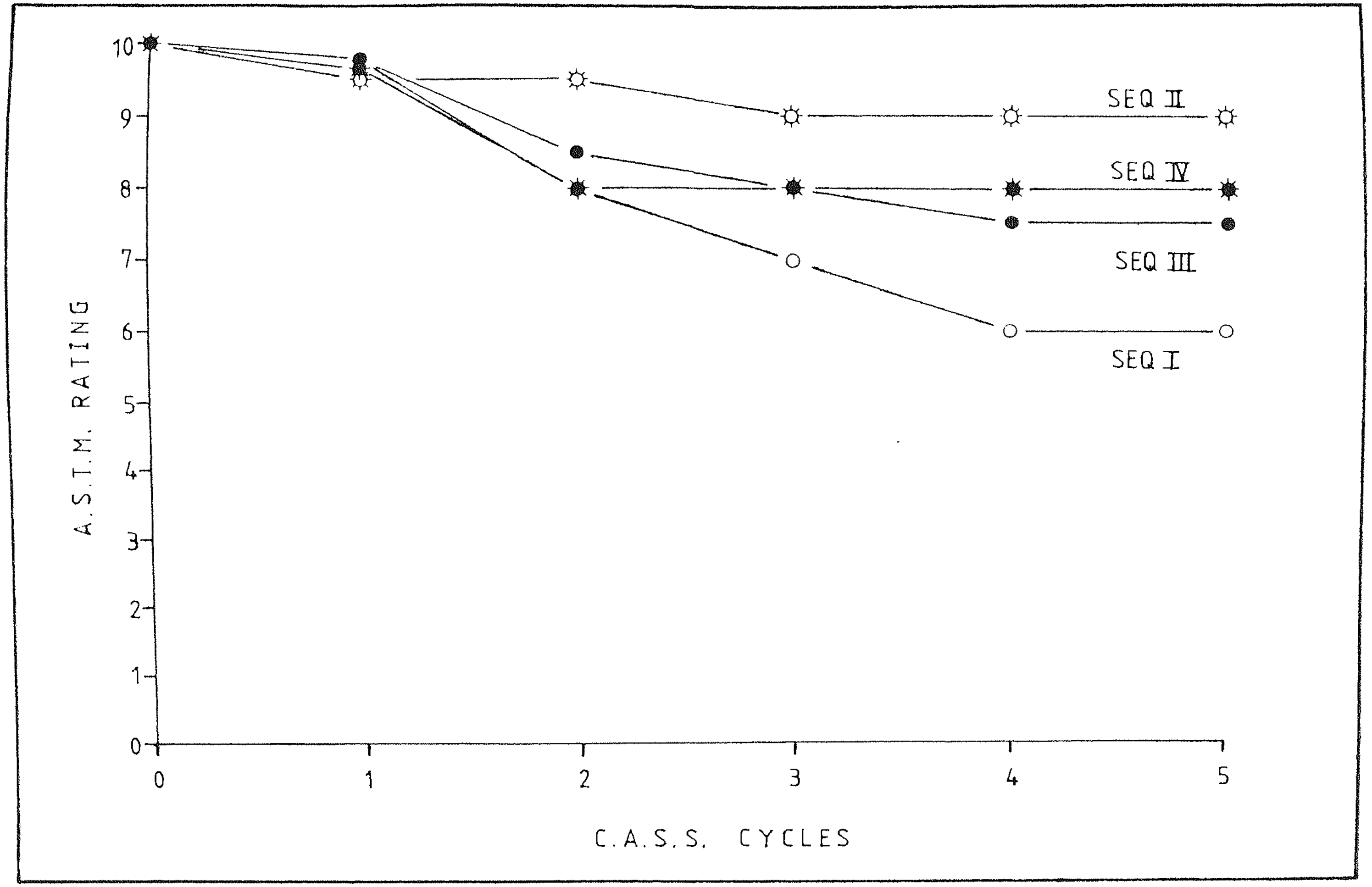


Fig.27a. Relationship between A.S.T.M. rating and number of C.A.S.S. cycles for alloy S1C plated with the 0·25 µm decorative chromium coating system. S1C pretreated using sequences I to IV (2 min immersion in room temperature M.A.Z. solution).

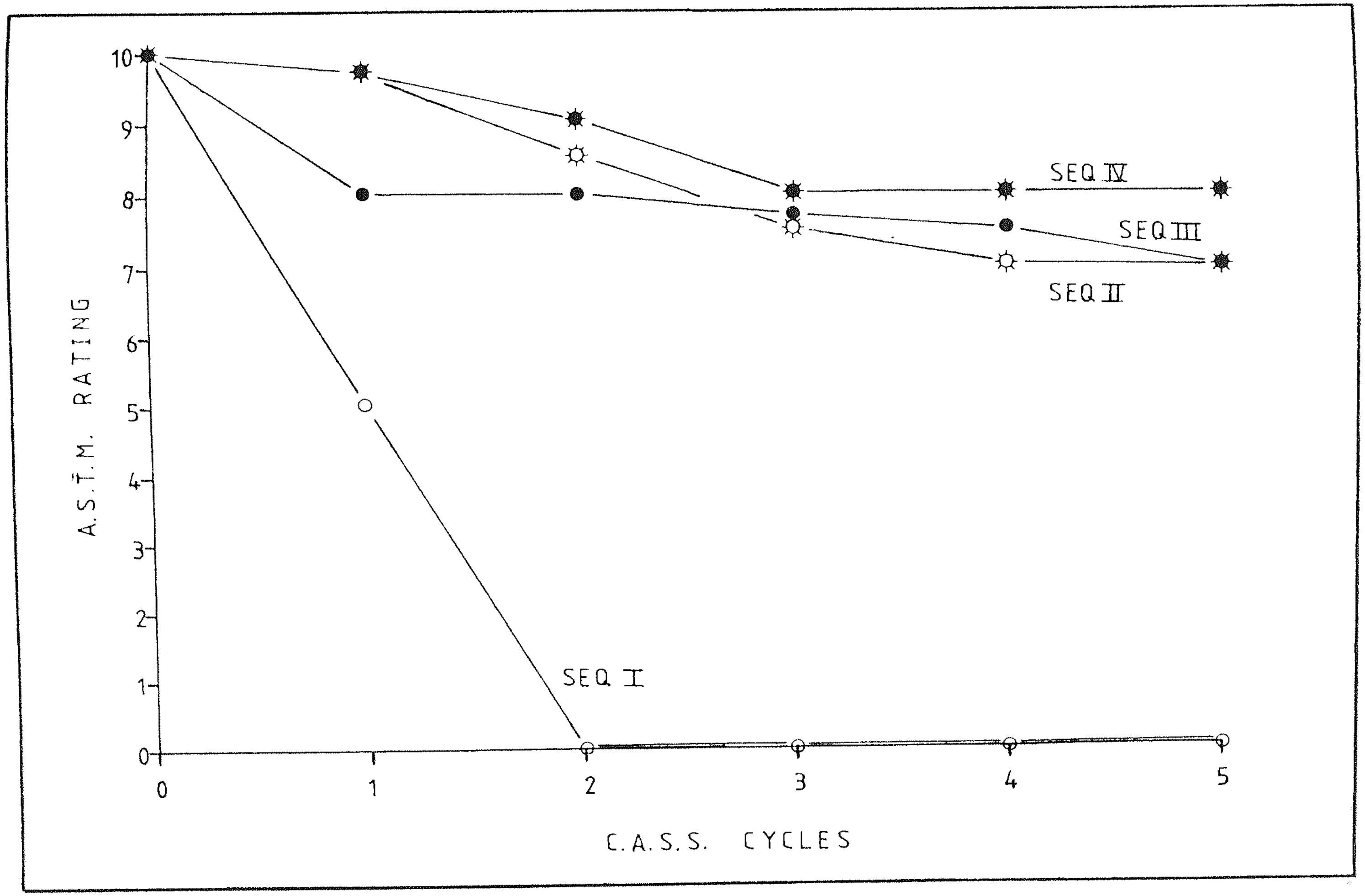


Fig.27b. Relationship between A.S.T.M. rating and number of C.A.S.S. cycles for alloy HE9 plated with the 0·25 µm decorative chromium coating system. HE9 pretreated using sequences I to IV (2 min immersion in room temperature M.A.Z. solution).

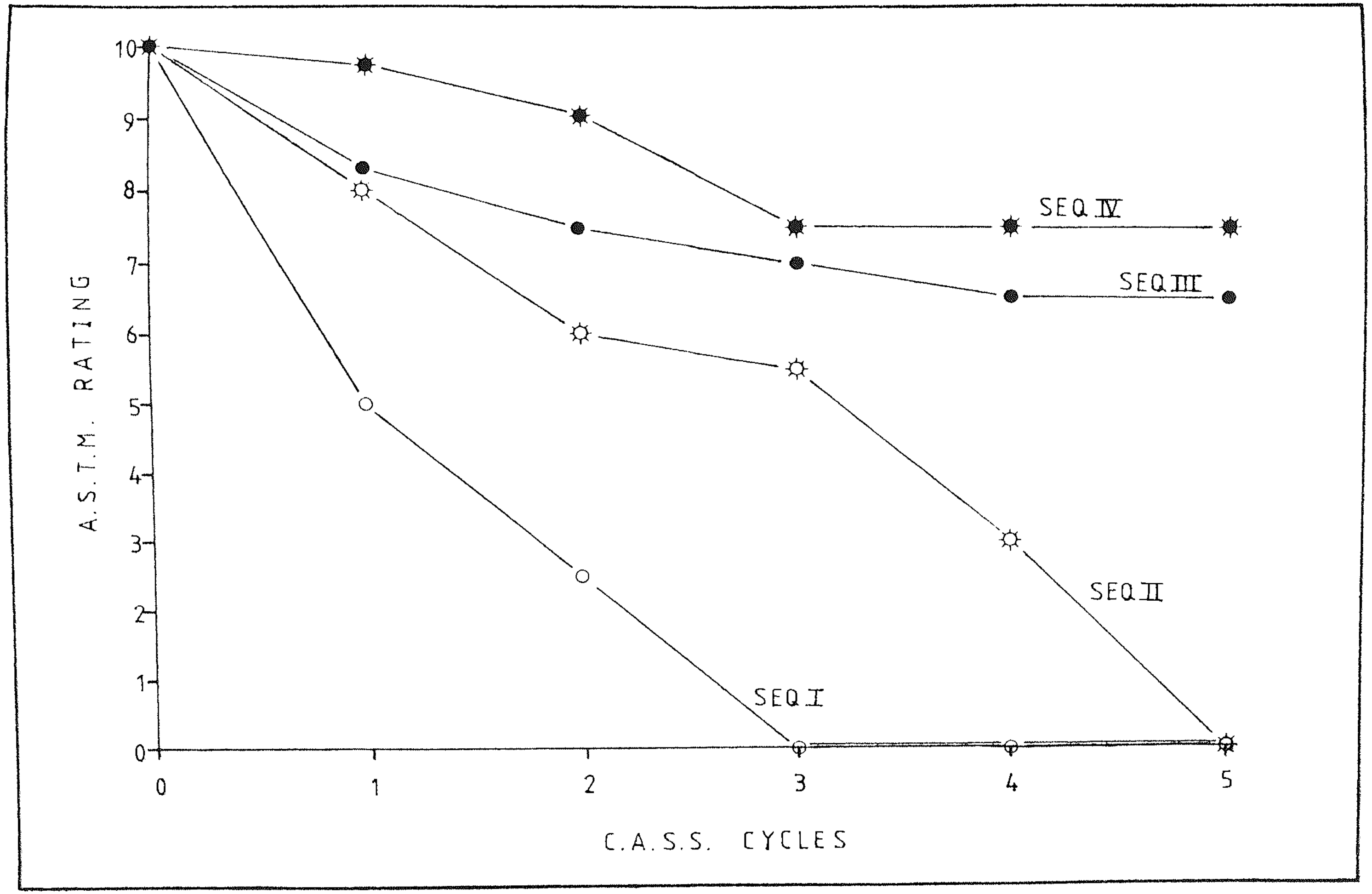


Fig.27c. Relationship between A.S.T.M. rating and number of C.A.S.S. cycles for alloy LM25 plated with the 0·25 µm decorative chromium coating system. LM25 pretreated using sequences I to IV (2 min immersion in room temperature M.A.Z. solution).

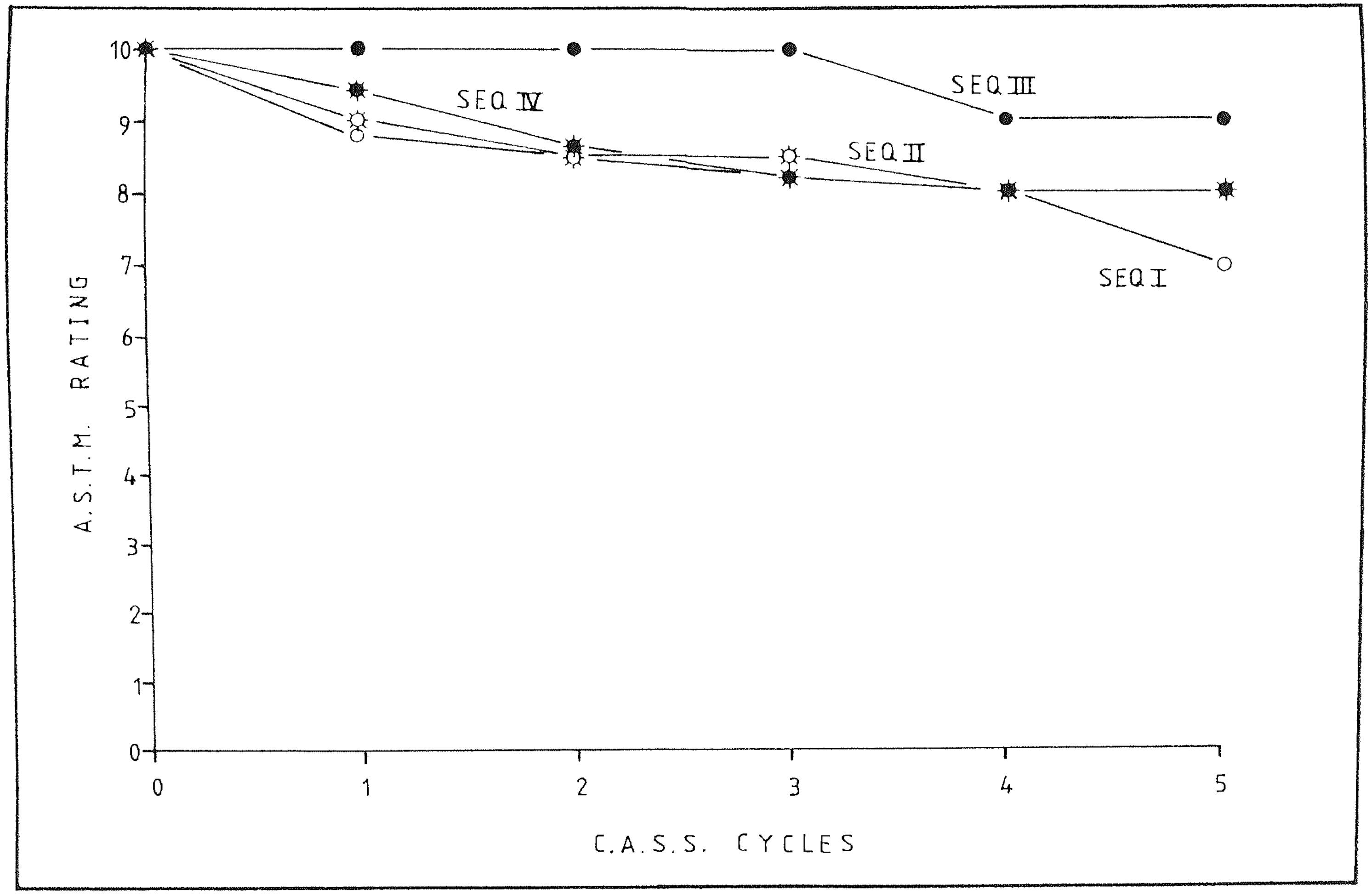


Fig.28a. Relationship between A.S.T.M. rating and number of C.A.S.S. cycles for alloy S1C plated with the thin 0·25 µm microporous chromium coating system. S1C pretreated using sequences I to IV (2 min immersion in room temperature M.A.Z. solution).

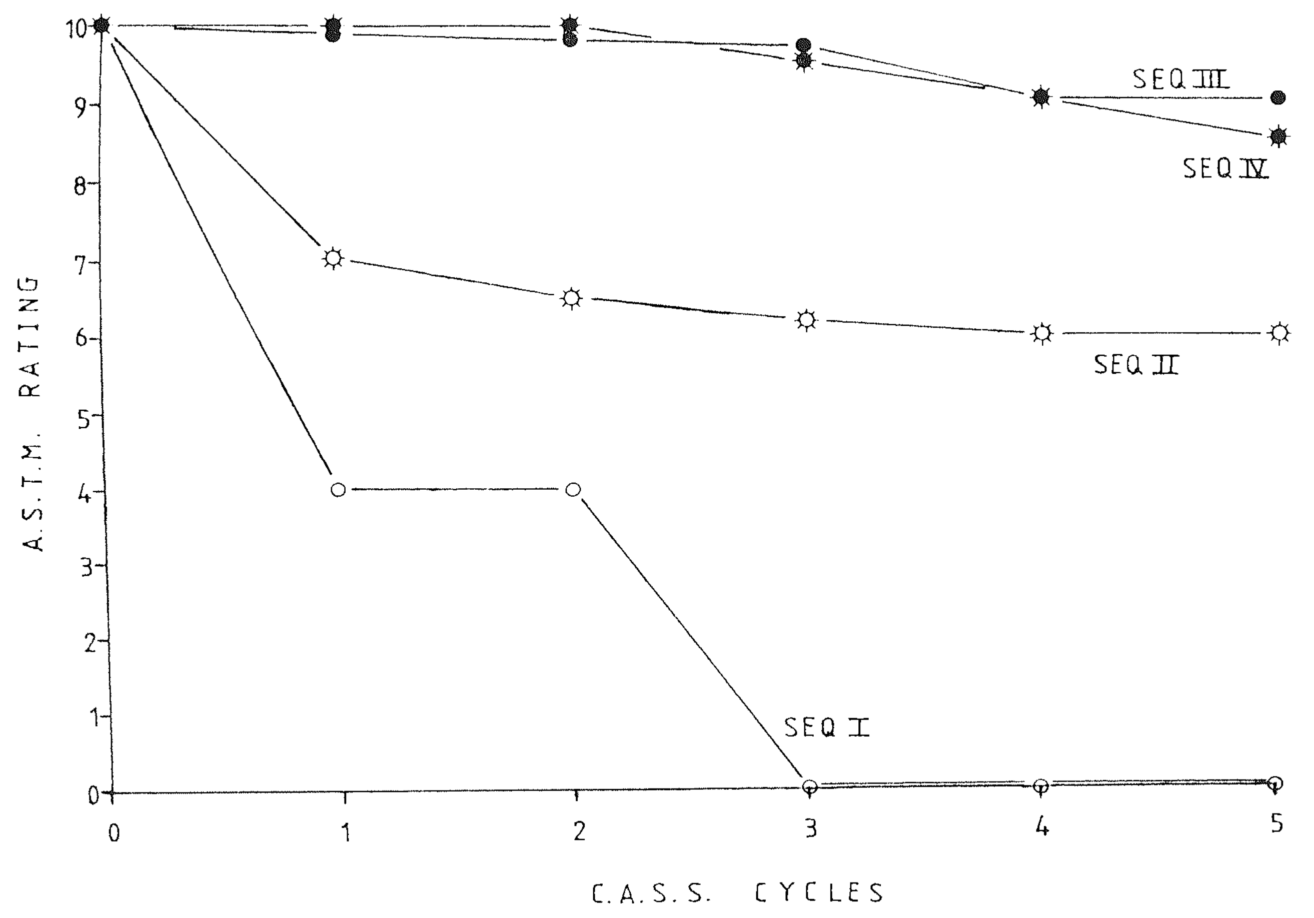


Fig.28b. Relationship between A.S.T.M. rating and number of C.A.S.S. cycles for alloy HE9 plated with the thin 0·25 µm microporous chromium coating system. HE9 pretreated using sequences I to IV (2 min immersion in room temperature M.A.Z. solution).

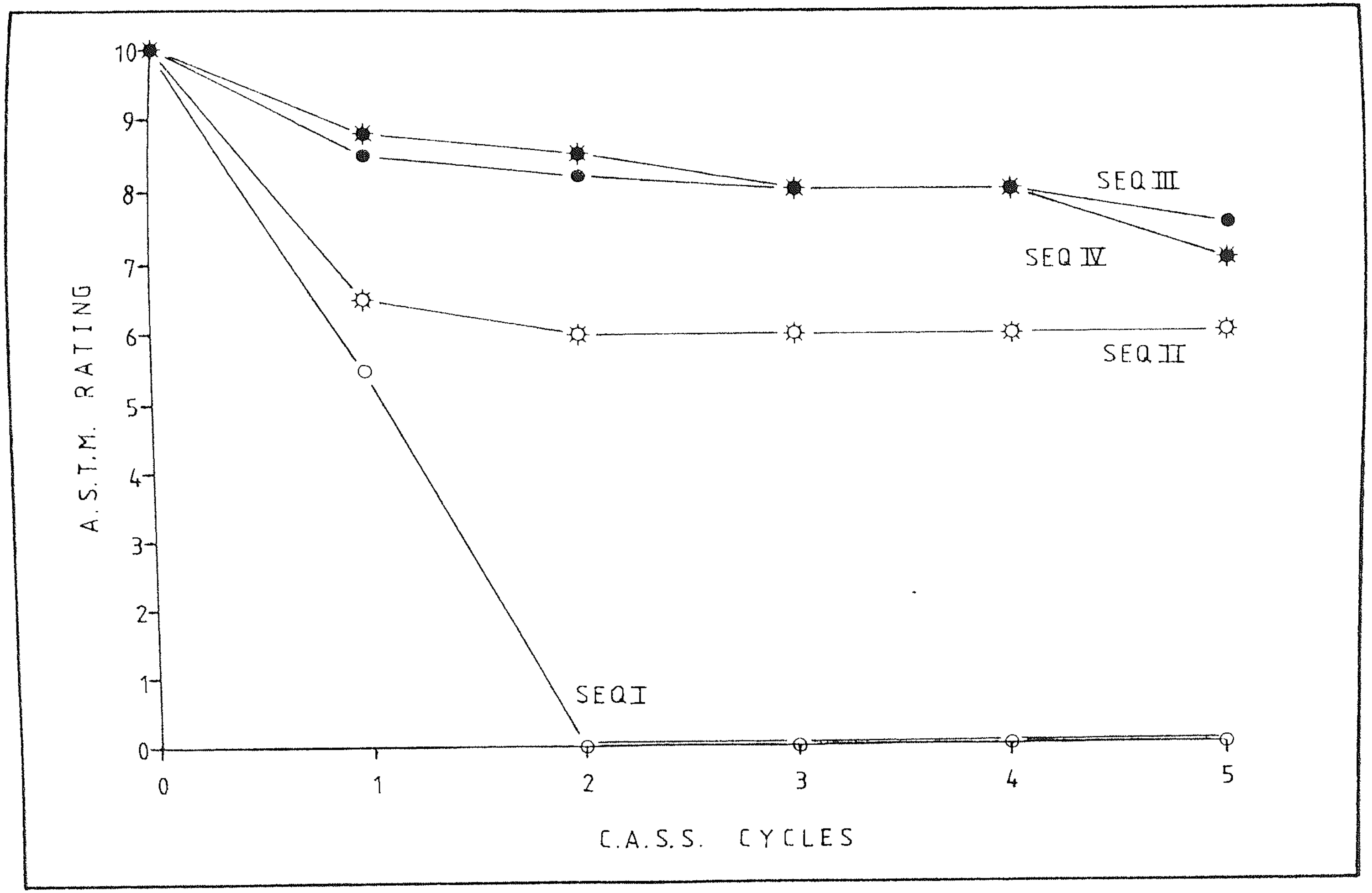


Fig.28c. Relationship between A.S.T.M. rating and number of C.A.S.S. cycles for alloy LM25 plated with the thin 0·25 µm microporous chromium coating system. LM25 pretreated using sequences I to IV (2 min immersion in room temperature M.A.Z. solution).

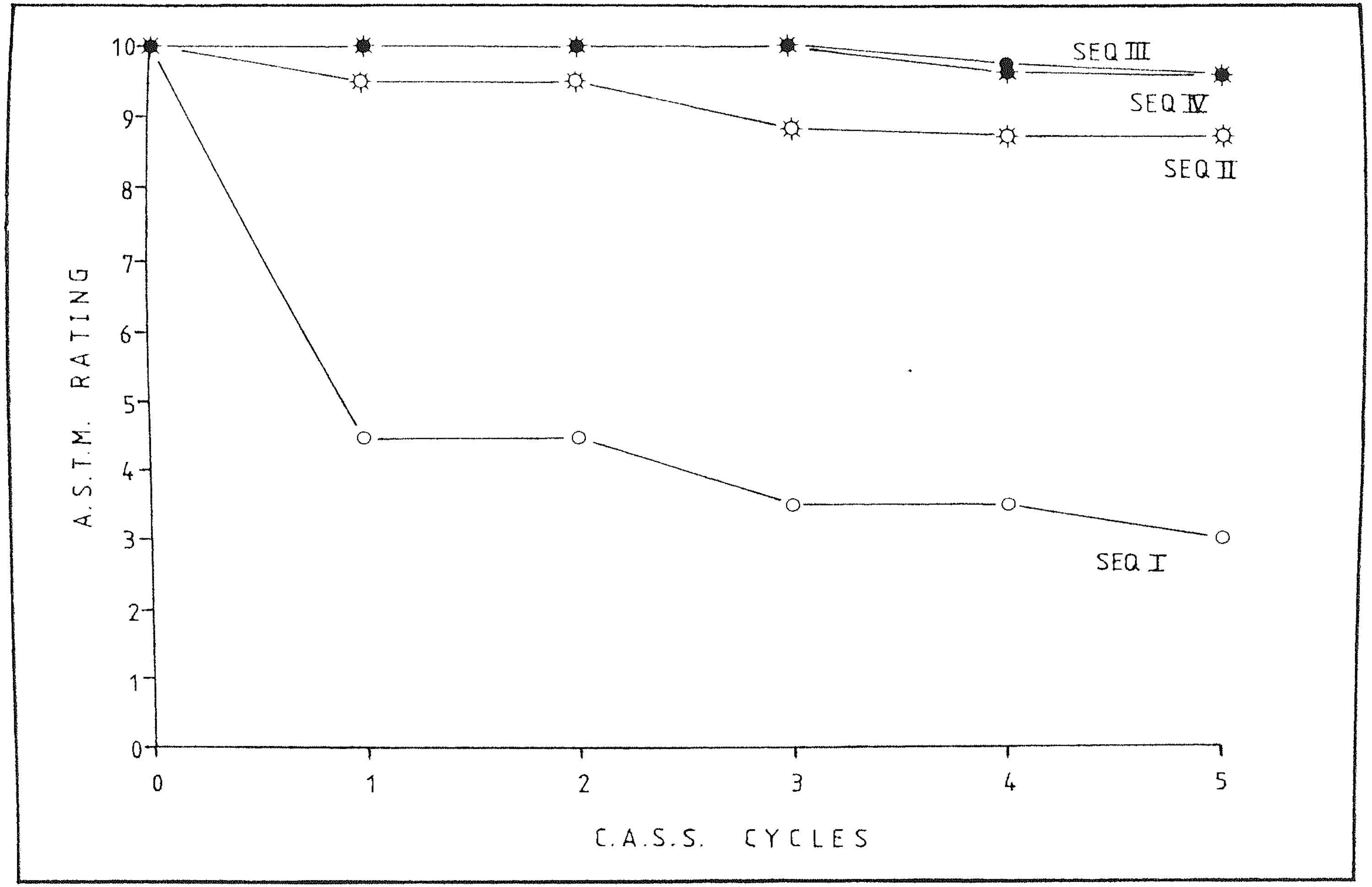


Fig.29a. Relationship between A.S.T.M. rating and number of C.A.S.S. cycles for alloy S1C plated with the thick 0·5 µm microporous chromium coating system. S1C pretreated using sequences I to IV (2 min immersion in room temperature M.A.Z. solution).

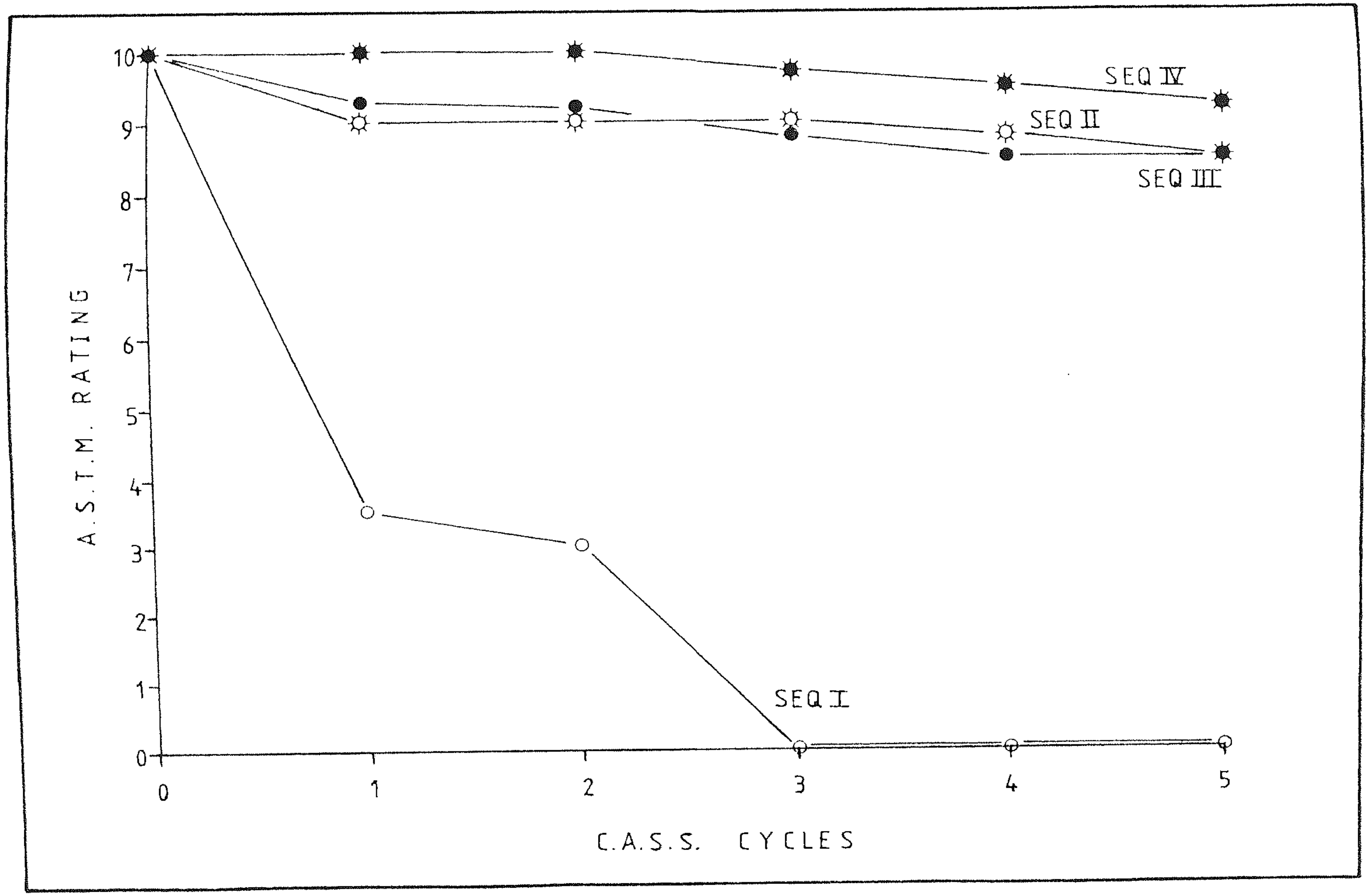


Fig.29b. Relationship between A.S.T.M. rating and number of C.A.S.S. cycles for alloy HE9 plated with the thick 0·5 µm microporous chromium coating system. HE9 pretreated using sequences I to IV (2 min immersion in room temperature M.A.Z. solution).

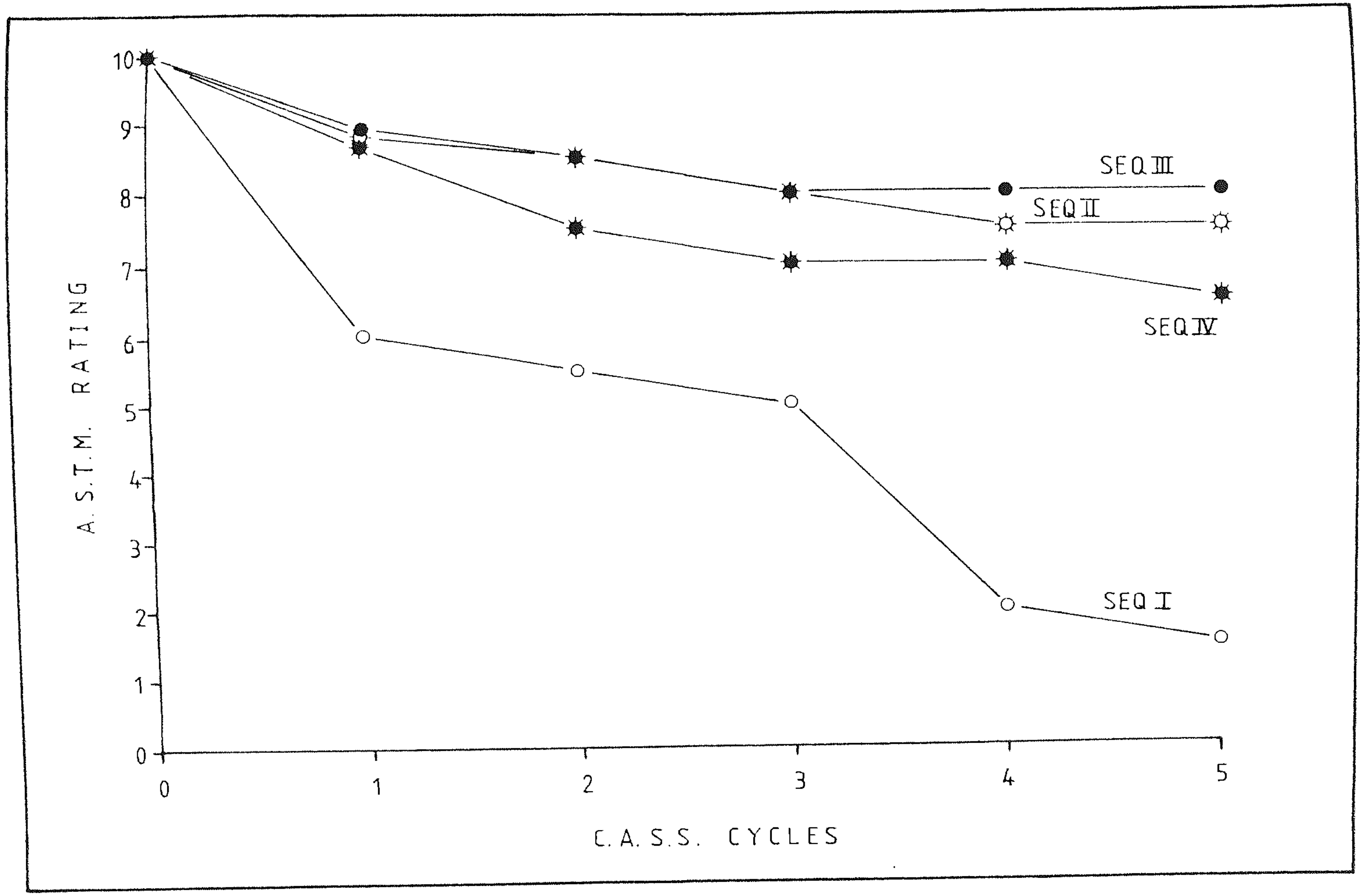


Fig.29c. Relationship between A.S.T.M. rating and number of C.A.S.S. cycles for alloy LM25 plated with the thick 0·5 μm microporous chromium coating system. LM25 pretreated using sequences I to IV (2 min immersion in room temperature M.A.Z. solution).

performance associated with sequence II was variable, and with sequence I usually unsatisfactory.

Even after 5 C.A.S.S. cycles a rating of 8 or above was recorded for :

1. S1C pretreated using sequences II, III and IV for all coating systems.
2. HE9 pretreated using sequences III and IV for all coating systems.
3. LM25 pretreated using sequence III in conjunction with the thick microporous chromium coating system.

3.2.6.2. Appearance of corroded panels

C.A.S.S. tested panels were examined using low power optical and scanning electron microscopy.

The various panels after 5 C.A.S.S. cycles, for the decorative, thin microporous and thick microporous chromium coating systems, respectively, are shown in Figs 30 to 32. As a C.A.S.S. cycle corresponds to approximately one year of outdoor service, the condition of the panels in Figs 30 to 32 represents the cumulative effect of a severe corrosion testing programme. A number of microporous chromium plated panels and especially those double-dip pretreated exhibit uncharacteristic, large corrosion pits. These generally occurred only after extended

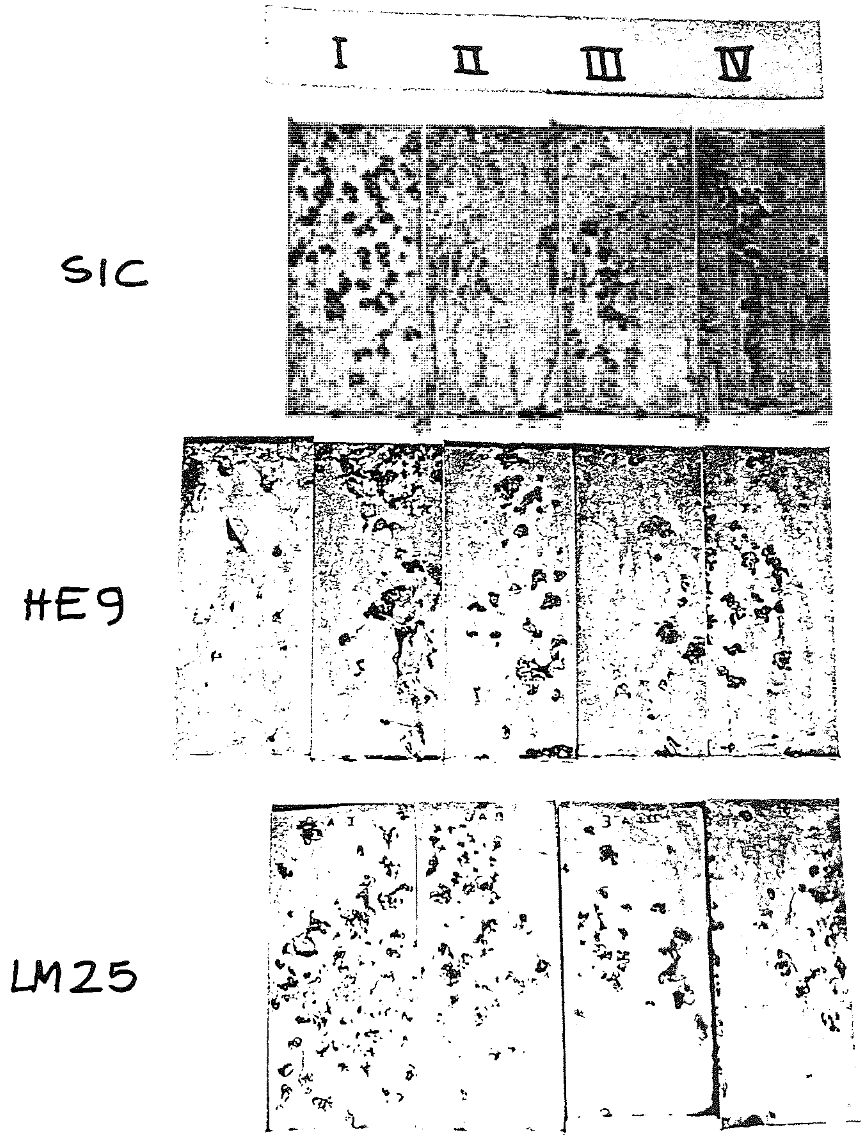


Fig.30. Panels of various aluminium alloys plated with the 0·25/um decorative chromium coating system after 5 cycles of C.A.S.S. testing. Alloys pretreated using sequences I to IV (2 min immersion in room temperature M.A.Z. solution). Panels are shown approximately half actual size.

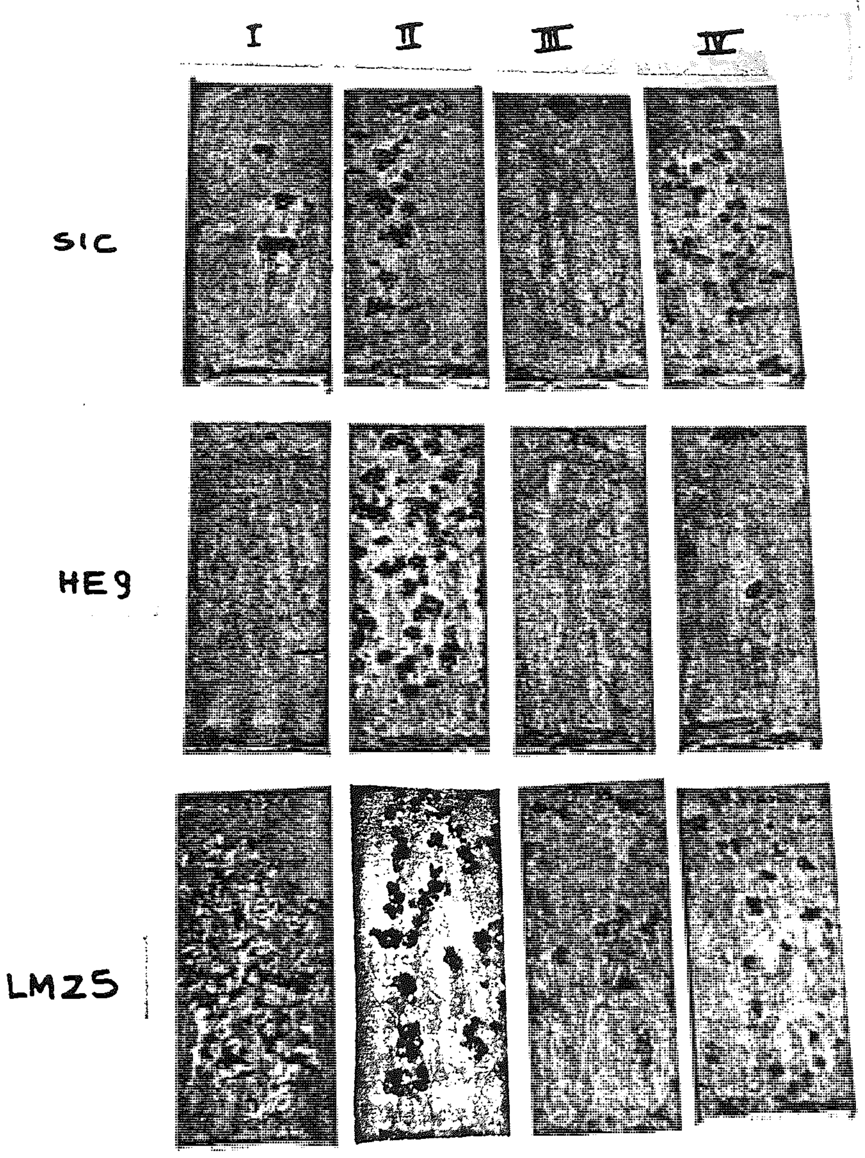


Fig.31. Panels of various aluminium alloys plated with the thin $0\cdot25\,\mu m$ microporous chromium coating system after 5 cycles of C.A.S.S. testing. Alloys pretreated using sequences I to IV (2 min immersion in room temperature M.A.Z. solution). Panels are shown approximately half actual size.

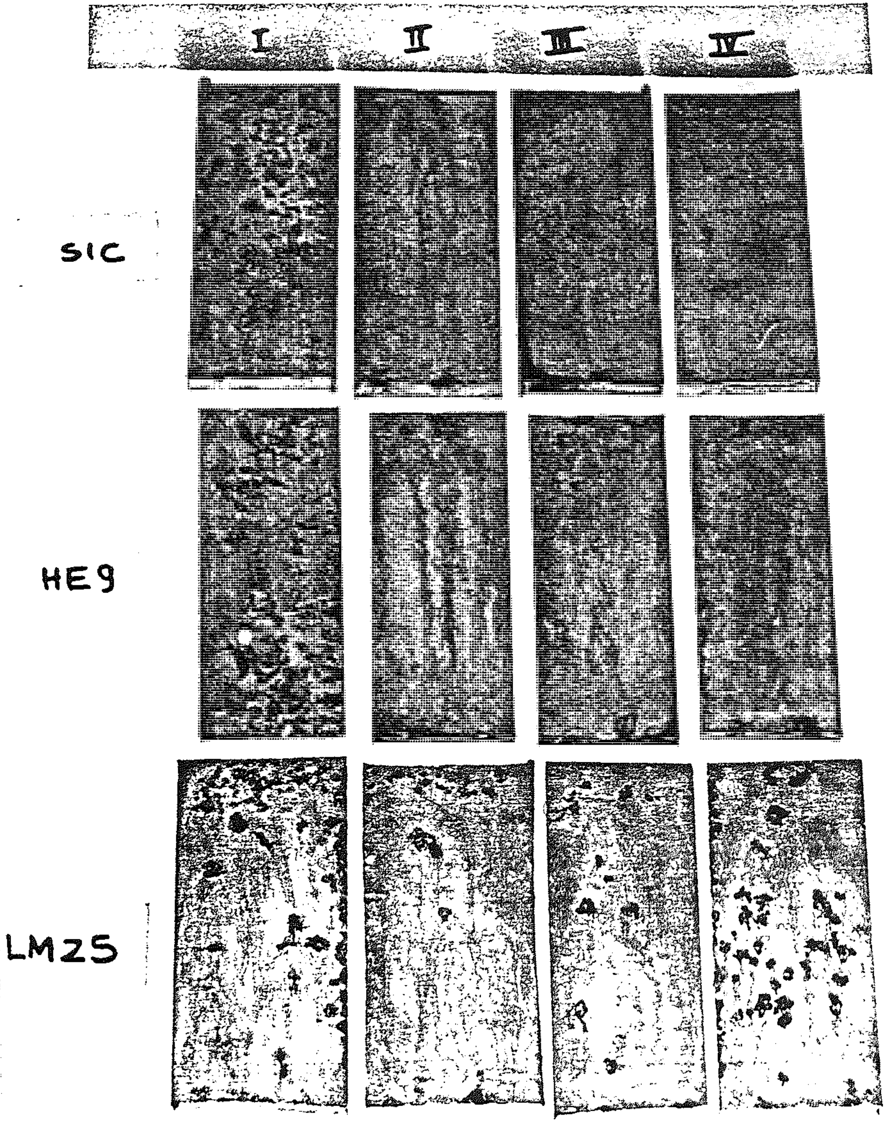


Fig.32. Panels of various aluminium alloys plated with the thick 0·5 µm microporous chromium coating system after 5 cycles of C.A.S.S. testing. Alloys pretreated using sequences I to IV (2 min immersion in room temperature M.A.Z. solution). Panels are shown approximately half actual size.

testing, as indicated by Figs 28 and 29. Figs 30 to 32 highlight effects indicated by Figs 27 to 29 and also show that the thicker microporous chromium coating systems gave slightly superior corrosion resistance overall. Furthermore sequence III was typically associated with the best performance. Note that the HE9 panel pretreated using sequence I and shown in Fig 31, whilst appearing satisfactory, suffered from severe blistering although the plated layer remained intact.

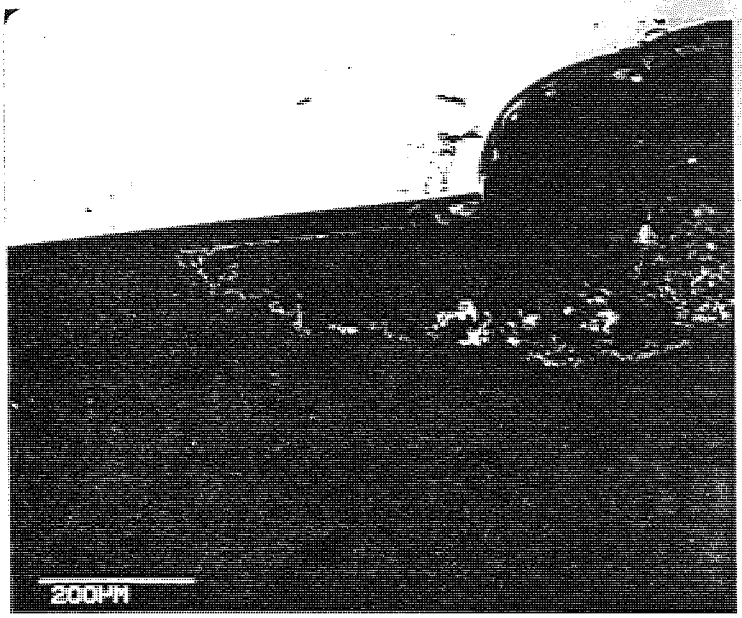
3.2.6.2.1. Decorative chromium coating system

Specimens plated with this coating system suffered relatively severe corrosive attack, Fig 30. Corrosion morphology included blistering, cracking and pin-hole attack. Large catastrophic corrosion sites often occurred after a few C.A.S.S. cycles.

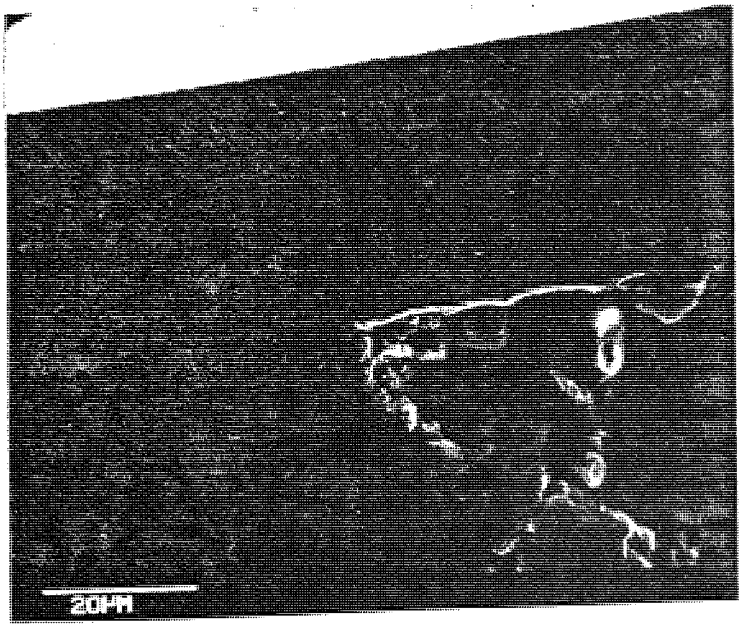
The majority of corrosion defects visible to the eye, initially appeared as tiny 'volcanoes', as electrodeposit was lifted by corrosion products. Subsequently, flakes of plating fell away leaving exposed pits. Size of pits varied between 0·1 - 5 mm in diameter.

There was particularly rapid and severe corrosion of HE9 and LM25, pretreated using sequence I. On HE9 blisters grew which eventually burst, releasing basis metal corrosion products. Wide pits formed on LM25 which were often accompanied by spalling of the plating. When this exfoliating electrodeposit was peeled away by hand, extensive undermining along the

Fig.33. Scanning electron micrograph of a cross-section through a corrosion site in a 0·25µm decorative chromium coating after 5 cycles C.A.S.S. Several small, deep pits developed within a larger corrosion defect. Alloy LM25 pretreated using sequence II (2 min immersion in room temperature M.A.Z. solution).



(a)



(b)

Fig.34. Scanning electron micrographs of a cross-section through a corrosion site in a 0·25 µm decorative chromium coating after 5 cycles C.A.S.S. Undercutting of aluminium but no preferential attack of the M.A.Z. interply. Alloy HE9 pretreated using sequence IV (2 min immersion in room temperature M.A.Z. solution).

substrate-electroplate interface was revealed. Coatings also detached easily from non-corroded regions which indicated a lack of adhesion. However, in contrast, S1C similarly pretreated suffered from severe pitting although the coating was well bonded to the substrate.

The wider pits often found on LM25 tended to act as the site for development of several smaller, deeper pits. This is shown in Fig 33, on a sample pretreated using sequence II.

The double-dip pretreatments, sequences III and IV, reduced the amount of undermining and spalling of the coating and also delayed its onset. A cross-section through a corrosion pit on HE9, pretreated using sequence IV, showing extensive undercutting of the aluminium substrate is illustrated in Fig 34. There was no undermining of the electroplate or preferential attack of the M.A.Z. layer. This further confirmed that the plating was only rapidly undermined where there was poor adhesion.

3.2.6.2.2. Thin microporous chromium coating system

This chromium overlay provided better corrosion resistance than decorative chromium, Fig 31.

Panels plated with the thin 0·25 μm microporous chromium often appeared almost perfect even after a number of C.A.S.S. cycles. However microscopy revealed minute pits, cracks and blisters. Corrosion at micropore sites was apparent in the form of

Fig.35. 'Crows-foot' corrosion sites in a thin 0·25 μm microporous chromium coating after 5 cycles C.A.S.S. Alloy HE9 pretreated using sequence IV (2 min immersion in room temperature M.A.Z. solution). Magnification × 500.

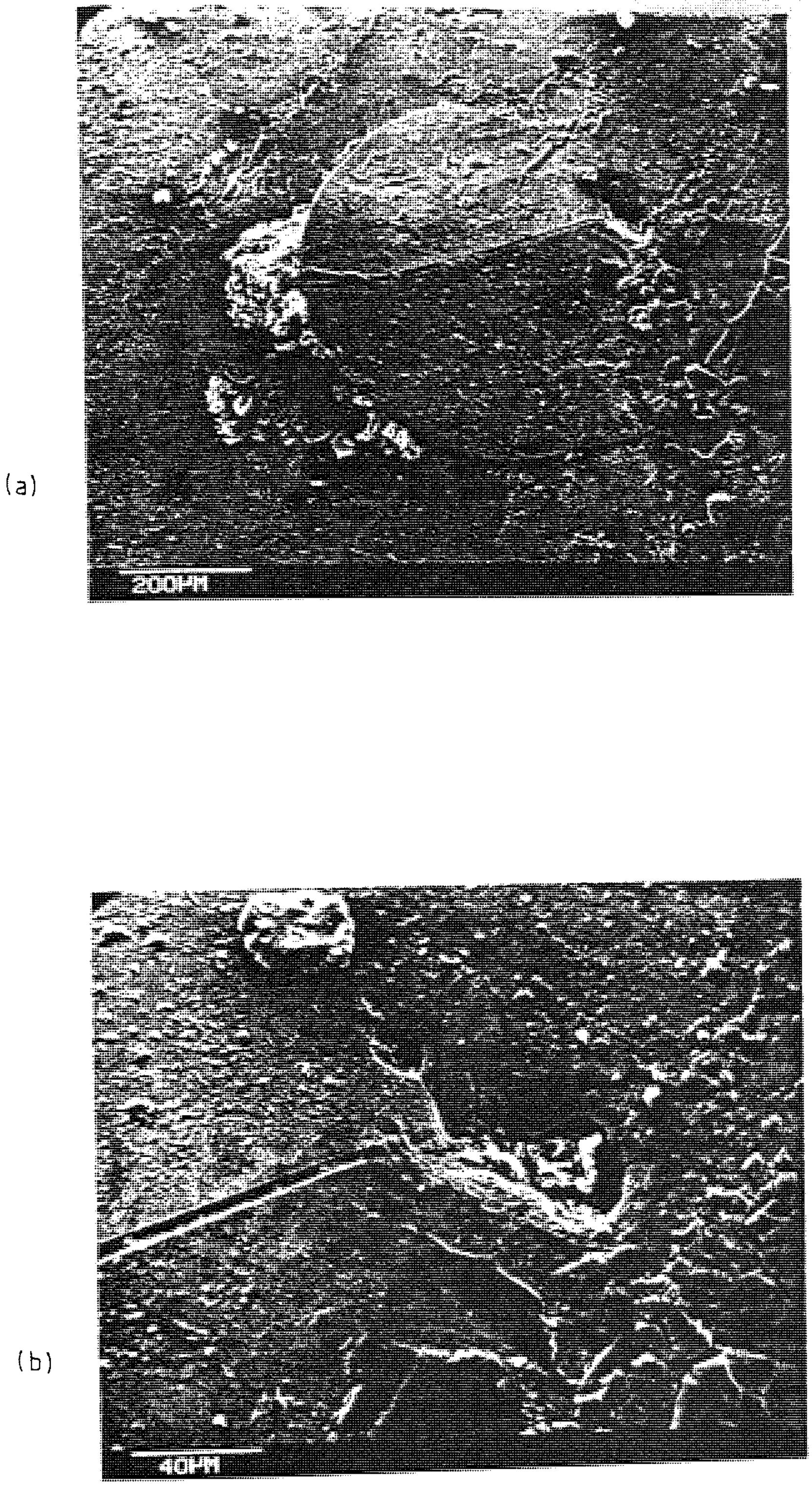


Fig.36. Scanning electron micrographs of a large corrosion site in a thin 0·25 µm microporous chromium coating after 5 cycles C.A.S.S. Disc of electroplate forced up by corrosion products. Alloy S1C pretreated using sequence III (2 min immersion in room temperature M.A.Z. solution).

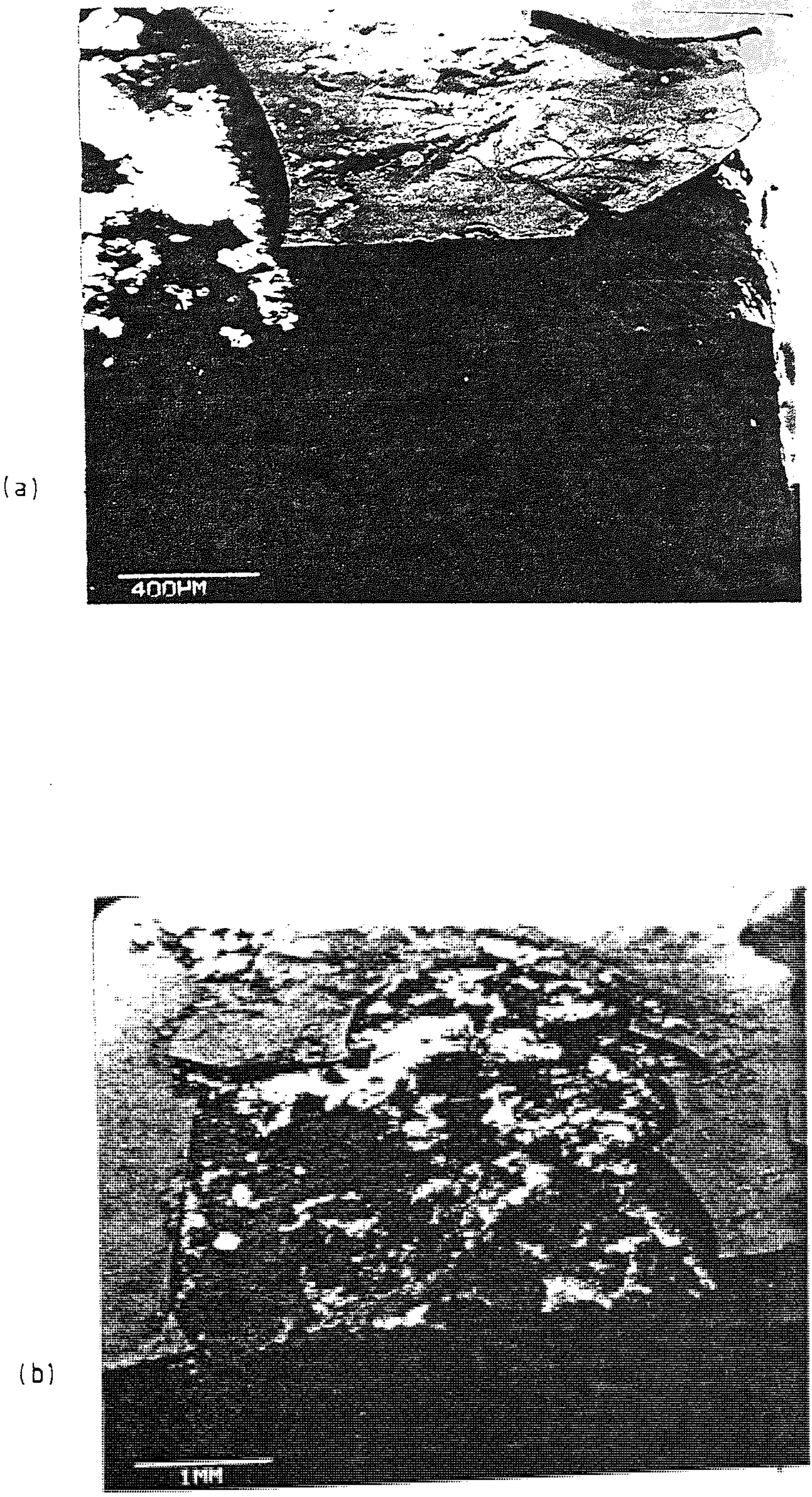


Fig.37. Scanning electron micrographs of a cross-section through an extensive corrosion defect in a thin 0·25 μm microporous chromium coating after 5 cycles C.A.S.S. Lack of electroplate adhesion, general corrosion of the substrate surface and exfoliation of the plating are evident. Alloy LM25 pretreated using sequence I (2 min immersion in room temperature M.A.Z. solution).

'crows-foot' cracks. 'Crows-foot' corrosion sites on HE9 pretreated using sequence IV are shown in Fig 35. Eventually certain crows-foot corrosion sites developed into much larger pits. This is highlighted in Fig 36, on S1C pretreated using sequence III. Fig 36a shows a disc of electrodeposit forced up by corrosion products which then exuded around the edges. Fig 36b illustrates the initial site of corrosion which may have been a micropore or other defect in the chromium layer. Blockage of the original hole by an increasing volume of corrosion products caused a pressure build up, leading to blistering and eventual coating rupture. Fully formed pits were similar to those observed with decorative chromium,i.e. undercutting of the aluminium occurred but there was no accelerated attack of the M.A.Z. interply.

A distinct lack of electroplate adhesion was evident with LM25 pretreated using sequence I, Fig 37. The coating was lifted by polishing, Fig 37a. Low adhesion allowed large areas of plate to exfoliate and the substrate corroded, Fig 37b.

3.2.6.2.3. Thick microporous chromium coating system

The corrosion resistance of this type of coating was generally superior to that of the other two chromium systems, Fig 32.

The high level of reflectivity of the chromium layer was retained longest by the thicker 0·5 μm microporous chromium coating system. The panels plated with the thicker microporous chromium also

Fig. 38. Scanning electron micrograph showing corrosion at cracks in a thick 0·5μm microporous chromium coating after 5 cycles C.A.S.S. Alloy S1C pretreated using sequence IV (2 min immersion in room temperature M.A.Z. solution).

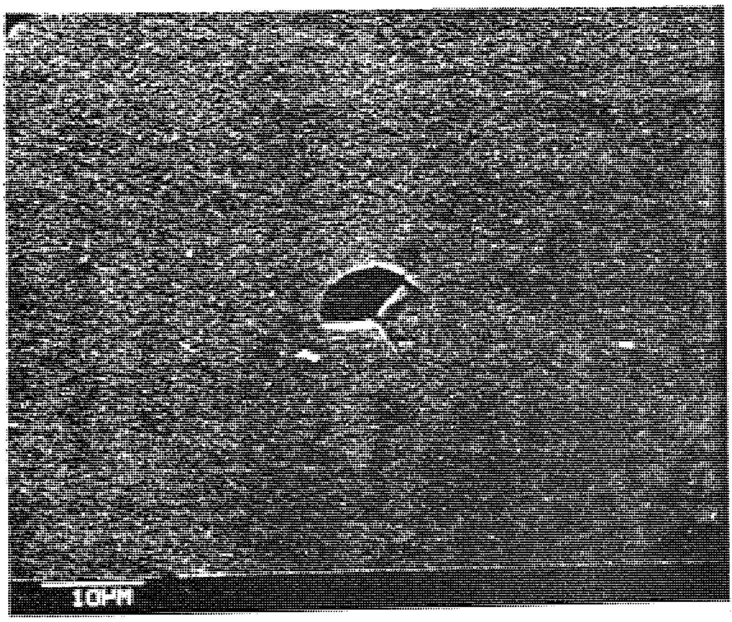


Fig. 39. Scanning electron micrograph showing a small micropore corrosion site in a thick 0·5μm microporous chromium coating after 5 cycles C.A.S.S. Alloy S1C pretreated using sequence III (2 min immersion in room temperature M.A.Z. solution).

exhibited a different corrosion morphology. Corrosion was evident at cracks in the chromium as shown in Fig 38 for S1C pretreated using sequence IV. Examination at higher magnification revealed that there was limited corrosion at micropore sites, Fig 39. However they were smaller and there were fewer than with the thinner microporous chromium.

Large pits when present, were similar to those in the case of decorative and thin microporous chromium overlays. These appeared at areas of poor adhesion or developed from micro-corrosion sites during extended testing. Undercutting of the substrate was evident with corrosion products eventually causing cracking and blistering of the coating. No preferential attack of the M.A.Z. layer was detected and the plating was undermined only when adhesion was minimal.

3.3. Comparison of Modified Alloy Zincate (M.A.Z.) and Simple Zincate (S.Z.) Solutions Operated at Room Temperature

The formulation of the dilute simple zincate (D.S.Z.) and concentrated simple zincate (C.S.Z.) solutions are given in section 2.3.1.1. The alloys used were S1C, HE9 and LM25.

3.3.1. Viscosity of zincate solutions

The viscosities of the zincate solutions, relative to water, measured at 20°C were as follows :

1. D.S.Z.	:	2·771
2. M.A.Z.	:	3·538
3. C.S.Z.	:	46·412

As the C.S.Z. solution was extremely viscous, thorough swilling was difficult. The D.S.Z. and M.A.Z. solutions posed no such practical problems.

3.3.2. Morphology of zincate films

The growth characteristics of the immersion films deposited from the different types of zincate solutions were compared. The D.S.Z. solution gave considerably coarser grained deposits than those from C.S.Z. solution, as shown in Fig 40. The latter had a less discrete growth form than the M.A.Z. deposits, Fig 41. However when using sequence I, the S.Z. solutions exhibited a tendency for accelerated vertical growth at certain more active sites. The resulting undesirable local variations in film thickness did not occur when using M.A.Z. solution.

The use of the double-dip technique produced thinner, finer grained deposits than the single dip with all three solutions. Furthermore the double-dip prevented the phenomena of non-uniform

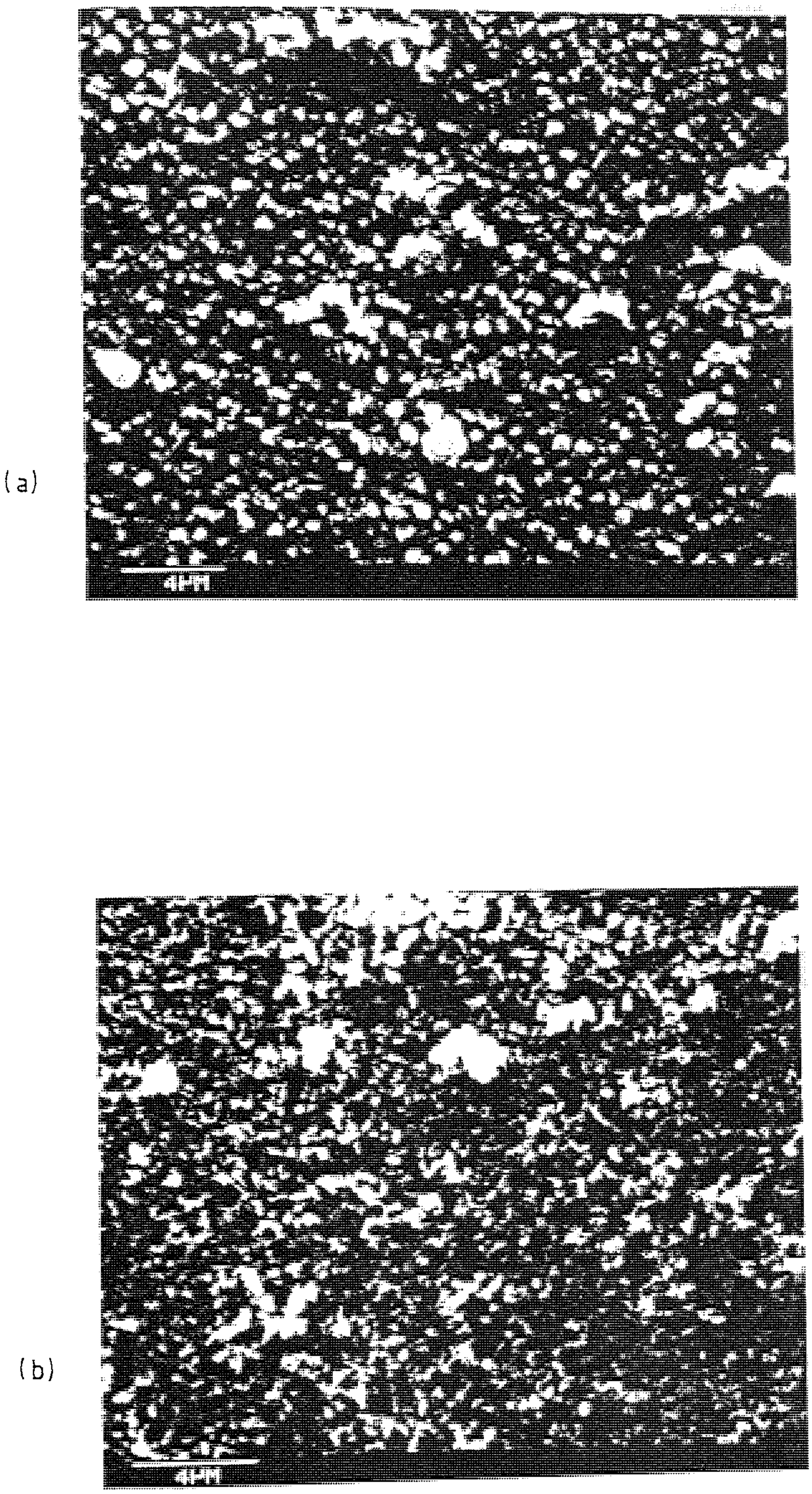


Fig. 40. Scanning electron micrographs of the surface of alloy S1C after pretreatment using sequence I :
(a) after 1 min immersion in room temperature D.S.Z. solution;
(b) after 1 min immersion in room temperature C.S.Z. solution.

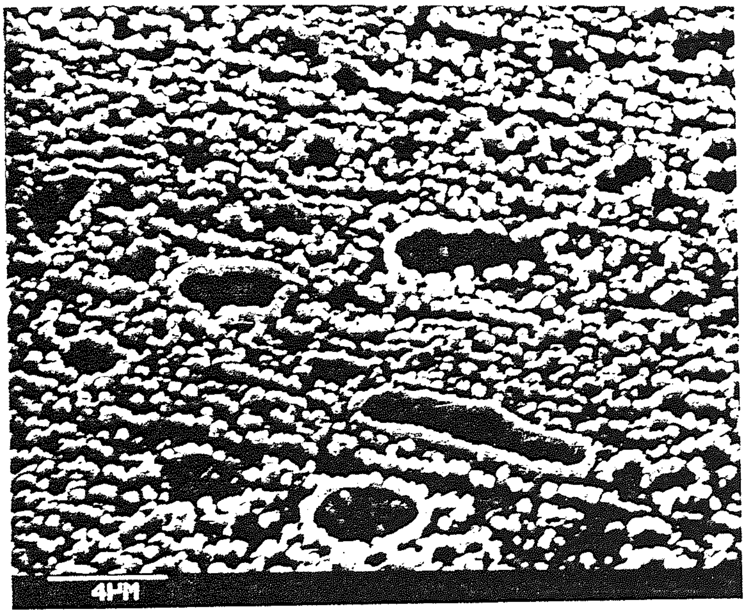


Fig. 41. Scanning electron micrograph of the surface of alloy S1C after pretreatment using sequence II and 30 s immersion in room temperature M.A.Z. solution.

vertical film growth observed when using the S.Z. solutions in conjunction with sequence I.

3.3.3. Quantitative analysis of zincate film composition

An atomic absorbtion spectrophometer was used for the analysis of zincate films stripped from S1C. While S.Z. films contained only zinc, the M.A.Z. deposits contained typically 84·5% zinc, 10% copper, 3% nickel, and 2·5% iron.

3.3.4. Determination of zincate film weight

Figs 42 to 44 show the change in film weight with immersion time in the different types of zincate solution for the three alloys pretreated using various sequences.

Formulation of the zincate solution affected film weight. Both S.Z. solutions yielded heavier deposits than the M.A.Z. solution. During the early stages of immersion, film growth from C.S.Z. solution was greatest. However, for an immersion longer than approximately 1 min, heavier deposits were obtained from the D.S.Z. solution.

Fig 42 illustrates that the curves for the M.A.Z. and C.S.Z. solutions have a similar characteristic shape in that rapid initial growth is followed by a longer period of much slower growth. In contrast, the increase in film weight from the D.S.Z. solution remained high and did not reduce with time.

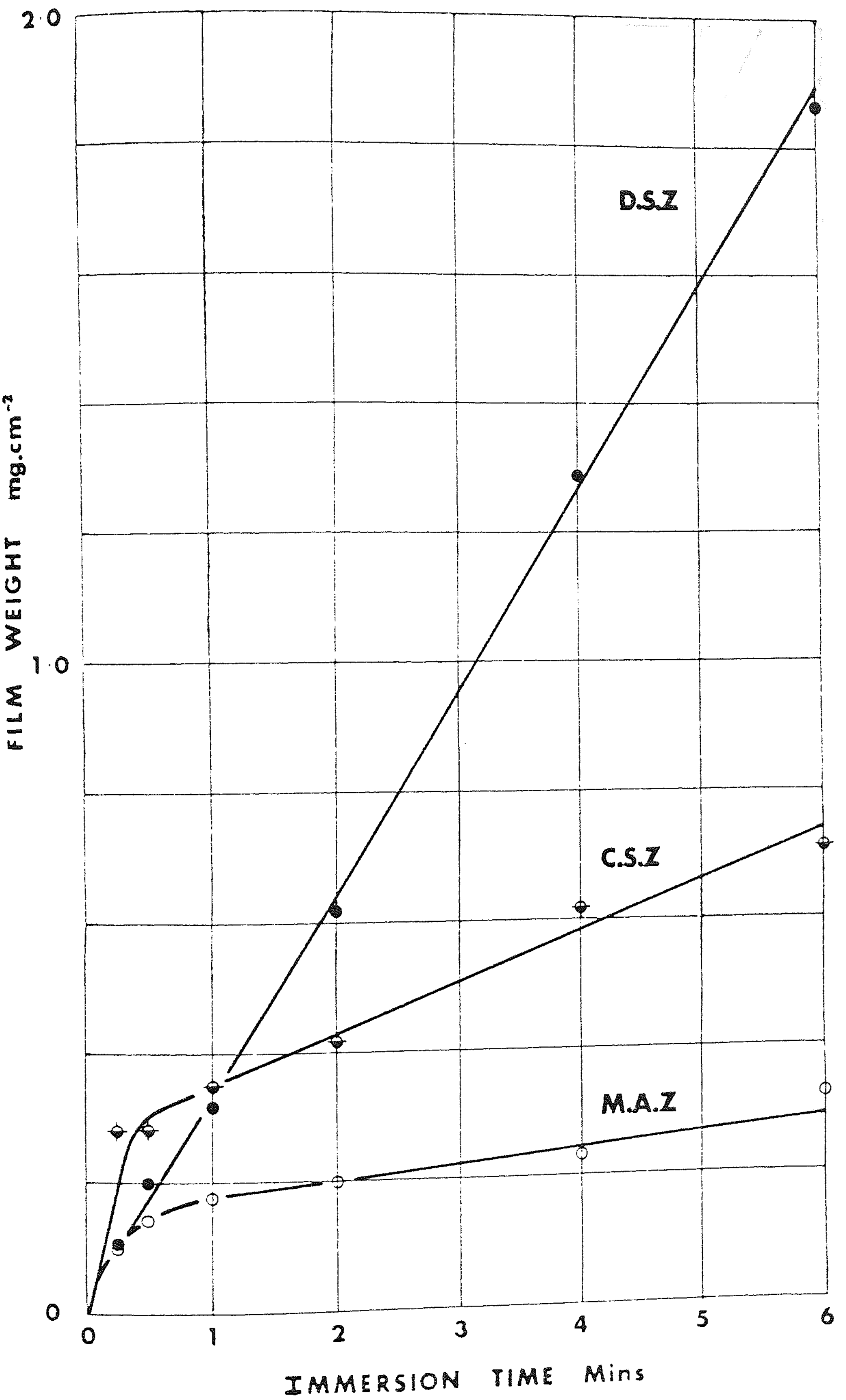


Fig. 42. Relationship between film weight and immersion time in various room temperature zincate solutions for alloy S1C pretreated using sequence I.

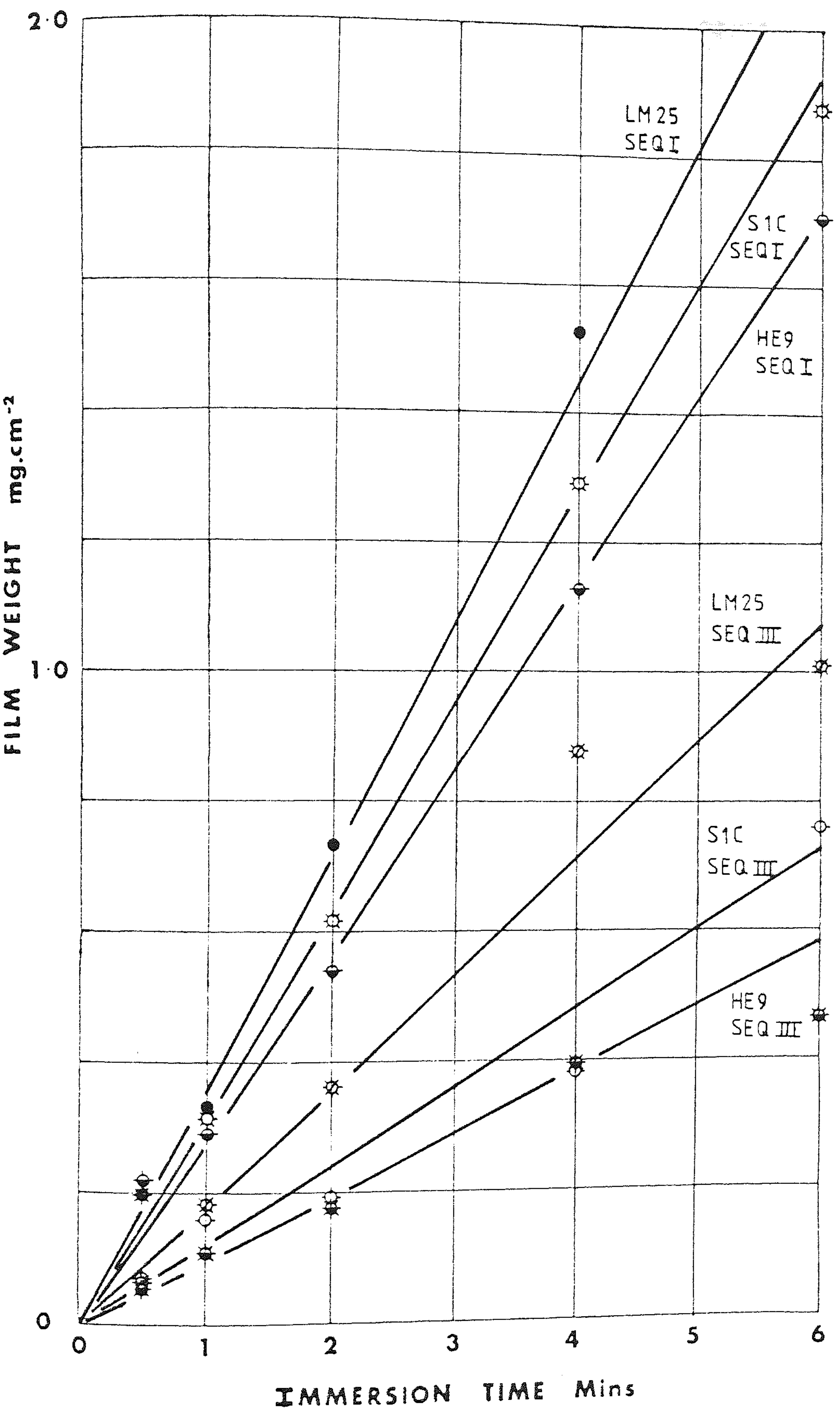


Fig. 43. Relationship between film weight and immersion time in room temperature D.S.Z. solution for various aluminium alloys after pretreatment using sequences I and III.

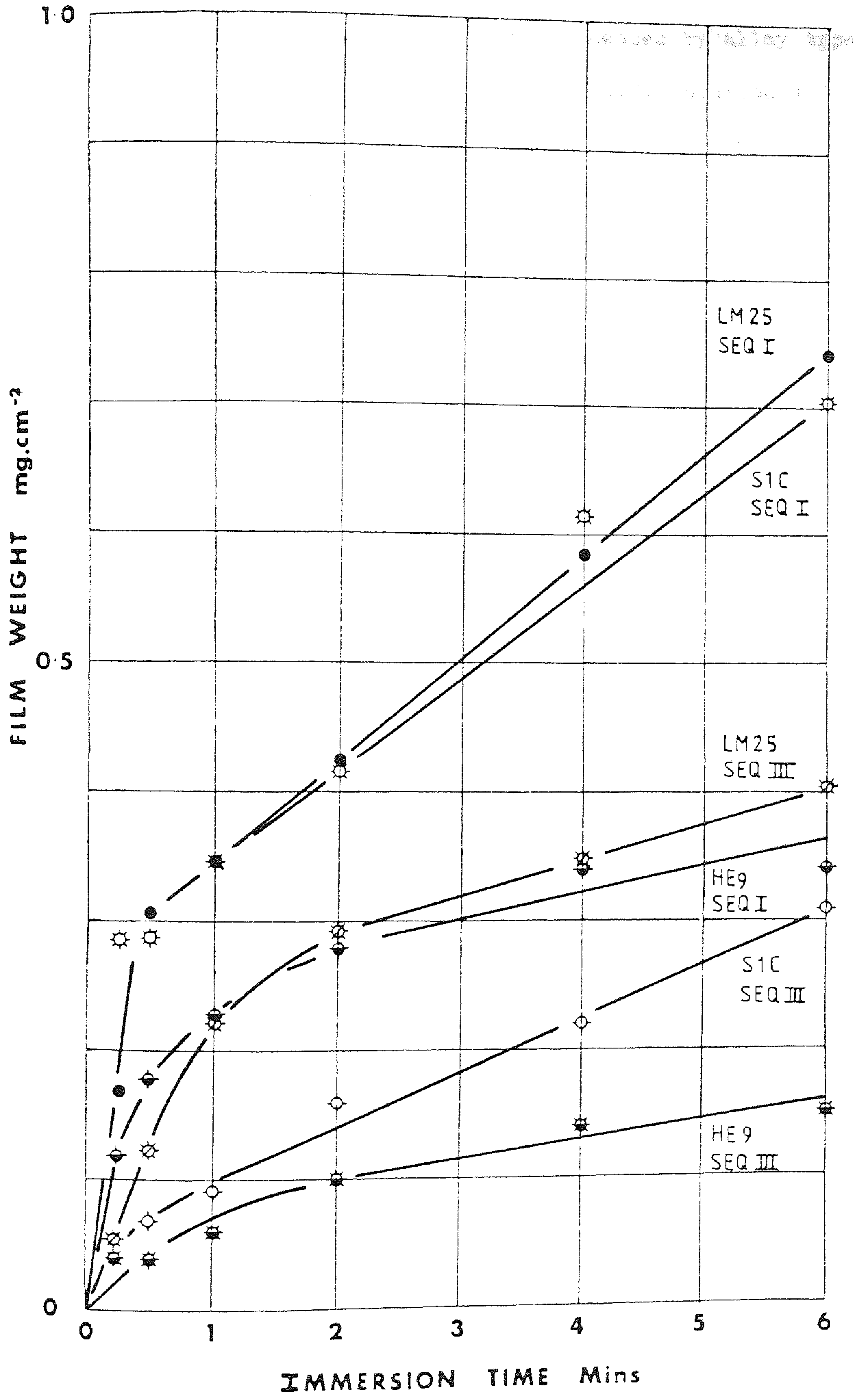


Fig. 44. Relationship between film weight and immersion time in room temperature C.S.Z. solution for various aluminium alloys after pretreatment using sequences I and III.

Film growth from the S.Z. solutions was influenced by alloy type and pretreatment. This is also true of the M.A.Z. solution and is illustrated in section 3.2.2. Figs 43 and 44 highlight the influence of pretreatment on film weight on the three alloys pretreated using sequence I and III, from D.S.Z. and C.S.Z. solutions respectively. The double-dip technique resulted in slower growing films than the single dip pretreatment for all three zincate solutions irrespective of alloy type.

3.3.5. Peel adhesion

The alloys were pretreated according to sequences I to IV using the three different zincate solutions and a standard immersion time of 2 min. All zincate films were directly plated with Watts nickel. When peel tested, all panels processed using the S.Z. solutions were merely encapsulated by the nickel plate and exhibited zero adhesion. Table XVII indicates that far superior adhesion results were achieved using the M.A.Z. solution.

From film weight results discussed previously, it was known that the S.Z. films grew considerably faster than the M.A.Z. type. This provided a possible explanation for the unsatisfactory performance of the S.Z. pretreatments. Therefore film weight curves were used to determine the S.Z. immersion times needed with the specific pretreatment sequences to produce the same final film weight as that obtained using a 2 min immersion in M.A.Z. solution. For the double-dip S.Z. pretreatments, the immersion time used for the first film remained at 2 min.

However, this did not solve the problem of zero electrodeposit adhesion.

Further investigations were restricted to the M.A.Z. solution which gave superior results and was developed because practical experience had revealed the inadequacies of the S.Z. formulations.

3.4. Alternative Methods of Operating the M.A.Z. Solution

The M.A.Z. solution was used in two other conditions apart from room temperature, (i) heated, usually at 50°C and (ii) cold but electrolytically. The alloys used in this study were S1C, LM25 and X-7046.

The M.A.Z. solution was used electrolytically or warmed, particularly to achieve greater success in plating the 'difficult' alloy X-7046. Films formed on this alloy using conventional immersion in room temperature M.A.Z. solution were slow growing, had a coarse grain size and gave poor coverage irrespective of pretreatment sequence. This resulted in zero adhesion of electrodeposit. From earlier work it was thought that a double-dip sequence which gave adequate etching was necessary to enable X-7046 to be plated satisfactorily. Ideally, the M.A.Z. deposit should exhibit rapid and total surface coverage and be thin, uniform and fine grained, i.e. similar to that obtained on S1C pretreated with sequence III using conventional immersion dips. The latter had an optimum weight of $0{\cdot}06 \pm 0{\cdot}01$ mg cm^{-2}.

3.4.1. Heated M.A.Z. solution

Previously, for all four standard pretreatment sequences and using 2 min dips in room temperature M.A.Z. solution, the best electroplate adhesion was achieved on S1C. For S1C pretreated using sequence I this corresponded to a film weight of approximately 0·2 mg cm^{-2}. On X-7046 identically pretreated, a similar film weight was obtained using the M.A.Z. solution at 50°C. Hence gently agitated M.A.Z. solution at this temperature was used in conjunction with the standard pretreatments as described in section 2.3. The final film was always deposited from 50°C M.A.Z. solution. For double-dip pretreatments, the first film was deposited from either room temperature or 50°C M.A.Z. solution always using a 2 min immersion.

Although the bulk of the work involved using the M.A.Z. solution at 50°C, it was also operated in the temperature range -1°C to 55°C.

3.4.1.1. Morphology of films deposited from 50°C M.A.Z. solution

On single dip pretreated S1C and LM25, the 50°C M.A.Z. films gave faster coverage but exhibited initial growth similar to that of conventional room temperature deposits. Figs 45a and 45b show films deposited on S1C pretreated using sequence I after 10 s immersion in room temperature and 50°C M.A.Z. solution respectively. However, the 50°C M.A.Z. deposits grew more quickly and unlike the conventional films continued to grow rapidly even when the substrate was completely covered. They thickened by

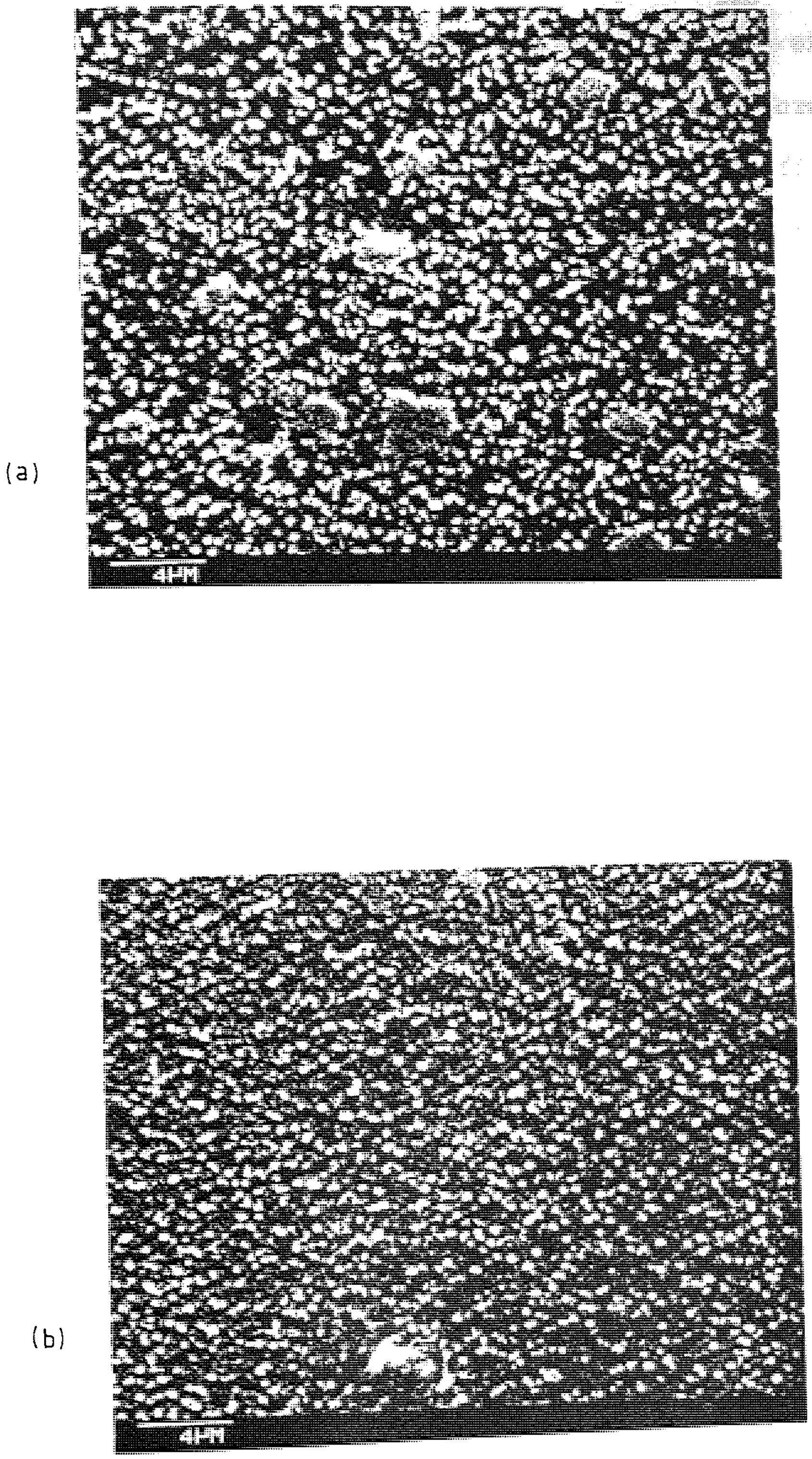


Fig. 45. Scanning electron micrographs of the surface of alloy S1C after pretreatment using sequence I : (a) after 10 s immersion in room temperature M.A.Z. solution; (b) after 10 s immersion in 50 °C M.A.Z. solution.

continued vertical development and coalescing of a number of the original growths. New randomly distributed growths also formed on the developing deposit. Extremely coarse grained, spongy films resulted. This is illustrated in Fig 46 which shows a 2 min 50 °C M.A.Z. deposit on S1C pretreated using sequence I.

Growth characteristics of the 50 °C M.A.Z. deposits were affected by pretreatment. Fig 47 illustrates the differences in morphology of films formed on LM25 pretreated using sequence III in conjunction with different combinations of room temperature and 50 °C M.A.Z. first and second dips. Of the three alloys considered, film growth on LM25 was most sensitive to changes in pretreatment.

For S1C and LM25 the double-dip technique resulted in thinner and slower growing 50 °C M.A.Z. deposits than single dip sequences. These films were also finer grained during the early stages of immersion and surface coverage was still rapid. After >30 s immersion they became similar to the single dip deposits as the growth forms became coarser. Growth of the 50 °C M.A.Z. deposits was accompanied by rapid substrate dissolution. The dissolution of an S1C surface caused during formation of a 2 min 50 °C M.A.Z. first film is shown in Fig 48. In this example, the first deposit had been removed by a 1 min 50% HNO acid dip and a second 50 °C M.A.Z. film allowed to develop for 10 s. Sequence IV was not used with S1C or LM25 as earlier work indicated it caused excessive attack and weakening of the surface layers.

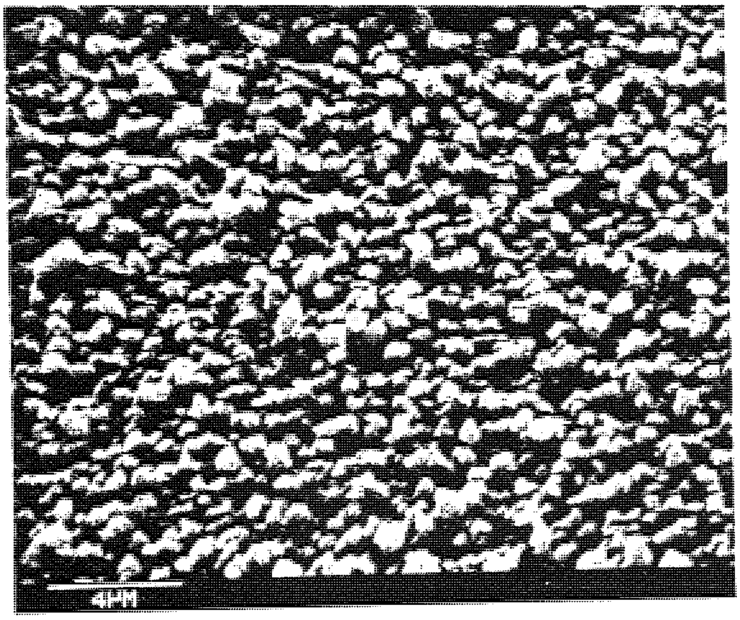


Fig. 46. Scanning electron micrograph of the surface of alloy S1C after pretreatment using sequence I and 2 min immersion in 50 °C M.A.Z. solution.

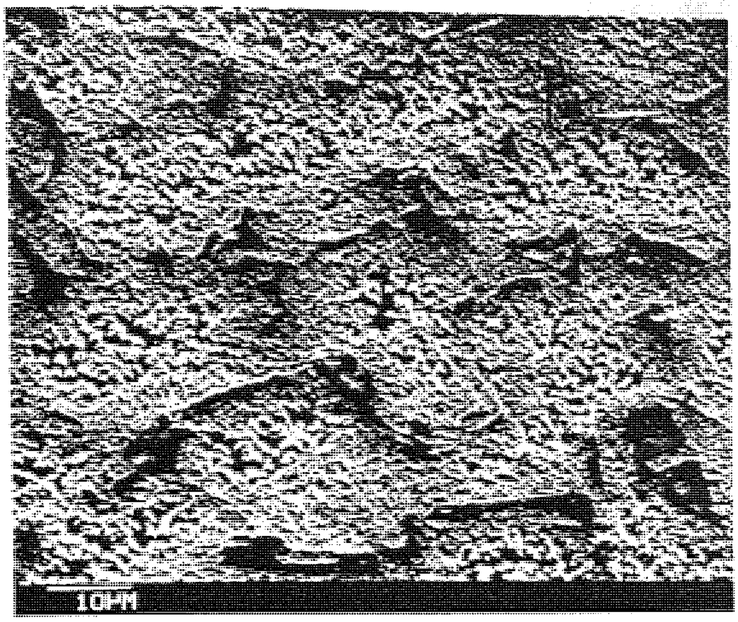


Fig. 47a. Scanning electron micrograph of the surface of alloy LM25 after pretreatment using sequence III with a 2 min first immersion and 1 min second immersion in room temperature M.A.Z. solution.

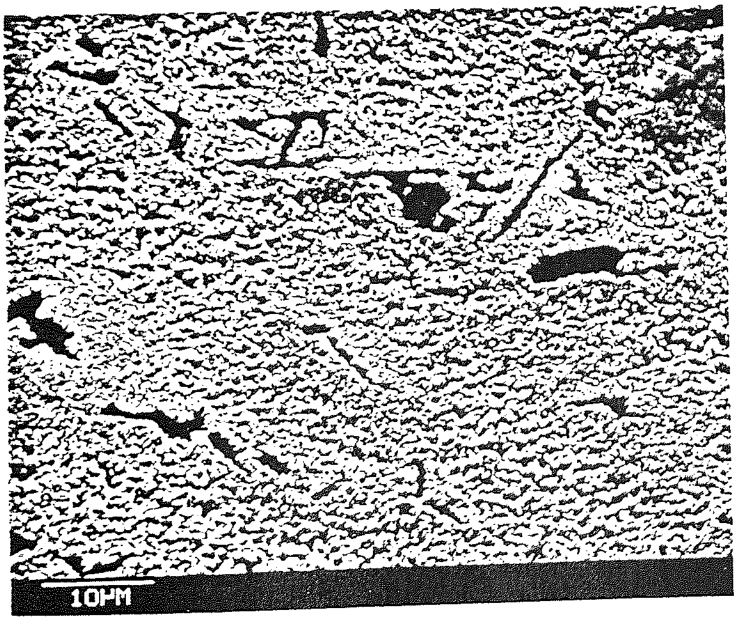


Fig. 47b. Scanning electron micrograph of the surface of alloy LM25 after pretreatment using sequence III with a 2 min first immersion in room temperature M.A.Z. solution and 1 min second immersion in 50 °C M.A.Z. solution.

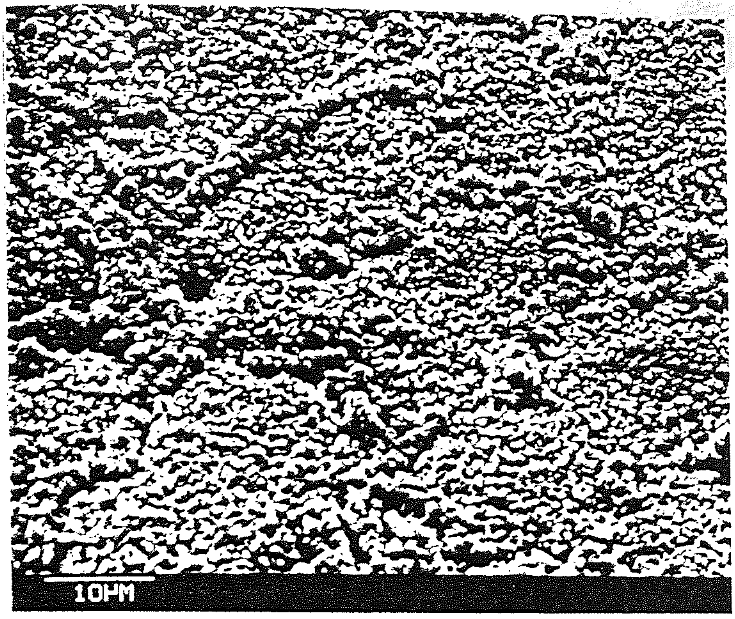


Fig. 47c. Scanning electron micrograph of the surface of alloy LM25 after pretreatment using sequence III with a 2 min first immersion and 1 min second immersion in 50°C M.A.Z. solution.

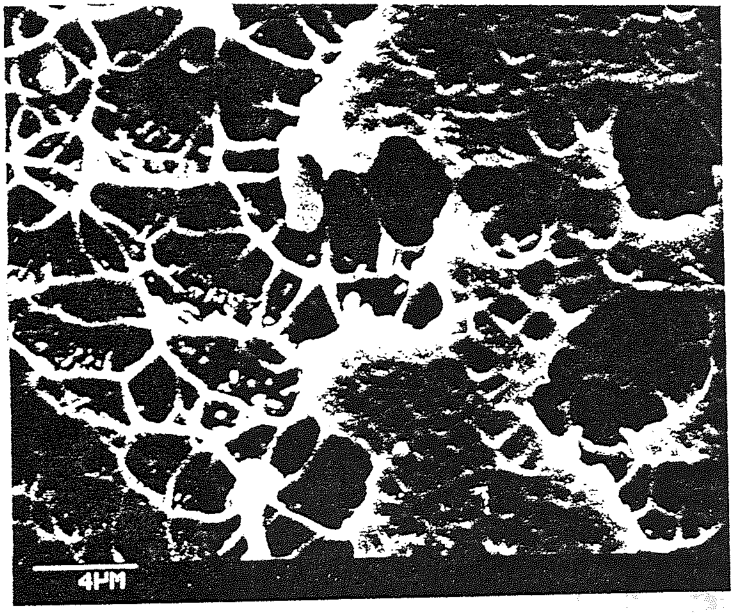


Fig. 48. Scanning electron micrograph of the surface of alloy S1C after pretreatment using sequence III with a 2 min first immersion and 10 s second immersion in 50 °C M.A.Z. solution. Extensive dissolution of the substrate caused during formation of the first film.

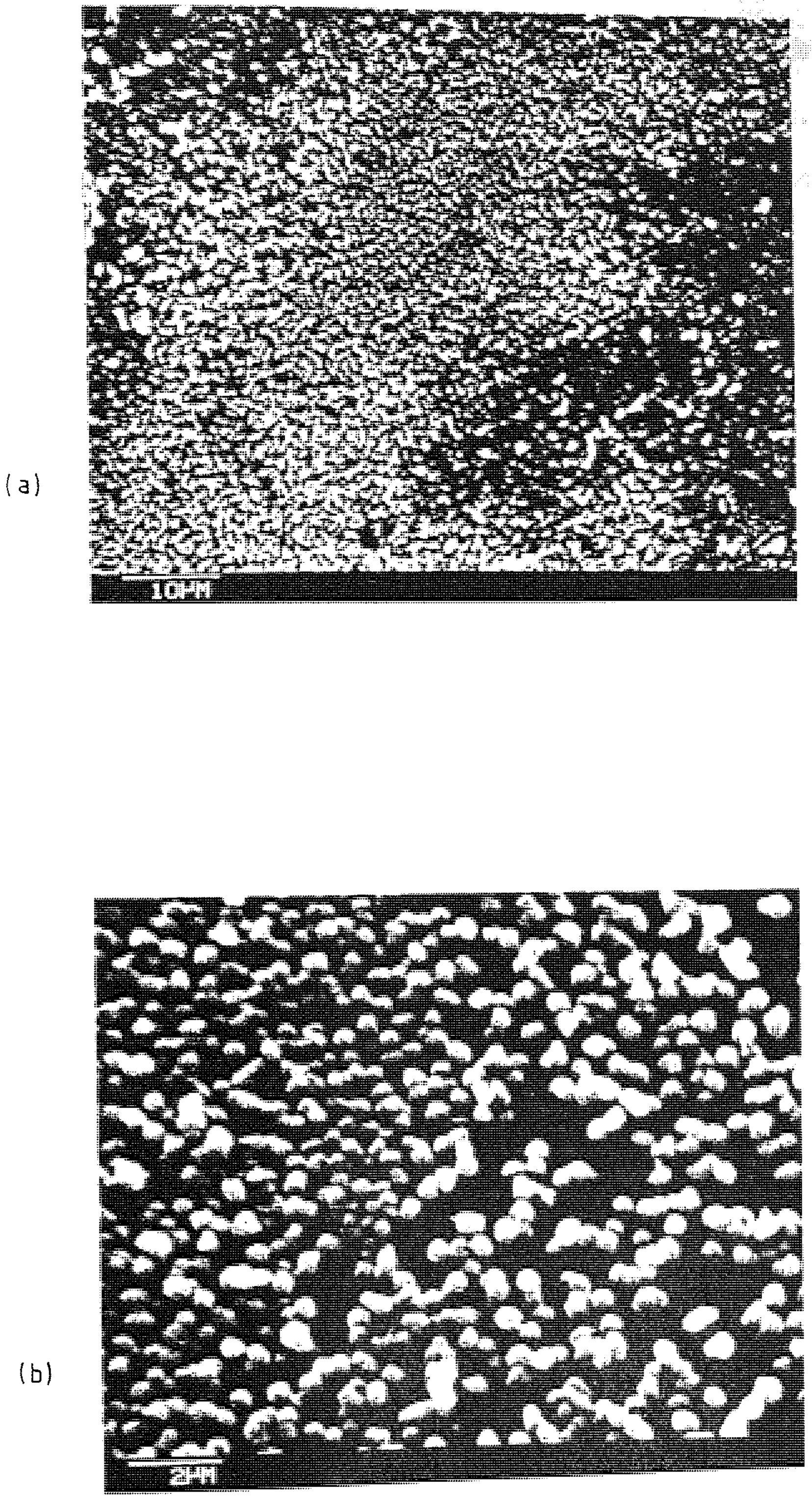


Fig. 49. Scanning electron micrographs of the surface of alloy X-7046 after pretreatment using sequence I and 1 min immersion in 50 °C M.A.Z. solution.

The rate of film growth on X-7046 was the least affected by using the M.A.Z. solution at 50°C or by changes in pretreatment. Single dip 50°C M.A.Z. deposits were initially coarse grained and became more so as immersion time increased. While growing slightly faster than from room temperature solution, they were much slower growing than on S1C and LM25 and gave poor coverage. The latter is highlighted in Fig 49, which shows coarse grained 1 min 50°C M.A.Z. deposits on X-7046 pretreated using sequence I. While double-dip pretreatments gave slower growing films on X-7046, unlike on S1C and LM25, the deposits which developed initially were coarse grained and exhibited poor coverage. Irrespective of pretreatment or immersion time, fine grained 50°C M.A.Z. films giving good coverage could not be produced on X-7046.

Kevex analysis indicated that typical 2 min room temperature and 50°C M.A.Z. deposits were of similar composition.

3.4.1.2. Determination of film weight from M.A.Z. solution at various temperatures

Figs 50 and 51 show the change in film weight with immersion time in M.A.Z. solution at 30°C and 50°C respectively, for the alloys pretreated using various sequences.

Fig 50 illustrates that on S1C and LM25 sequence I pretreated, the relatively high film growth rate typical of the early stages of immersion continued for a considerable time when the M.A.Z. solution was warmed. Only the X-7046 sequence I curve shows the

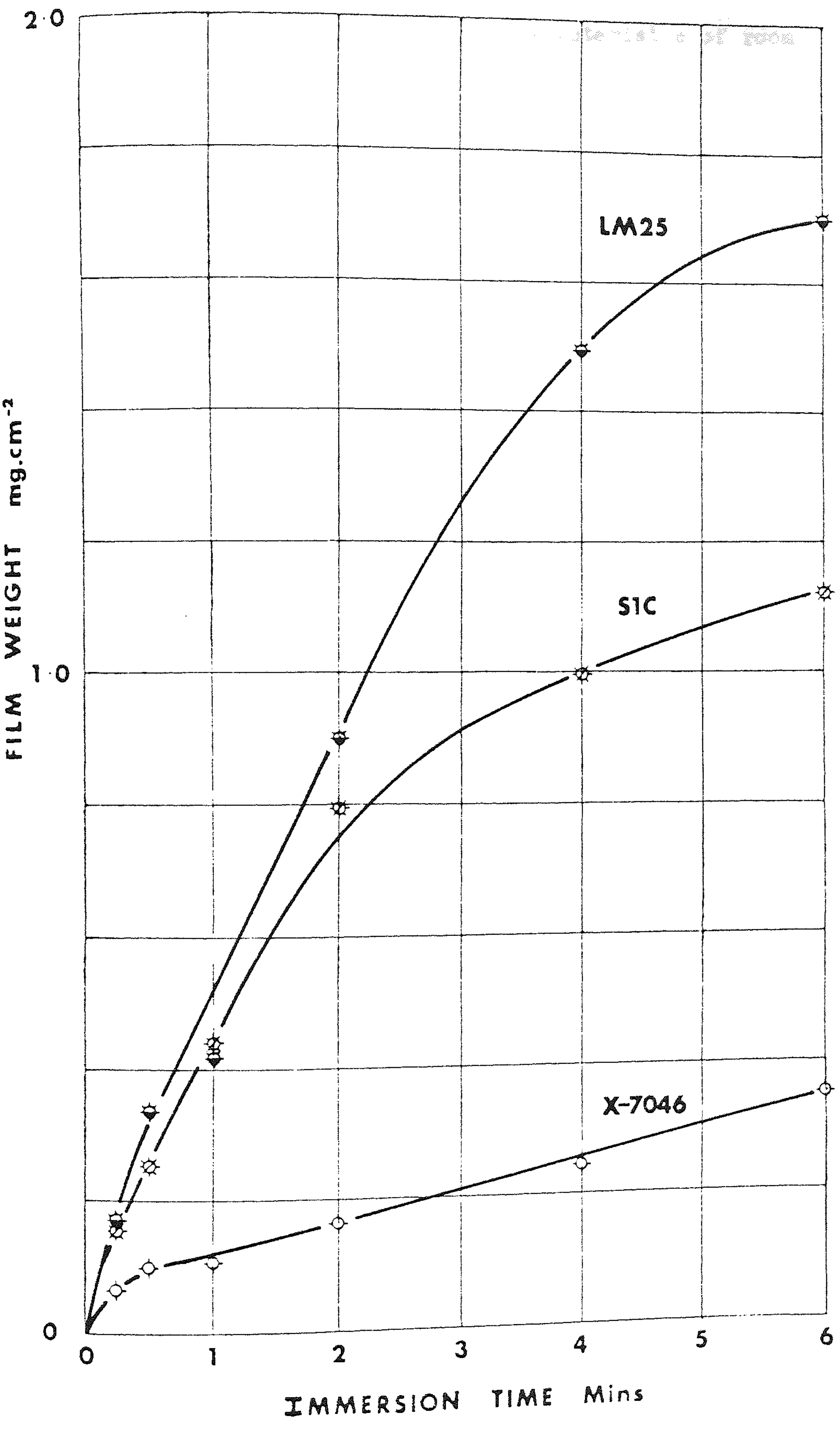


Fig.50. Relationship between film weight and immersion time in 30 °C M.A.Z. solution for various aluminium alloys after pretreatment using sequence I.

extended period of slower growth more characteristic of room temperature M.A.Z. immersion.

Fig 51 shows that film growth on S1C and LM25 was far more sensitive to an increase in M.A.Z. solution temperature than X-7046. Changes in pretreatment also had a much greater effect on the weight of 50°C M.A.Z. deposits on S1C and LM25 than on X-7046. It should be noted that the film weight curves for S1C and LM25, pretreated using sequence III with a 50°C M.A.Z. first dip, shown in Figs 51a and 51b respectively, are misleading. This is due to the great increase in 'true surface area' caused by dissolution during formation of the rapidly growing 50°C M.A.Z. first film.

On S1C and LM25 pretreated using sequence I, after 4 min immersion the 50°C M.A.Z. deposits became so thick that they started to crack and blister. The substrate became re-exposed to solution and the original deposit tended to exfoliate. Fig 52 illustrates part of an S1C panel used for film weight measurements after being pretreated using sequence I and immersed in 50°C M.A.Z. solution for 6 min. Areas of deposit can be seen to be missing in Fig 52a, while Fig 52b shows where thick coarse grained film has ruptured and started to lift off the substrate.

Fig 53 illustrates the relationship between film weight and M.A.Z. solution temperature, in the range -1°C to 55°C, for various alloys and sequences. It indicates that there may be problems when using M.A.Z. solution in a non-thermostatically

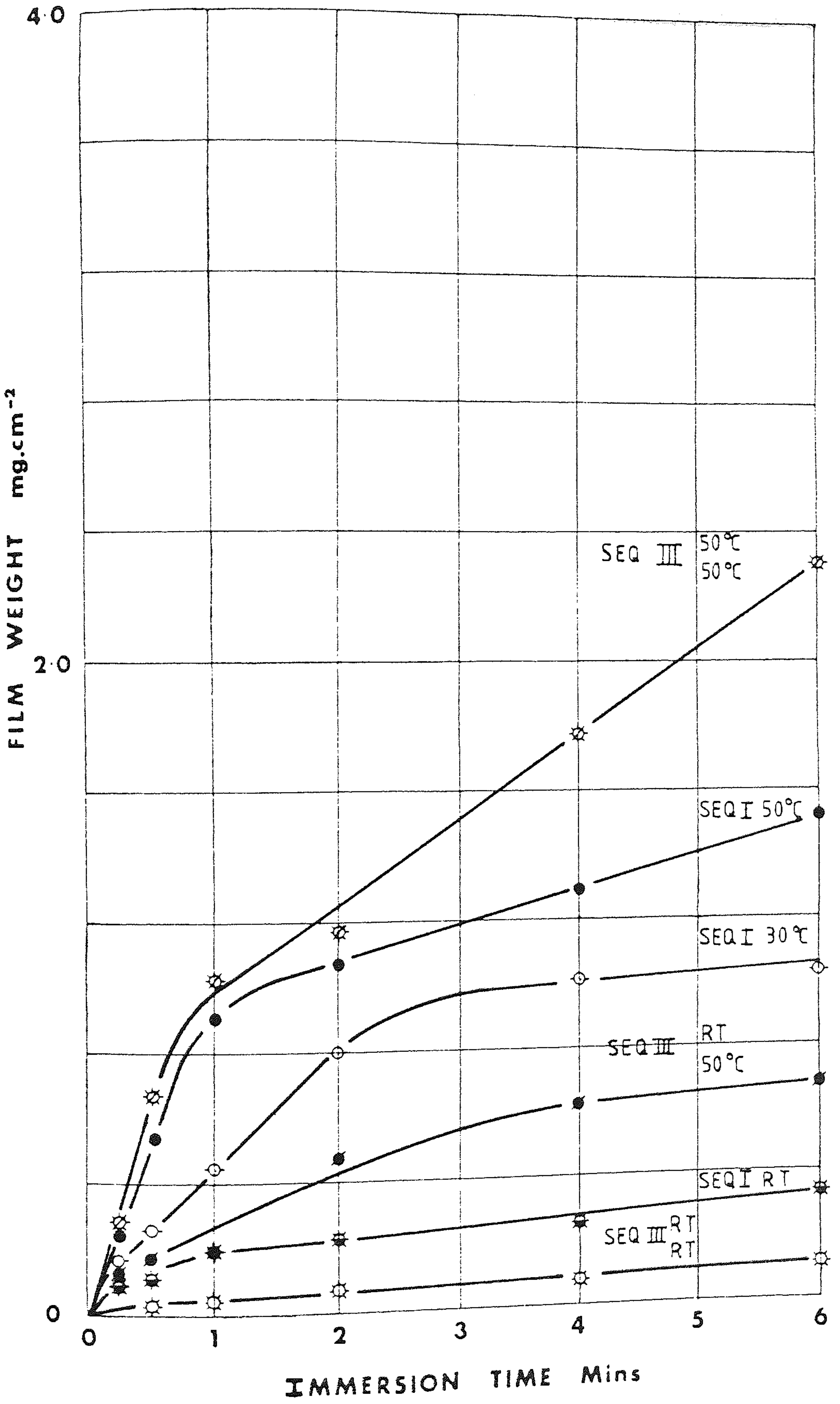


Fig.51a. Relationship between film weight and immersion time for alloy S1C pretreated using sequences I and III with immersion dips in M.A.Z. solution at various temperatures.

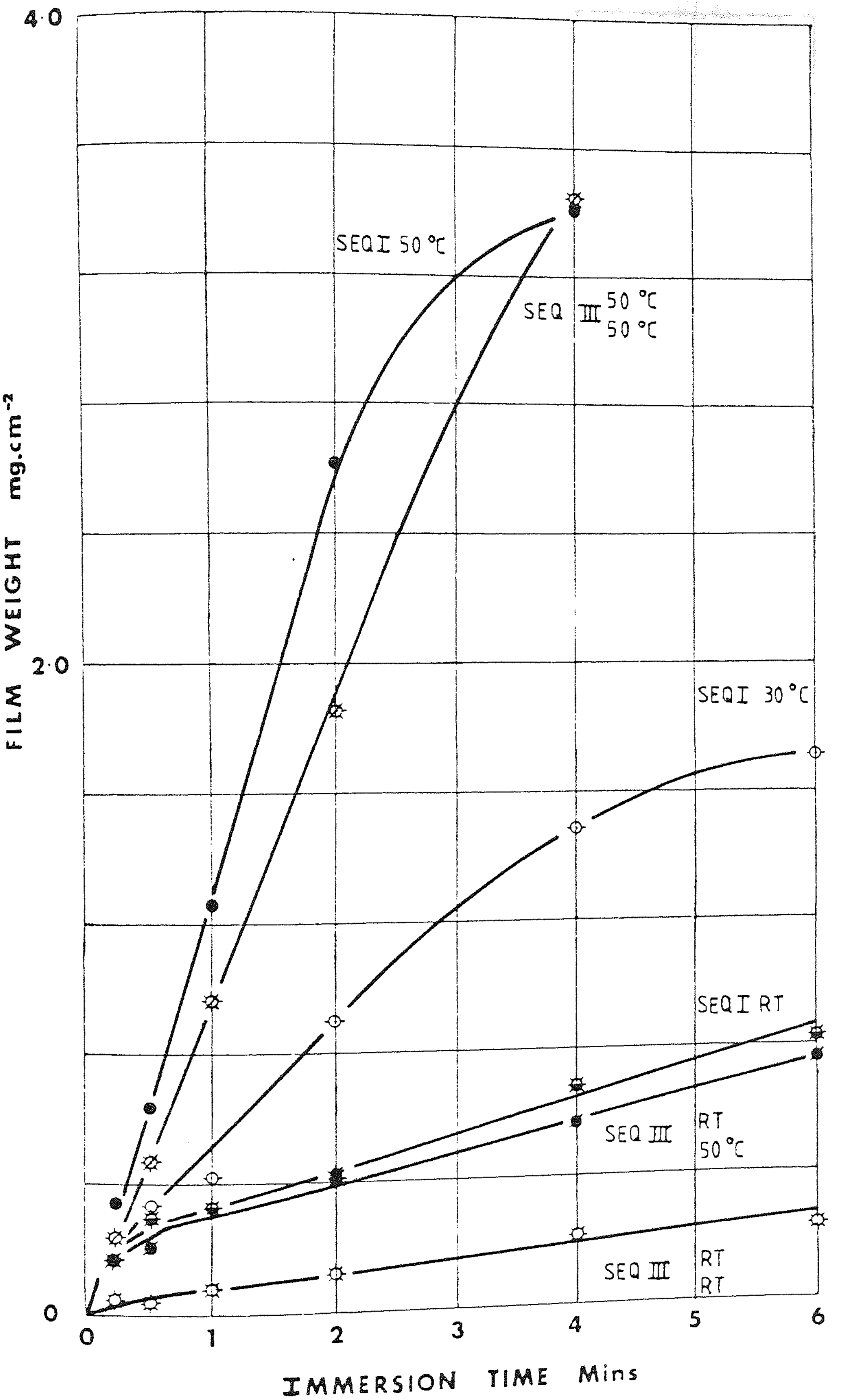


Fig.51b. Relationship between film weight and immersion time for alloy LM25 pretreated using sequences I and III with immersion dips in M.A.Z. solution at various temperatures.

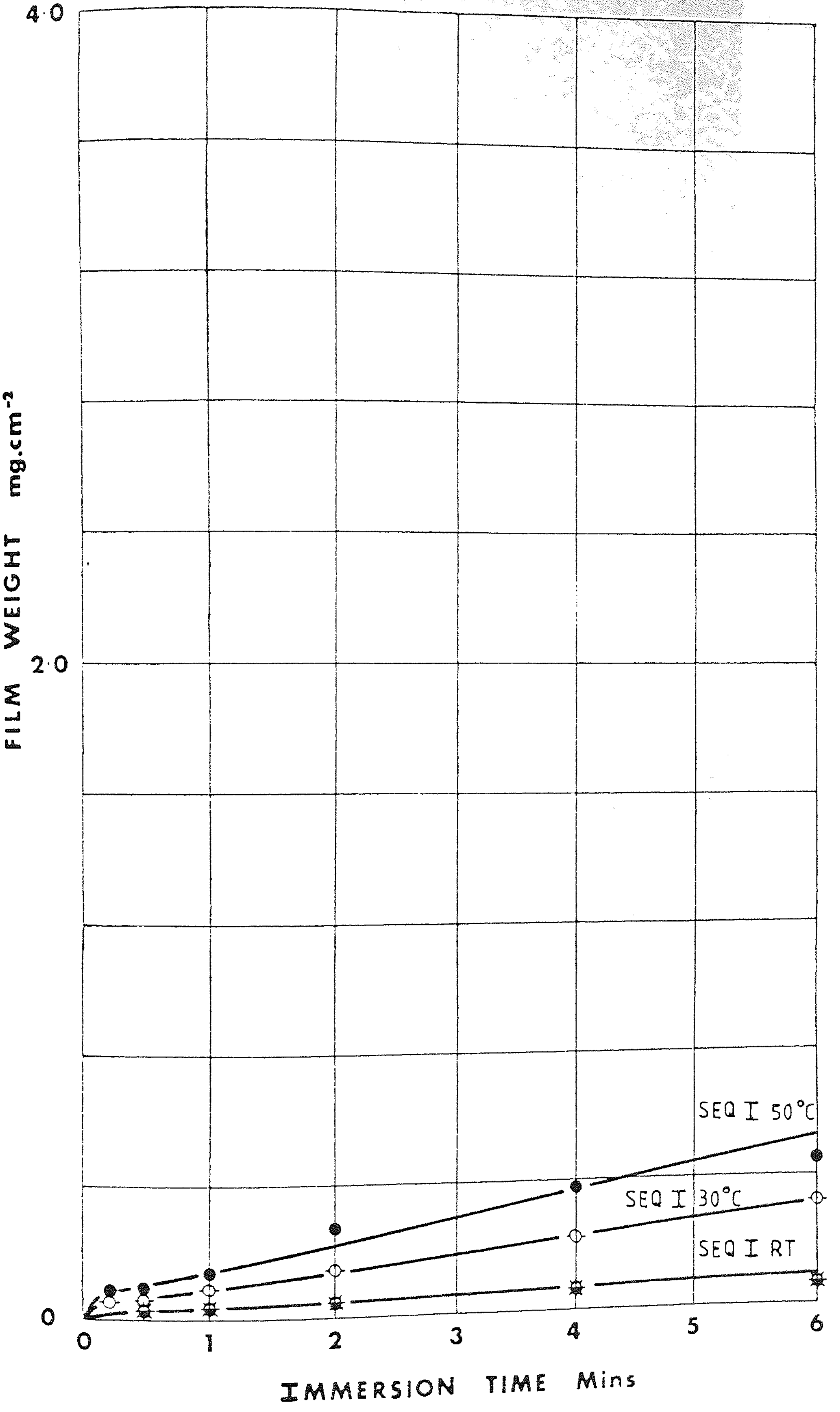


Fig.51c. Relationship between film weight and immersion time for alloy X-7046 pretreated using sequences I and III with immersion dips in M.A.Z. solution at various temperatures.

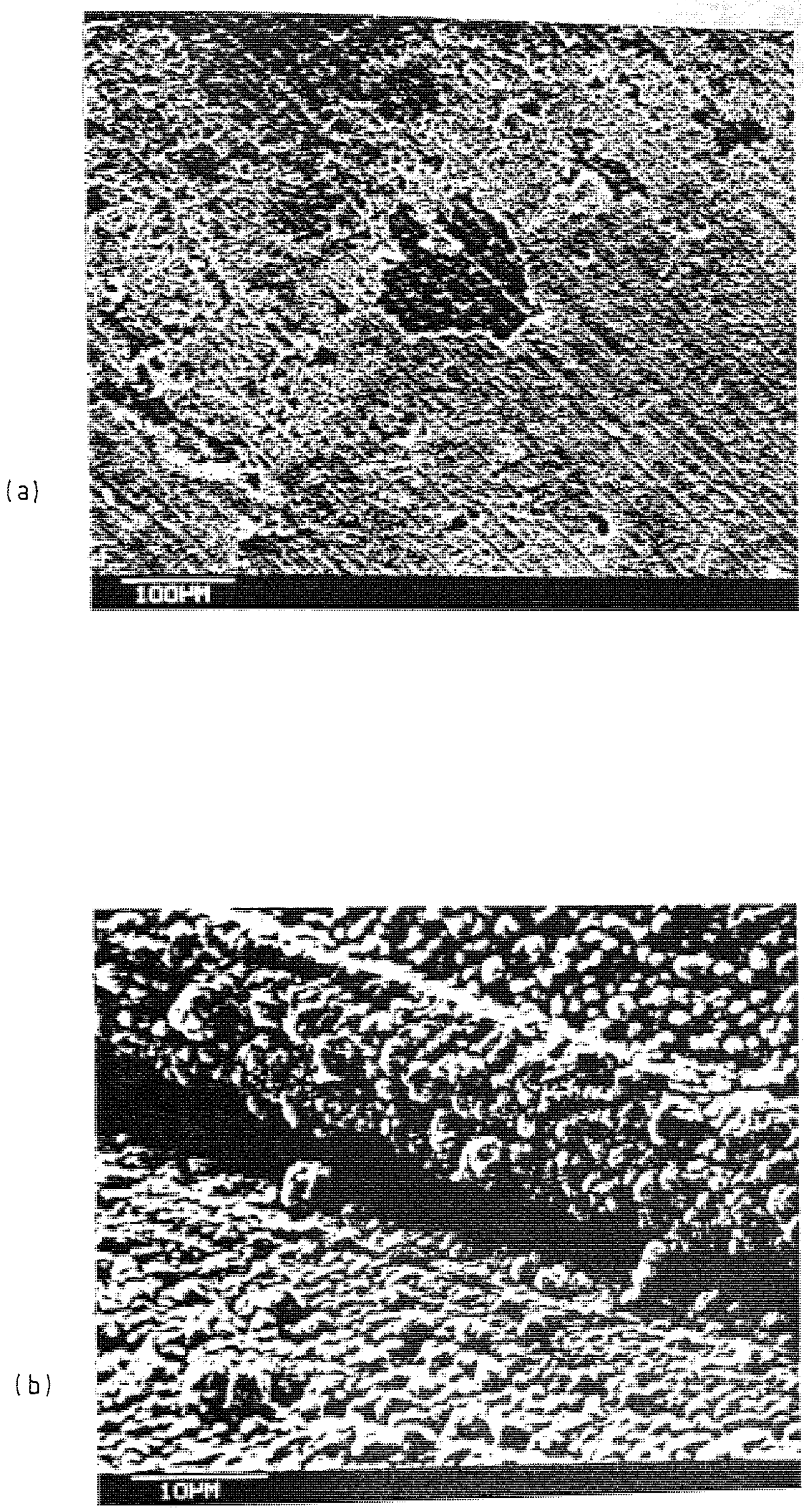


Fig.52. Scanning electron micrographs of the surface of alloy S1C after pretreatment using sequence I and 6 min immersion in 50°C M.A.Z. solution showing where : (a) areas of deposit have exfoliated; (b) the thick coarse grained deposit has ruptured and started to lift off the substrate.

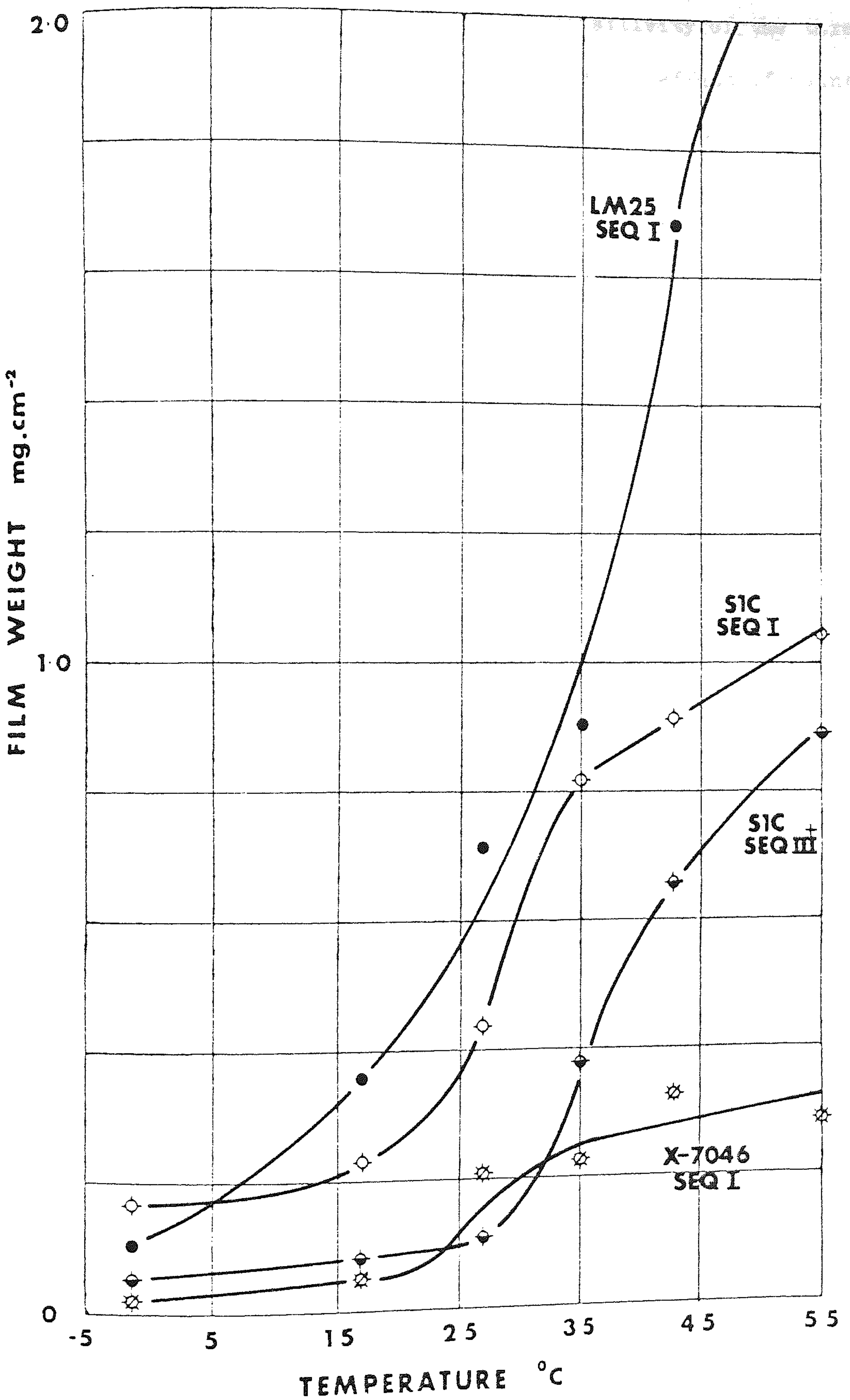


Fig.53. Relationship between film weight and M.A.Z. solution temperature for various aluminium alloys and pretreatment sequences - 2 min final immersion. (For sequence III$^+$ 2 min first immersion in room temperature M.A.Z. solution).

controlled environment. The difference in sensitivity of the three alloys to changes in solution temperature and the effect of using a double rather than single dip pretreatment for S1C are also illustrated.

3.4.1.3. Peel adhesion using 50°C M.A.Z. films

For this adhesion testing programme the alloys were pretreated and then electroplated with Watts nickel. M.A.Z. solution at 50°C was incorporated into the standard pretreatment sequences I to IV. With the double-dip pretreatments the first dip, in either room temperature or 50°C M.A.Z. solution, was always 2 min. Deposits produced at 50°C were thicker than those from room temperature solution. Therefore final dips in 50°C M.A.Z. solution for times predicted by film weight graphs, as well as the usual 2 min, were used.

An M.A.Z. film was not the only requisite for good electrodeposit adhesion. For example, single dip pretreatments in conjunction with 50°C M.A.Z. deposits failed to produce adhesion on any of the alloys irrespective of immersion time.

The double-dip pretreatment, sequence III, using either a room temperature or 50°C M.A.Z. first film gave satisfactory levels of adhesion on S1C and LM25. Peel adhesion results are given in Table XXI, where each value represents the mean of six results. This table illustrates that electroplate adhesion was affected by alloy type, the type of sequence III pretreatment used and

TABLE XXI. ADHESION OF WATTS NICKEL ELECTRODEPOSITS TO ALUMINIUM ALLOYS S1C AND LM25 AFTER VARIOUS PRETREATMENT SEQUENCES INVOLVING IMMERSION IN 50 °C M.A.Z. SOLUTION.

Processing sequence		Mean ($\bar{X}$) peel adhesion value KN/m		
	Duration of second 50 °C M.A.Z. dip s	Alloy type		
		S1C	LM25	Comments
SEQ III $\begin{smallmatrix}\text{R.T., 2 min}\\ 50\,^\circ\text{C}\end{smallmatrix}$	15	16·8 (5·2)	3·9 (0·6)	Unsatisfactory, non-uniform failure surfaces. Areas of zero adhesion.
	30	28·5 (8·0)	7·1 (0·7)	Satisfactory, uniform failure surfaces.
	120	17·1 (2·1)	4·6 (0·7)	Unsatisfactory, non-uniform failure surfaces. Areas of zero adhesion.
SEQ III $\begin{smallmatrix}50\,^\circ\text{C, 2 min}\\ 50\,^\circ\text{C.}\end{smallmatrix}$	15	6·4 (1·8)	5·1 (1·4)	Unsatisfactory, non-uniform failure surfaces. Areas of zero adhesion.
	30	20·7 (4·6)	12·4 (2·2)	Satisfactory, uniform failure surfaces.
	120	13·8 (1·0)	3·3 (0·5)	S1C: satisfactory, LM25: unsatisfactory, failure surfaces.

(Standard deviations given in brackets).

Mean peel adhesion on S1C and LM25 pretreated using SEQ III $\begin{smallmatrix}\text{R.T., 2 min}\\ \text{R.T., 2 min}\end{smallmatrix}$ was 23·6 KN m^{-1} and 4·4 KN m^{-1}, respectively.

TABLE XXII. ADHESION OF WATTS NICKEL ELECTRODEPOSITS TO ALUMINIUM ALLOY X-7046 AFTER VARIOUS PRETREATMENT SEQUENCES INVOLVING IMMERSION IN 50°C M.A.Z. SOLUTION.

Processing sequence		Mean ($\bar{X}$) peel adhesion value KN/m	
	Duration of second 50 °C M.A.Z. dip s	Alloy type X-7046	Comments
SEQ III $\genfrac{}{}{0pt}{}{\text{R.T.,2 min}}{50\,^{\circ}\text{C}}$	30	0	Alloy surface
	60	0	attacked by
	120	0	plating solution.
SEQ III $\genfrac{}{}{0pt}{}{50\,^{\circ}\text{C, 2 min}}{50\,^{\circ}\text{C}}$	60	0	Alloy surface attacked by plating solution.
	120	0	
SEQ IV $\genfrac{}{}{0pt}{}{\text{R.T.,2 min}}{50\,^{\circ}\text{C}}$	30	1·5 (0·2)	Unsatisfactory, non-uniform
	60	1·5 (0·3)	failure surfaces.
	120	1·5 (0·3)	Some surface attack.
SEQ IV $\genfrac{}{}{0pt}{}{50\,^{\circ}\text{C, 2 min}}{50\,^{\circ}\text{C}}$	60	4·2 (0·6)	Many areas of no attack but zero adhesion. A few regions of positive adhesion.
	120	2·3 (0·3)	

(Standard deviations given in brackets).

Mean peel adhesion on X-7046 pretreated using SEQ III $\genfrac{}{}{0pt}{}{\text{R.T.,2 min}}{\text{R.T.,2 min}}$ or SEQ IV $\genfrac{}{}{0pt}{}{\text{R.T.,2 min}}{\text{R.T.,2 min}}$ was zero.

the duration of the 50°C M.A.Z. second dip. Unlike S1C, on LM25 both 50°C M.A.Z. sequence III pretreatments resulted in significantly better adhesion of electroplate than that obtained using the standard pretreatment sequences with room temperature M.A.Z. solution.

None of the pretreatments using 50°C M.A.Z. solution produced satisfactory electrodeposit adhesion on X-7046. Table XXII shows peel adhesion results obtained on X-7046, where each value represents the mean of six results. Unlike for S1C and LM25, it can be seen that sequence III proved totally unsuitable for the pretreatment of X-7046. Only sequence IV, the double-dip pretreatment incorporating the 5% HF etch, produced any adhesion at all on this alloy. This was the first instance that adhesion, no matter how unsatisfactory, had been achieved on X-7046. Sequence IV was not used with S1C or LM25 as it caused over-etching which had a detrimental effect on adhesion.

3.4.1.3.1. Appearance of failure surfaces after peel adhesion testing

The characteristics of the failure surfaces were similar to those discussed in section 3.2.4.2.

Unlike the conventional M.A.Z. pretreatments, a mean electroplate adhesion value in excess of 7·5 KN m^{-1} was not always indicative of successful plating when using a 50°C M.A.Z. pretreatment. In Table XXI it can be seen that sometimes even though the adhesion level was acceptable, the failure surfaces were non-uniform. In such cases there were numerous regions of very low adhesion, of up to 2 mm in diameter, visible.

Where there was low adhesion on S1C and LM25, the failure surfaces indicated that extreme dissolution of the substrate occurred during formation of the 50°C M.A.Z. deposits.

The improvement in adhesion achieved on LM25 was accompanied by an increase in the amount of substrate detached on the peeled foil.

The failure surfaces of X-7046 pretreated using sequence IV on which slight electrodeposit had been recorded, exhibited some areas of low adhesion. There was however, zero adhesion on the majority of the surface which included regions attacked by the plating solution.

3.4.2. Operating the M.A.Z. solution electrolytically

Room temperature M.A.Z. solution, gently agitated, was operated electrolytically using inert anodes in conjunction with the four standard pretreatment sequences, section 2.3. The final film was always deposited electrolytically. Because M.A.Z. solution was not formulated as a plating solution, for practical reasons and to avoid difficulties including introduction of critical immersion times, the solution was operated within the range 0·5 A dm^{-2} to 2·0 A dm^{-2}. For double-dip pretreatments the first film was deposited from M.A.Z. solution either electrolytically or by conventional immersion. Initially the first dip was always for 2 min. However to improve adhesion on X-7046, in the latter stages of the work the effect of increasing the duration of the first dip was investigated.

By operating the M.A.Z. solution electrolytically it was hoped to artificially create the conditions on the surface of X-7046 that would result in the formation of films having the preferred characteristics.

3.4.2.1. Morphology of electrolytic M.A.Z. films

Even when an external current was applied, the surface characteristics of the aluminium still affected the growth of the M.A.Z. deposit. Figs 54a and 54b show films deposited for 3 min from M.A.Z. solution operated electrolytically at 2·0 A dm^{-2}, on 240 grit polished non-pretreated S1C and pure zinc, respectively. The latter is an example of a material which has a negligible natural driving force for film growth. Consequently fine grained, uniform electrolytic M.A.Z. deposits formed on pure zinc, Fig 54b. In contrast, the natural driving force of S1C had a predominant effect on M.A.Z. film growth even when an external current was superimposed. This resulted in the formation of a much thicker, coarser deposit which exhibited dendritic growth, Fig 54a.

Fig 54 represents an extreme situation where S1C was unpretreated and therefore in its most chemically reactive condition.

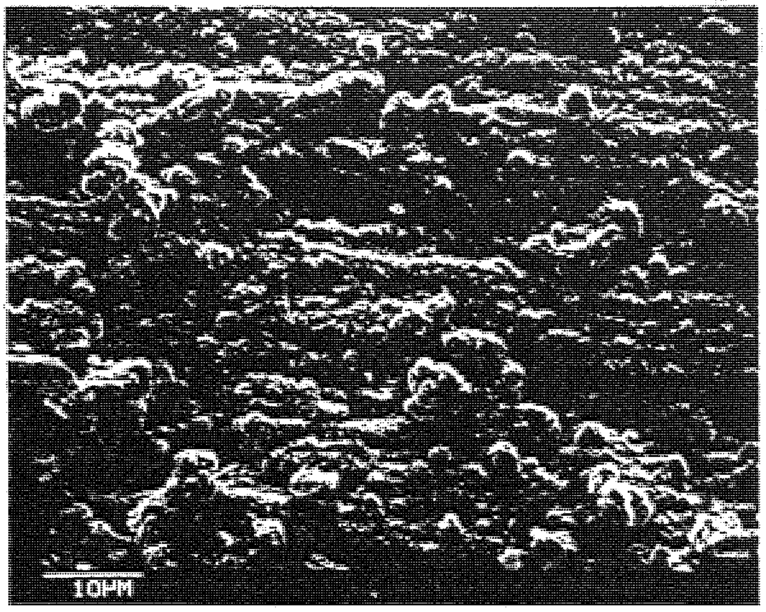


Fig. 54a. Scanning electron micrograph of the surface of alloy S1C 240 grit finished and non-pretreated after 3 min immersion in room temperature M.A.Z. solution operated electrolytically at 2·0 A dm^{-2}.

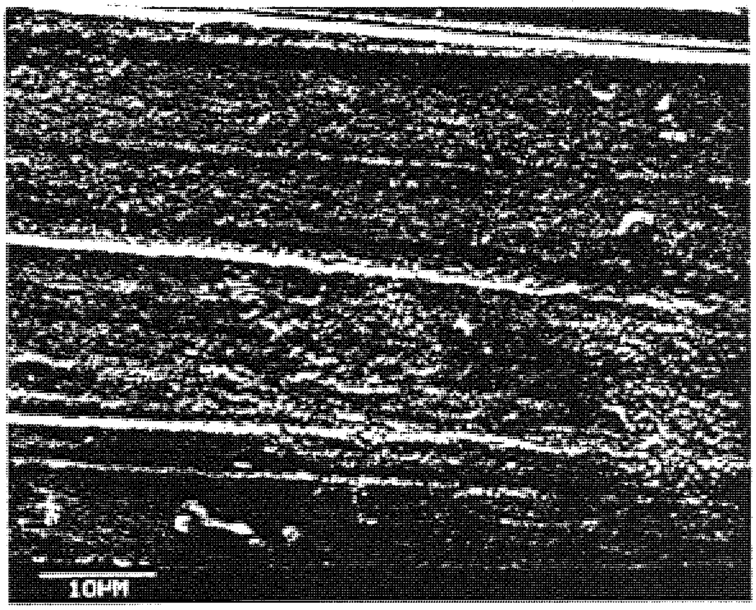


Fig. 54b. Scanning electron micrograph of the surface of zinc 240 grit finished and non-pretreated after 3 min immersion in room temperature M.A.Z. solution operated electrolytically at 2·0 A dm^{-2}.

However, it indicated that even when depositing the M.A.Z. films electrolytically the galvanic effect of the aluminium alloy substrates could not be ignored.

Figs 55a and 55b respectively illustrate the morphology of 1 min 1·0 A dm^{-2} M.A.Z. deposits produced on S1C and LM25 pretreated using sequence I. The equivilent film produced on X-7046 was uniform, exhibited good surface coverage and was similar, though finer grained and even more featureless than that shown in Fig 55a on S1C. Compared to S1C and LM25, X-7046 has a negligible natural driving force for film growth. This was the first example of a satisfactory M.A.Z. deposit on X-7046. In contrast, the deposit on LM25, Fig 55b, was coarse grained and the surface coverage poor. This was due to a strong natural driving force being dominant, even after pretreatment. This resulted largely from the presence of silicon platelets in the surface which were not covered with film. Fig's 55c and 55d respectively show that on S1C and LM25 pretreated using sequence I, with a 1 min immersion time thicker deposits were produced when the M.A.Z. solution was operated at 2 A dm^{-2}. Total coverage was also achieved more quickly. While the silicon platelets still tended to remain uncovered, use of the larger superimposed current did modify the film growth characteristics on LM25, Fig 55d.

On S1C the double-dip pretreatment, sequence III, only resulted in significantly thinner and finer grained final electrolytic M.A.Z. deposits when a conventional immersion first dip was used.

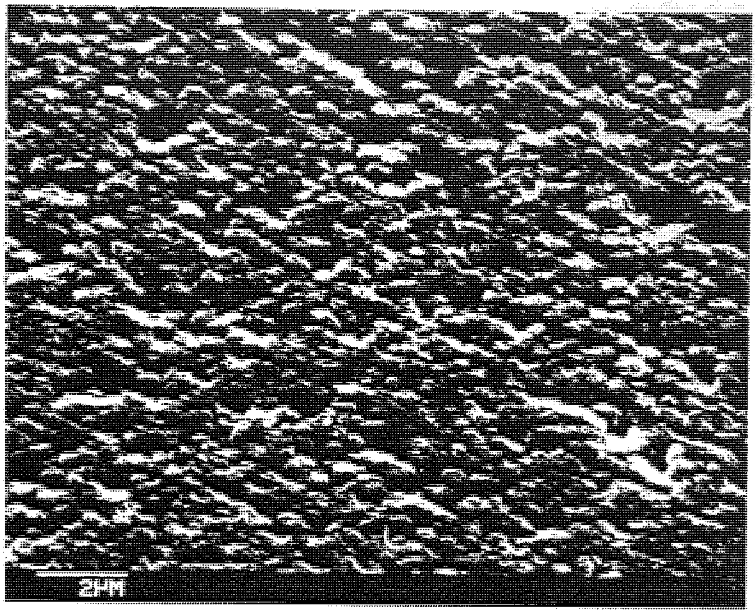


Fig.55a. Scanning electron micrograph of the surface of alloy S1C after pretreatment using sequence I and 1 min immersion in room temperature M.A.Z. solution operated electrolytically at 1·0 A dm^{-2}.

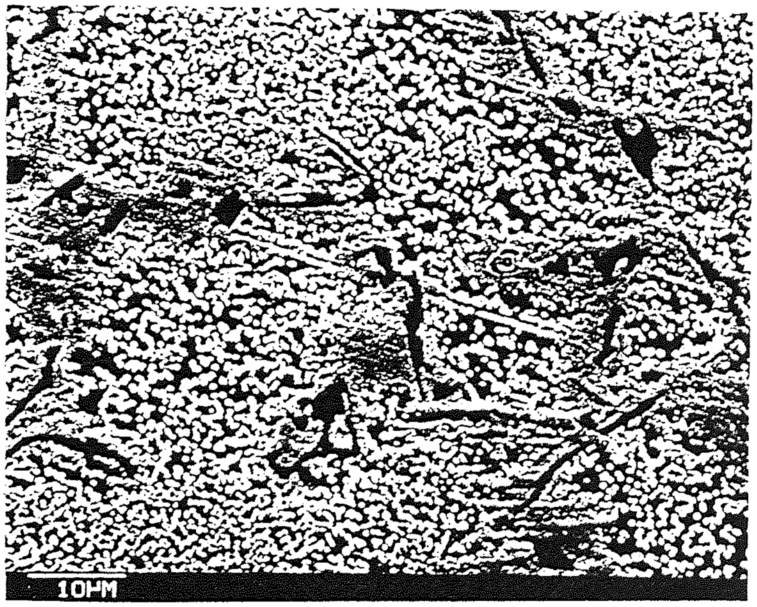


Fig.55b. Scanning electron micrograph of the surface of alloy LM25 after pretreatment using sequence I and 1 min immersion in room temperature M.A.Z. solution operated electrolytically at 1·0 A dm^{-2}.

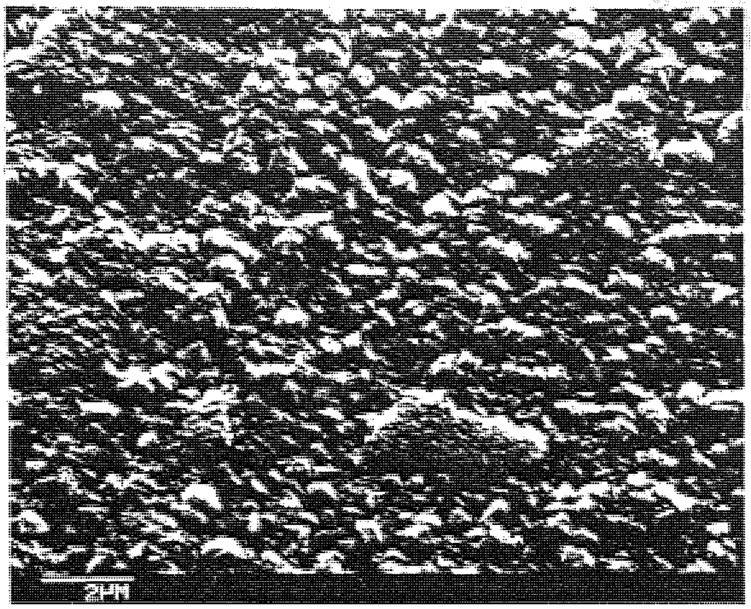


Fig.55c. Scanning electron micrograph of the surface of alloy S1C after pretreatment using sequence I and 1 min immersion in room temperature M.A.Z. solution operated electrolytically at 2·0 A dm^{-2}.

Fig.55d. Scanning electron micrograph of the surface of alloy LM25 after pretreatment using sequence I and 1 min immersion in room temperature M.A.Z. solution operated electrolytically at 2·0 A dm^{-2}.

This is not surprising since the surface exposed after removal of an electrolytic rather than ordinary immersion first film would be more reactive and less uniform. This is because less attack of the surface occurs during formation of an electrolytic type M.A.Z. deposit.

With LM25 however, when using sequence III the type of first film applied was of only minor significance. Unless the final electrolytic M.A.Z. film was deposited at approximately 2·0 A dm^{-2} or above, the natural tendencies for formation of a relatively coarse grained deposit exhibiting poor coverage predominated.

S1C and LM25 were not pretreated using sequence IV due to the excessive surface attack which resulted.

The electrolytic M.A.Z. deposits produced on X-7046 were affected little by changes in pretreatment. Using an operating current density of between 0·5 A dm^{-2} to 2·0 A dm^{-2}, although thickness varied, all films were fine grained, uniform and exhibited rapid coverage. Fig 56 highlights that using sequence IV rather than sequence II had little influence on the morphology of 4 min 1·0 A dm^{-2} deposits produced on X-7046. In this example a 4 min immersion time was used to make the presence of these generally featureless deposits more apparent. It can be seen however that sequence IV in conjunction with a 6 min conventional immersion first dip, Fig 56b, resulted in greater surface attack than sequence II, Fig 56a. This was mainly due to the extra 5% HF etch rather than dissolution caused during formation of the slow growing first film.

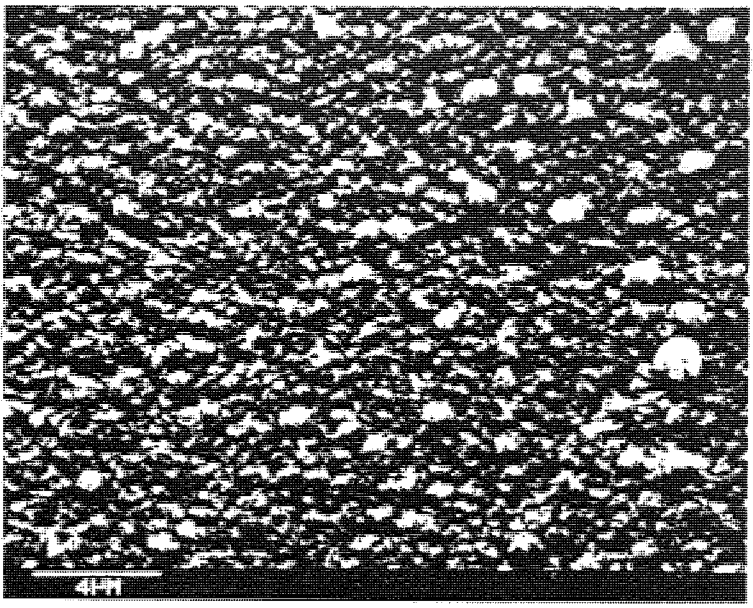


Fig.56a. Scanning electron micrograph of the surface of alloy X-7046 after pretreatment using sequence II and 4 min immersion in room temperature M.A.Z. solution operated electrolytically at 1·0 A dm^{-2}.

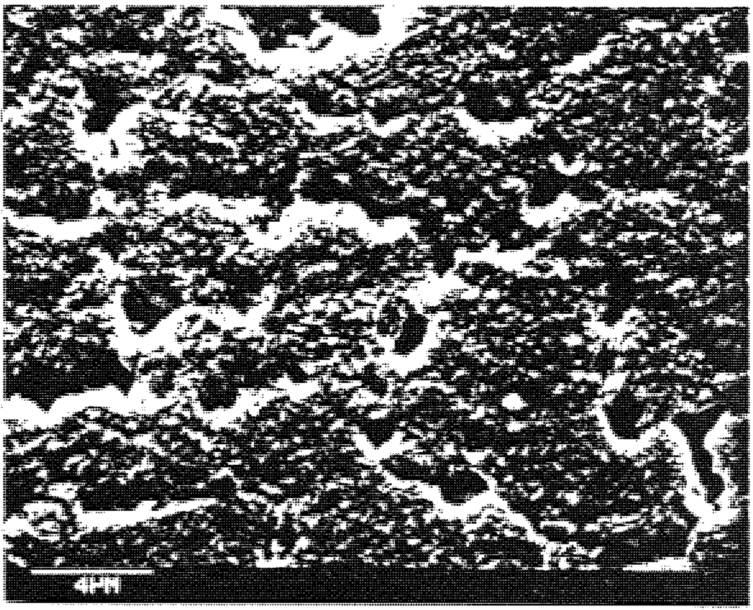


Fig.56b. Scanning electron micrograph of the surface of alloy X-7046 after pretreatment using sequence IV with a 6 min conventional first immersion and 4 min 1·0 A dm^{-2} electrolytic second immersion in room temperature M.A.Z solution.

The electrolytic deposits on all the alloys became coarser grained when they developed beyond a certain thickness; further growth taking place at fewer growth centres.

Kevex analysis revealed that typical 2 min M.A.Z. deposits produced electrolytically or by conventional immersion were of similar composition.

3.4.2.2. Determination of film weight from M.A.Z. solution operated electrolytically

Figs 57 to 60 show the change in film weight with immersion time in electrolytically operated M.A.Z. solution for the alloys pretreated using various sequences.

Fig 57 shows that on non-pretreated S1C and brass, the initial growth rate of a 1 A dm^{-2} electrolytic M.A.Z. deposit was much greater on S1C which has a large inherent natural driving force for film growth. As film weight increased and the galvanic effect of the S1C substrate diminished, the growth rate on S1C became similar to the linear rate on brass where the natural driving force was negligible.

Fig 58 shows the influence of the operating current density on M.A.Z. film weight for the alloys pretreated using sequence I. Under conditions of conventional immersion, i.e. 0 A dm^{-2}, the driving force for film growth was lowest on X-7046. Film growth on this alloy was influenced most by electrolytic use of M.A.Z. solution. The opposite was true of LM25 which exhibited the

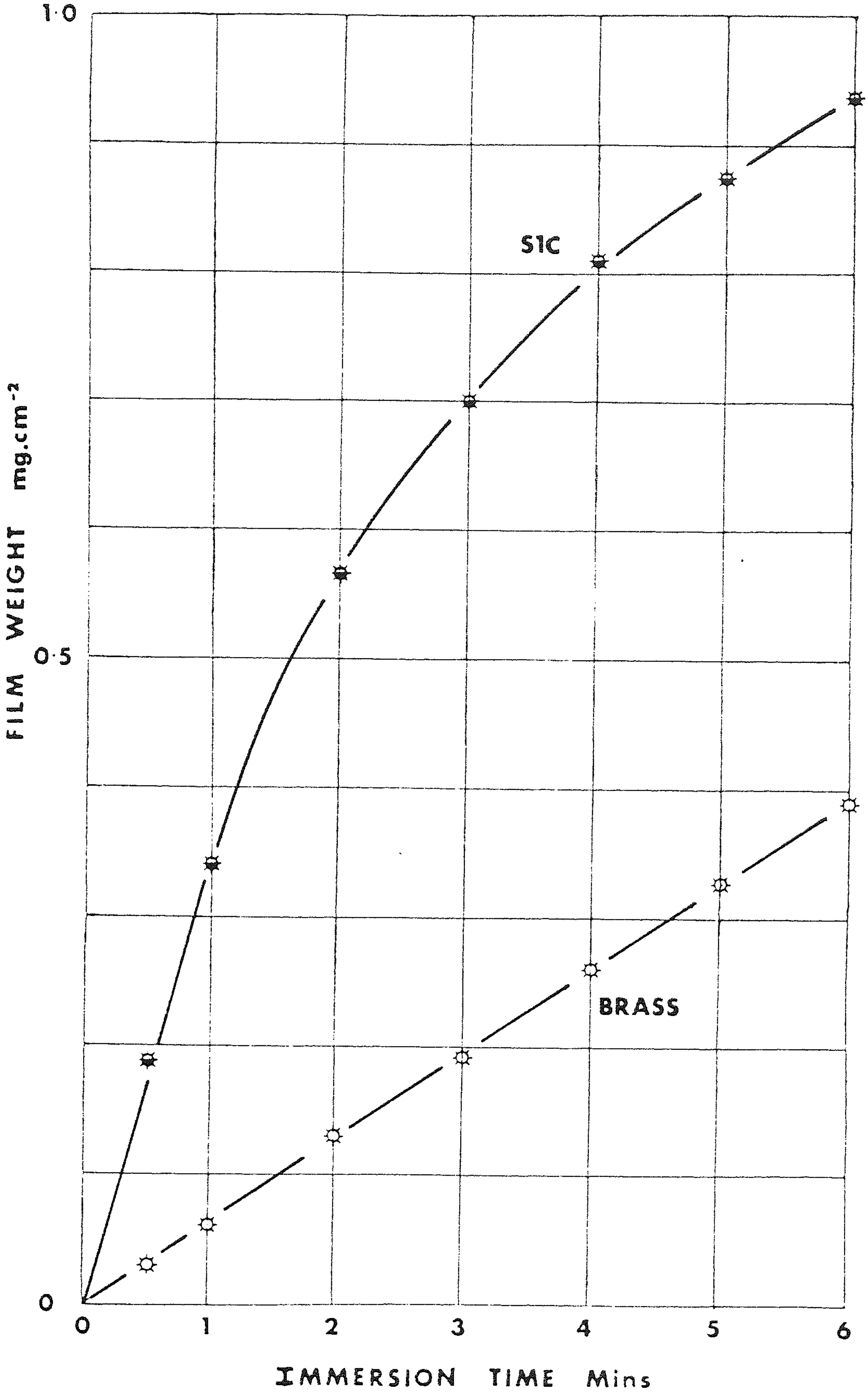


Fig.57. Relationship between film weight and immersion time in room temperature M.A.Z. solution operated electrolytically at 1·0 A dm^{-2} for alloy S1C and brass after no pretreatment.

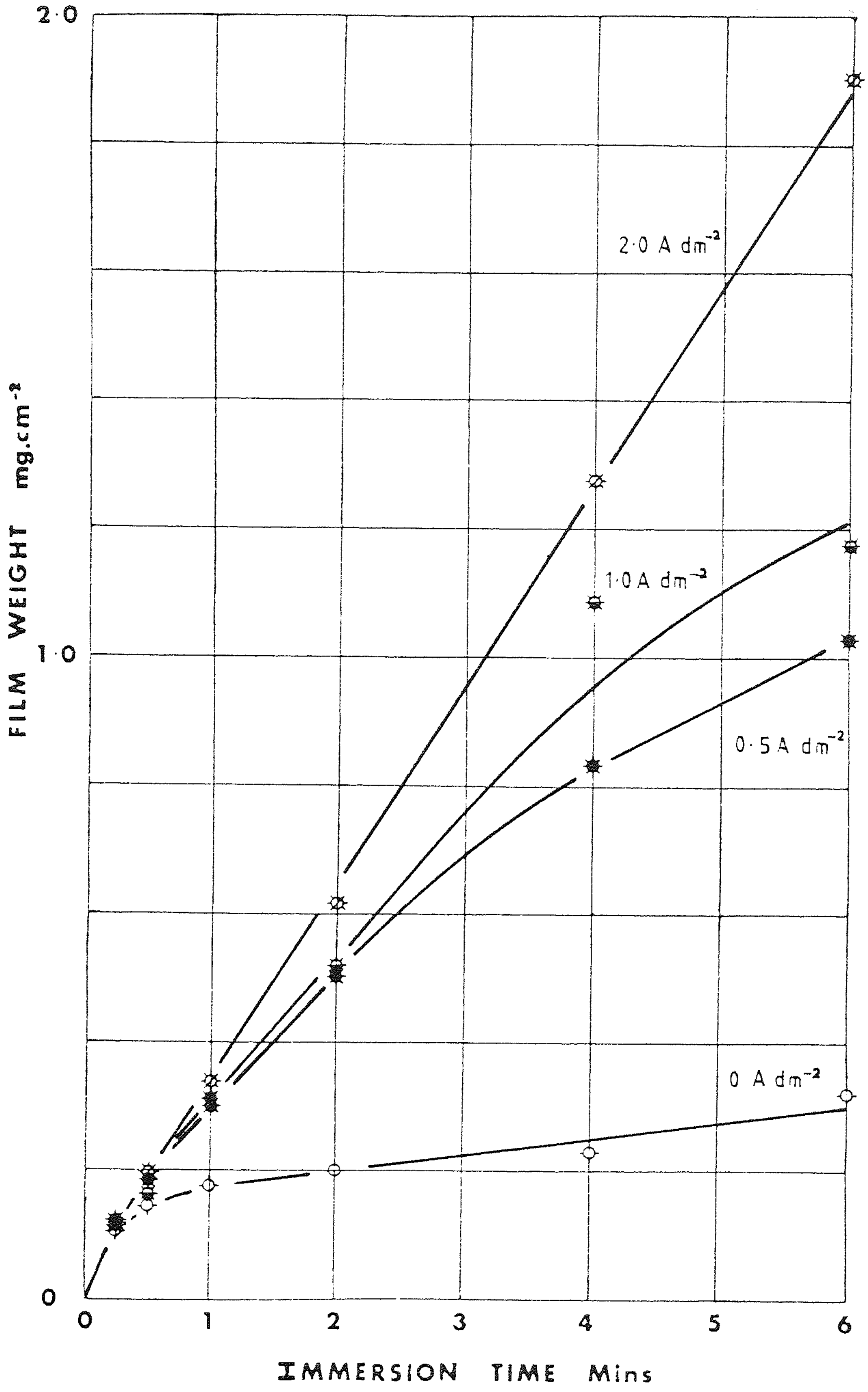


Fig.58a. Relationship between film weight and immersion time in room temperature M.A.Z. solution operated electrolytically at various current densities for alloy S1C after pretreatment using sequence I.

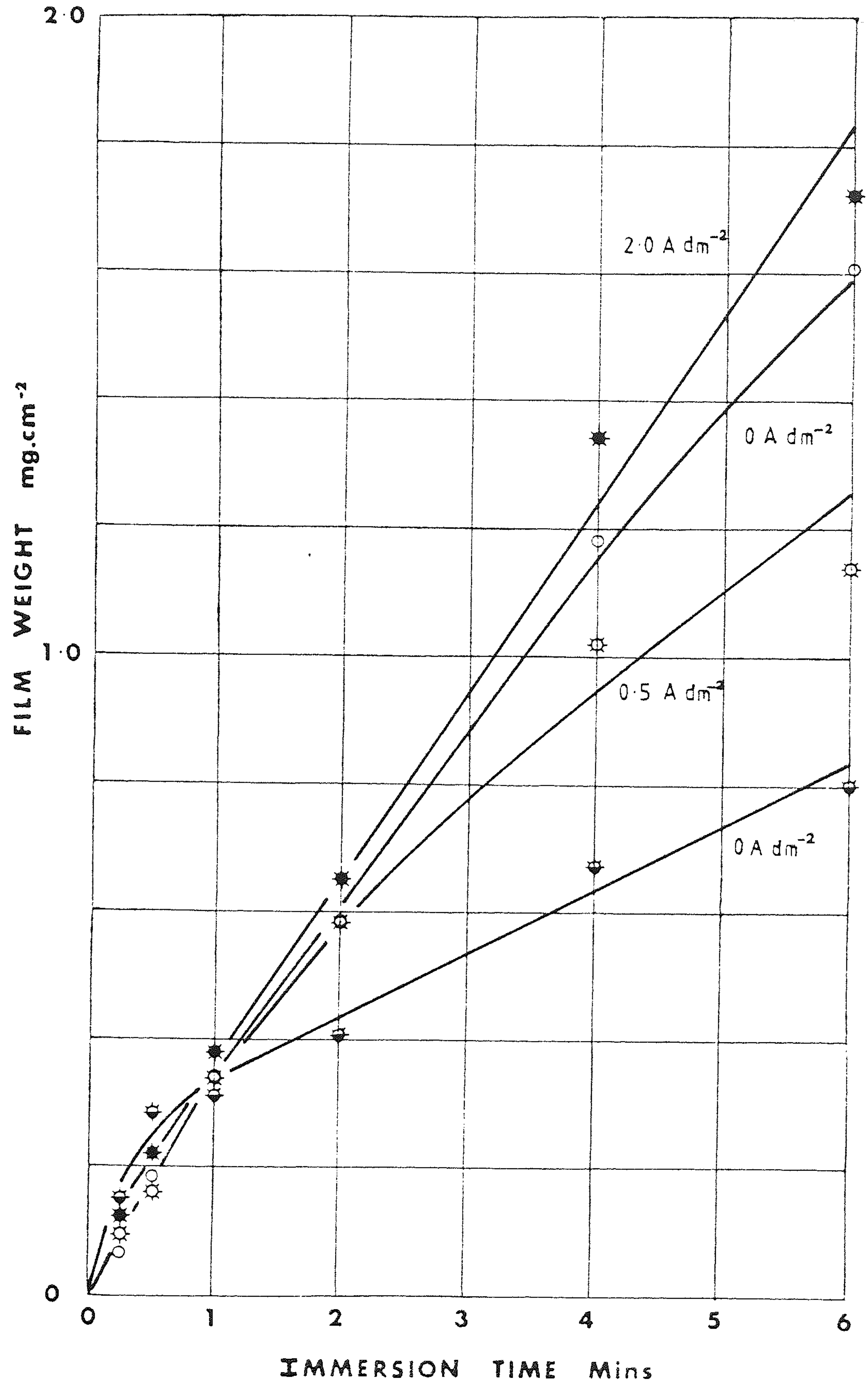


Fig.58b. Relationship between film weight and immersion time in room temperature M.A.Z. solution operated electrolytically at various current densities for alloy LM25 after pretreatment using sequence I.

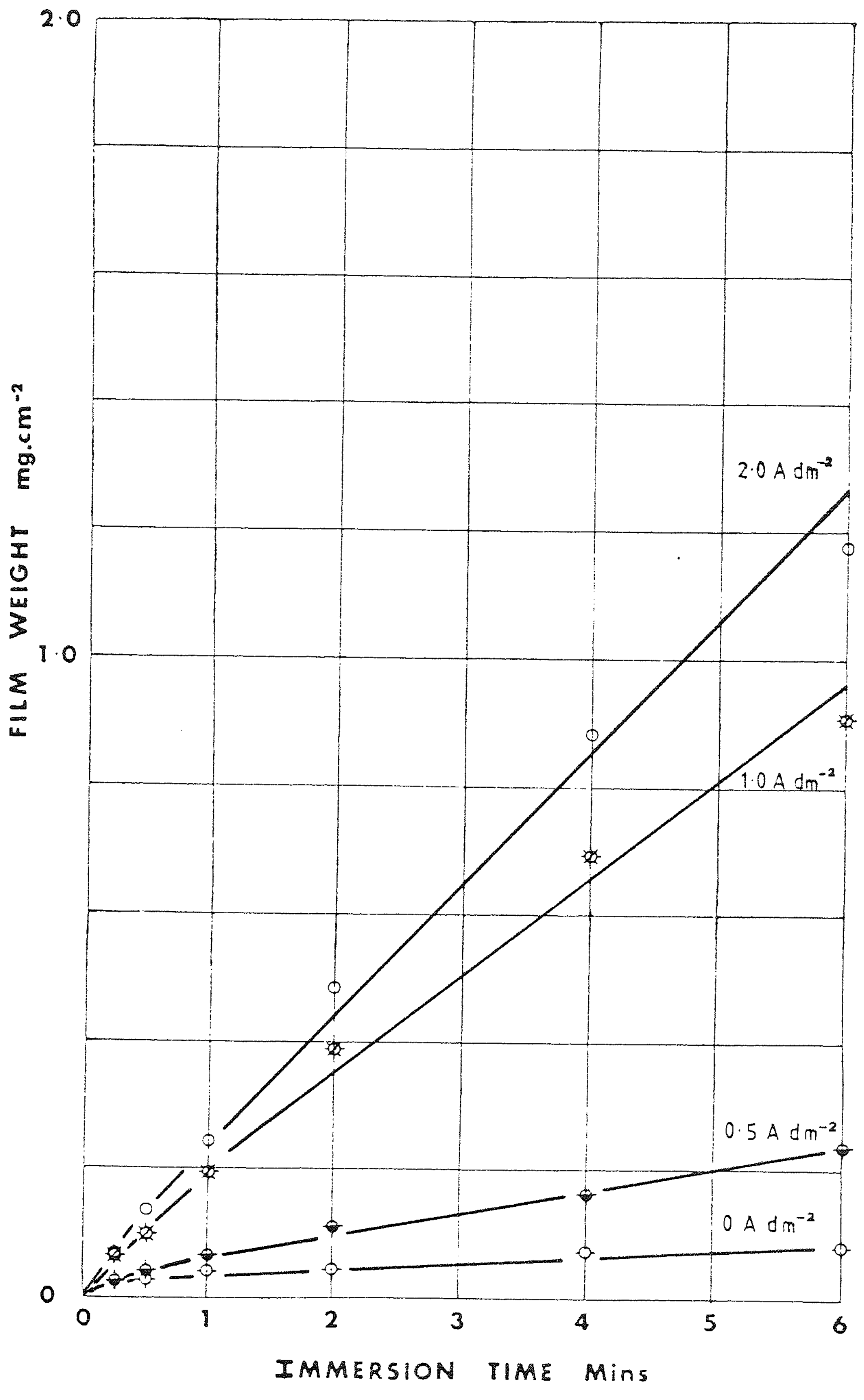


Fig.58c. Relationship between film weight and immersion time in room temperature M.A.Z. solution operated electrolytically at various current densities for alloy X-7046 after pretreatment using sequence I.

greatest tendency for film growth with conventional immersion.

For S1C and LM25 pretreated using the double-dip sequence III, the weight of the final electrolytic M.A.Z. film was affected considerably more by a conventional 2 min first dip rather than by an electrolytic one. This is illustrated in Fig 59 for S1C, operating the M.A.Z. solution at 1·0 A dm^{-2}.

Due to its relatively small natural driving force, the growth of electrolytic M.A.Z. films on X-7046 was least affected by pretreatment. This is shown in Fig 60 for 0·5 A dm^{-2} deposits, (expanded scale). The differences in film weight due to changes in pretreatment were small and probably the result of variations in true surface area caused by pretreatment.

Operating the M.A.Z. solution electrolytically was the first technique developed which was capable of producing relatively thick deposits on X-7046. Because X-7046 had such a small influence on the growth of the electrolytic M.A.Z. deposits, the growth rate obtained was primarily determined by the operating current density.

The various electrolytic M.A.Z. film weight curves were compared with that of S1C pretreated using sequence III incorporating conventional immersion dips. The latter curve shown in Fig 59, after a 2 min immersion time indicates the approximate film weight required to achieve good adhesion of electrodeposit. This comparison showed that for plating, to avoid a very short and highly critical immersion time the operating current density

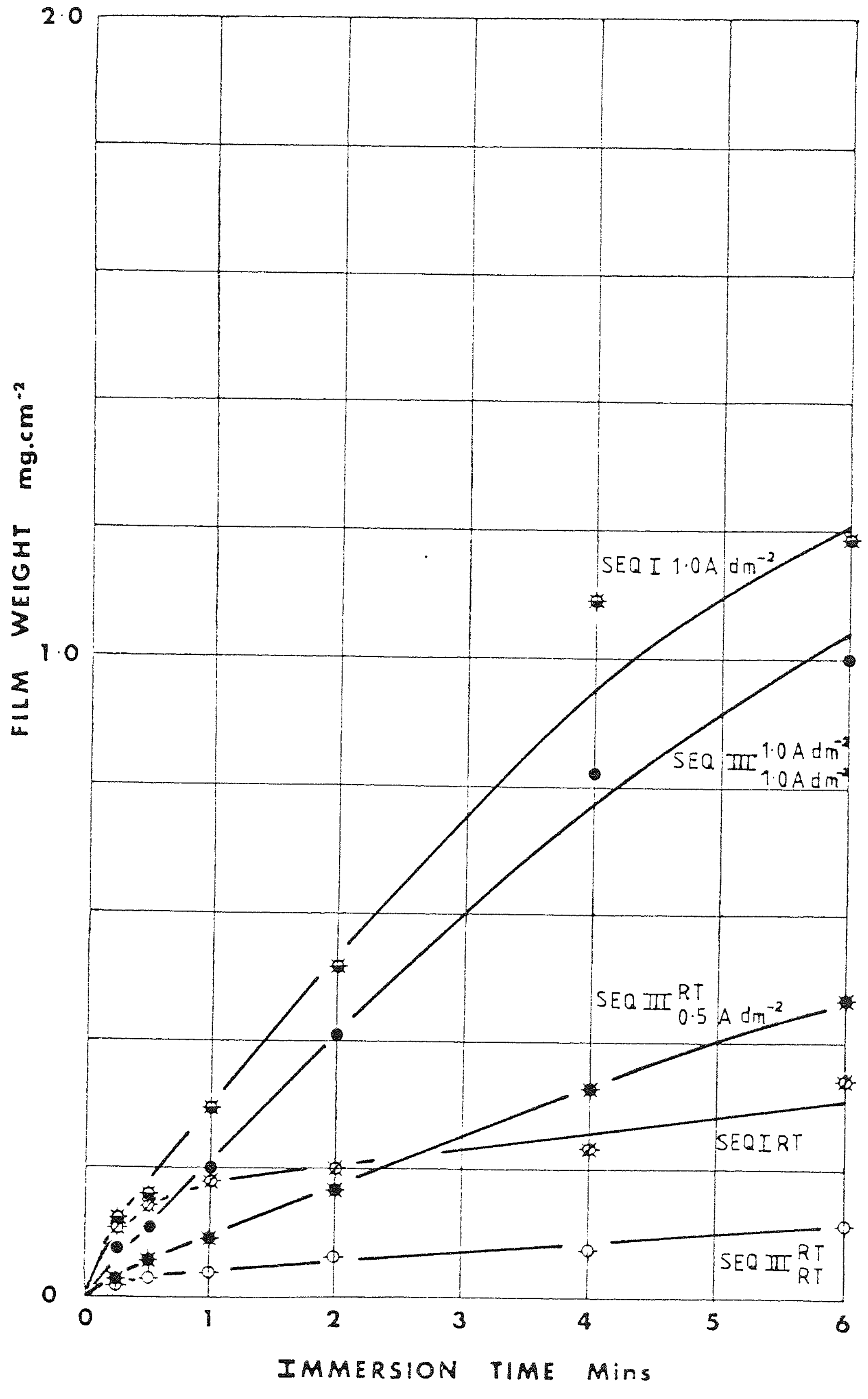


Fig.59. Relationship between film weight and immersion time for alloy S1C pretreated using sequences I and III with conventional immersion and 1·0 A dm^{-2} electrolytic immersion dips in room temperature M.A.Z. solution.

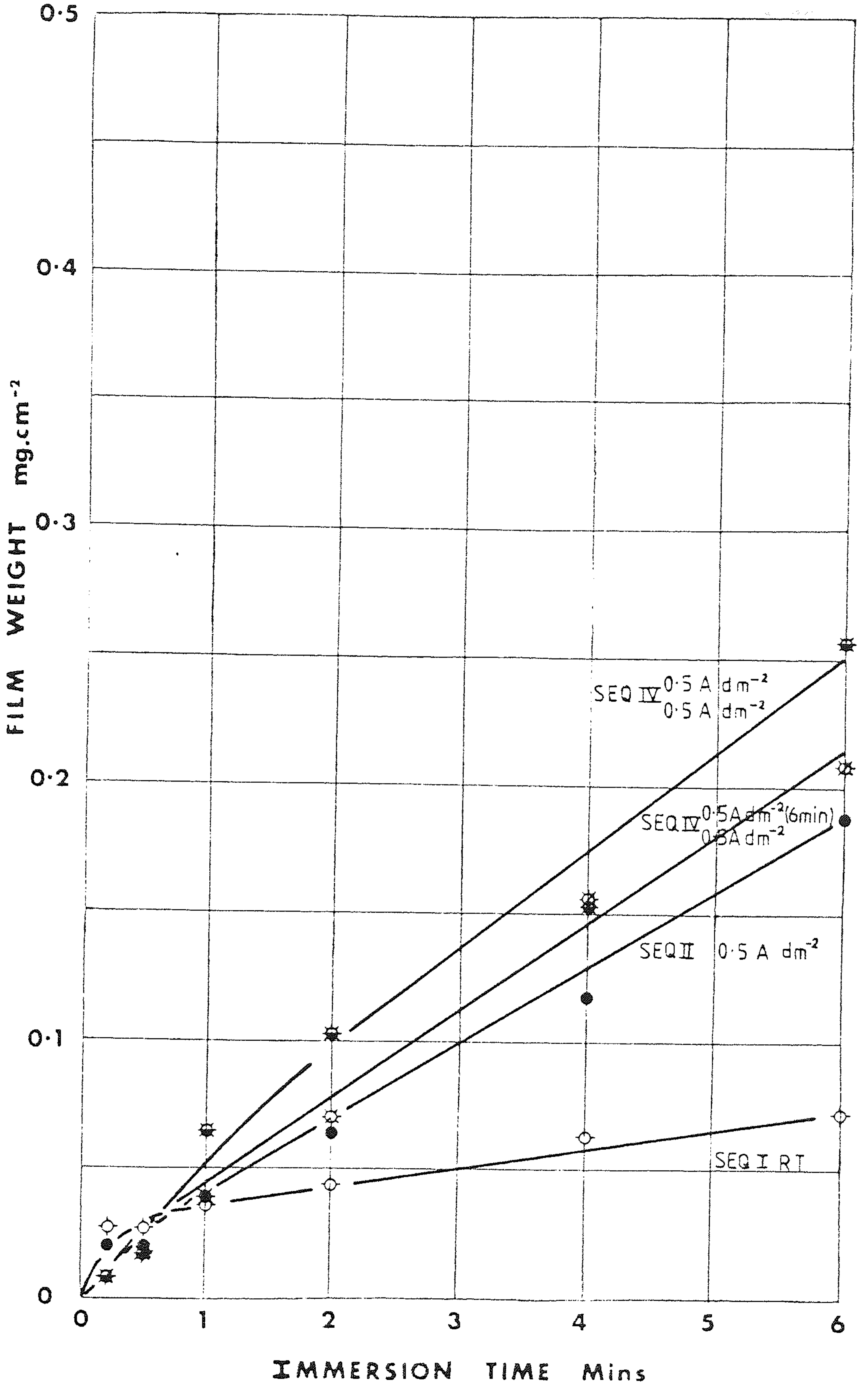


Fig.60. Relationship between film weight and immersion time for alloy X-7046 pretreated using various sequences with conventional immersion and 0·5 A dm^{-2} electrolytic immersion dips in room temperature M.A.Z. solution.

of the M.A.Z. solution must be relatively low, e.g. 0·5 A dm^{-2}. This was quite satisfactory for the pretreatment of X-7046 whereas for LM25 a current density of 2·0 A dm^{-2} was needed to achieve adequate film growth characteristics.

3.4.2.3. Peel adhesion using electrolytic M.A.Z. films

In this adhesion study the alloys were Watts nickel plated following pretreatment. M.A.Z. solution operated electrolytically at either 0·5 A dm^{-2} or 1 A dm^{-2} was incorporated into the standard pretreatment sequences I to IV. Initially with the double-dip pretreatments, a 2 min conventional or electrolytic first M.A.Z. dip was used. However for X-7046, this immersion time was increased to improve adhesion. Depending on the operating current density, electrolytic M.A.Z. deposits were faster growing than those produced by conventional immersion. The time taken for the selected film weight was obtained from film weight graphs, e.g. Figs 58 to 60. Therefore final electrolytic dips of duration indicated by film weight measurements, as well as the usual 2 min, were utilized.

Irrespective of immersion time, the single dip electrolytic pretreatments did not produce adhesion on any of the three alloys.

Tables XXIII to XXV contain the results of peel adhesion tests for the alloys pretreated using various electrolytic M.A.Z. double-dip sequences. Each value represents the mean of six results.

TABLE XXIII. ADHESION OF WATTS NICKEL ELECTRODEPOSITS TO ALUMINIUM ALLOYS S1C AND LM25 AFTER VARIOUS PRETREATMENT SEQUENCES INVOLVING ELECTROLYTIC M.A.Z. IMMERSION.

Processing sequence		Mean ($\bar{X}$) peel adhesion value KN/m		
	Duration of second electrolytic M.A.Z. dip s	Alloy type S1C	LM25	Comments
SEQ III R.T., 2 min 1 A dm^{-2}	30	21·2 (4·2)	0	S1C : unsatisfactory, non-uniform failure surfaces.
	60	23·0 (5·5)	0	
	120	2·7 (0·4)	0	'Snake-skin adhesion effect'.
SEQ III 1 A dm^{-2}, 2 min 1 A dm^{-2}	15	12·6 (3·2)	0	Regions of very high but also zero adhesion.
	30	29·0 (2·1)	0	
	120	9·7 (1·9)	0	LM25 : encapsulation only.
SEQ III R.T., 2 min 0·5 A dm^{-2}	30	18·0 (2·1)	4·2 (0·8)	S1C : satisfactory, uniform failure surfaces.
	60	18·0 (3·9)	3·9 (0·5)	
	120	15·1 (4·1)	1·9 (0·3)	LM25 : low adhesion.
SEQ III 0·5 A dm^{-2}, 2min 0·5 A dm^{-2}	15	16·2 (2·6)	3·1 (0·4)	
	30	18·9 (3·2)	3·9 (0·5)	
	120	11·6 (3·5)	1·9 (0·5)	

(Standard deviations given in brackets).

TABLE XXIV. ADHESION OF WATTS NICKEL ELECTRODEPOSITS TO ALUMINIUM ALLOY X-7046 AFTER VARIOUS PRETREATMENT SEQUENCES INVOLVING ELECTROLYTIC M.A.Z. IMMERSION.

Processing sequence		Mean ($\bar{X}$) peel adhesion value KN/m	
	Duration of second electrolytic M.A.Z. dip s	Alloy type X-7046	Comments
SEQ III R.T.,2 min 0·5 A dm^{-2}	30	0	Alloy surface attacked by plating solution.
	60	0	
	120	0	
SEQ III 0·5 A dm^{-2},2 min 0·5 A dm^{-2}	30	0	
	60	0	
	120	0	
SEQ IV R.T.,2 min 0·5 A dm^{-2}	30	1·7 (0·2)	Satisfactory uniform failure surfaces. No surface attack.
	60	1·9 (0·2)	
	120	4·8 (1·9)	
SEQ IV 0·5 A dm^{-2},2 min 0·5 A dm^{-2}	30	3·9 (1·5)	
	60	7·0 (1·5)	
	120	0	

(Standard deviations given in brackets).

TABLE XXV. ADHESION OF WATTS NICKEL ELECTRODEPOSITS TO ALUMINIUM ALLOY X-7046 AFTER VARIOUS PRETREATMENT SEQUENCES INVOLVING ELECTROLYTIC M.A.Z. IMMERSION BUT SHOWING THE EFFECT OF INCREASING THE DURATION OF THE FIRST M.A.Z. DIP

Processing sequence		Mean ($\bar{X}$) peel adhesion value KN/m	
	Duration of second electrolytic M.A.Z. dip s	Alloy type X-7046	Comments
SEQ IV R.T.,2 min 0·5 A dm^{-2}	60	1·9 (0·2)	Satisfactory, uniform failure surfaces. No surface attack.
	120	4·8 (1·9)	
SEQ IV R.T.,6 min 0·5 A dm^{-2}	60	3·1 (0·8)	
	120	9·7 (1·0)	
SEQ IV R.T.,6 min 0·5 A dm^{-2} (2 min etches)*	120	6·6 (2·3)	
SEQ IV 0·5 A dm^{-2},2 min 0·5 A dm^{-2}	60	7·0 (1·5)	Satisfactory, uniform failure surfaces. No surface attack.
	120	0	
SEQ IV 0·5 A dm^{-2},6 min 0·5 A dm^{-2}	60	12·4 (1·2)	
	120	6·6 (0·2)	
SEQ IV 0·5 A dm^{-2},6 min 0·5 A dm^{-2} (2 min etches)*	60	8·5 (1·8)	

(Standard deviations given in brackets).

* Standard etch time 1 min.

Table XXIII indicates the peel results recorded on S1C and LM25 pretreated using electrolytic M.A.Z. deposits in conjunction with sequence III. Poor adhesion was always obtained on LM25. For S1C, adhesion levels in excess of 20 KN m^{-1} were obtained using 0·5 A dm^{-2} and 1 A dm^{-2} M.A.Z. deposits. However the failure surfaces of S1C pretreated with 1·0 A dm^{-2} films were non-uniform and characterized by streaks of zero adhesion. Therefore in all subsequent work only 0·5 A dm^{-2} deposits were utilized.

Table XXIV illustrates that the electrolytic M.A.Z. modification of sequence III was totally ineffective for the pretreatment of X-7046. Sequence IV, which was not used with S1C or LM25 due to the effects of over-etching, did however produce adhesion, though not of an acceptable level on X-7046.

Previously, where the double-dip technique had produced good adhesion on alloys such as S1C and HE9 using conventional M.A.Z. immersion, the first 2 min film was relatively thick and gave total coverage. The weight of the first 2 min conventional or 0·5 A dm^{-2} M.A.Z. deposit on X-7046 was in contrast much lower. Using the electrolytic M.A.Z. sequence IV pretreatment but increasing the duration of this first dip from 2 min to 6 min resulted in a significant improvement in adhesion on X-7046, as shown in Table XXV. Satisfactory levels in excess of 7·5 KN m^{-1} were achieved. This improvement was not merely due to extra indiscriminate surface attack as use of longer etches of up to 3 min with sequence II, the single dip equivalent, did not produce adhesion. Thus the formation of the first film had some selective 'etching' or 'conditioning' effect which resulted in superior adhesion. Table XXV also shows that the benefits of a satisfactory pretreatment could be reduced by over-etching.

3.4.2.3.1. Appearance of failure surfaces after peel adhesion testing

The characteristics of the failure surfaces were similar to those discussed previously.

However Table XXIII indicates that although sequence III, incorporating 1 A dm^{-2} M.A.Z. deposits, developed mean electrodeposit adhesion levels in excess of 20 KN m^{-1} on S1C, the failure surfaces were extremely non-uniform. These were covered with regions of high but also near zero adhesion and considered unacceptable. This was termed the 'snakeskin adhesion effect' and did not occur when the M.A.Z. solution was operated at 0·5 A dm^{-2}.

The failure surfaces of X-7046 pretreated using SEQ IV $\substack{\text{R.T.,2 min}\\ \text{0·5 A dm , 1 min}}$ and SEQ IV $\substack{\text{R.T.,6 min}\\ \text{0·5 A dm , 2 min}}$ are shown in Figs 61 and 62, respectively. The adhesion levels on these test pieces were 1·9 KN m^{-1} and 9·7 KN m^{-1} respectively. Fig 61 indicates that on X-7046 the sequence IV pretreatment caused extensive attack of grain boundaries. Fig 62 illustrates a failure, characteristic of a low ductility substrate. It shows that failure occurred primarily at the X-7046 - electrodeposit interface but that grains weakened by etching were also detached.

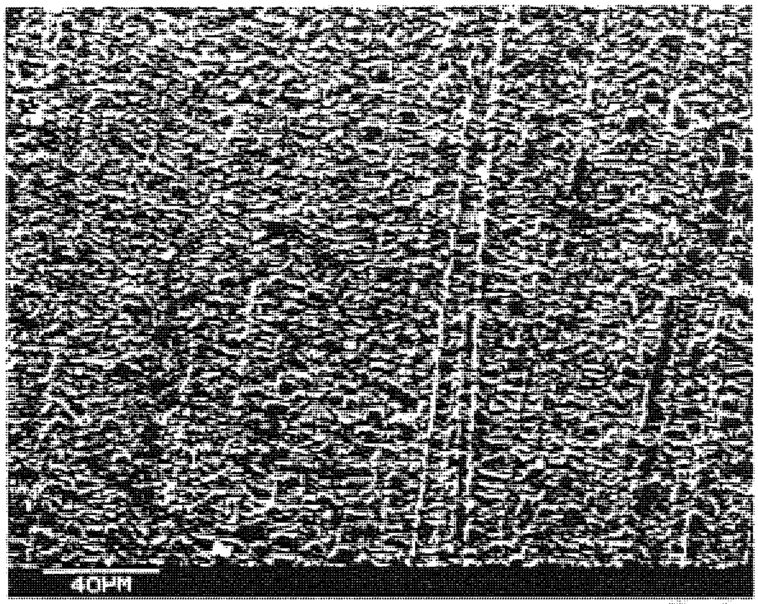


Fig.61. Scanning electron micrograph of the surface of alloy X-7046 pretreated using sequence IV with a 2 min conventional first immersion and 1 min 0·5 A dm^{-2} electrolytic second immersion in room temperature M.A.Z. solution, after peeling off the nickel foil. The peel adhesion was 1·9 KN m^{-1}.

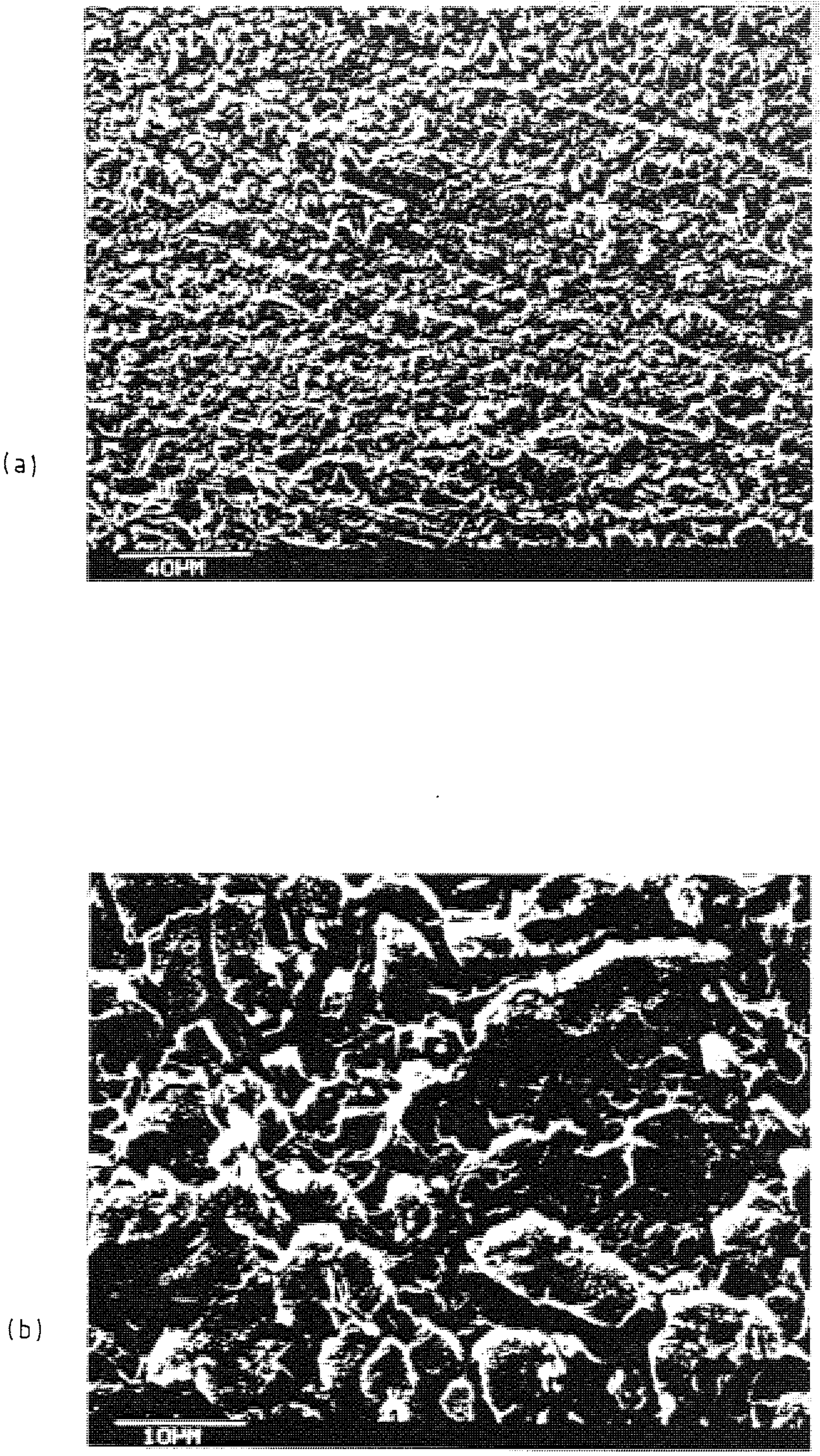


Fig.62. Scanning electron micrographs of the surface of alloy X-7046 pretreated using sequence IV with a 6 min conventional first immersion and 2 min 0·5 A dm^{-2} electrolytic second immersion in room temperature M.A.Z. solution, after peeling off the nickel foil. The peel adhesion was 9·7 KN m^{-1}.

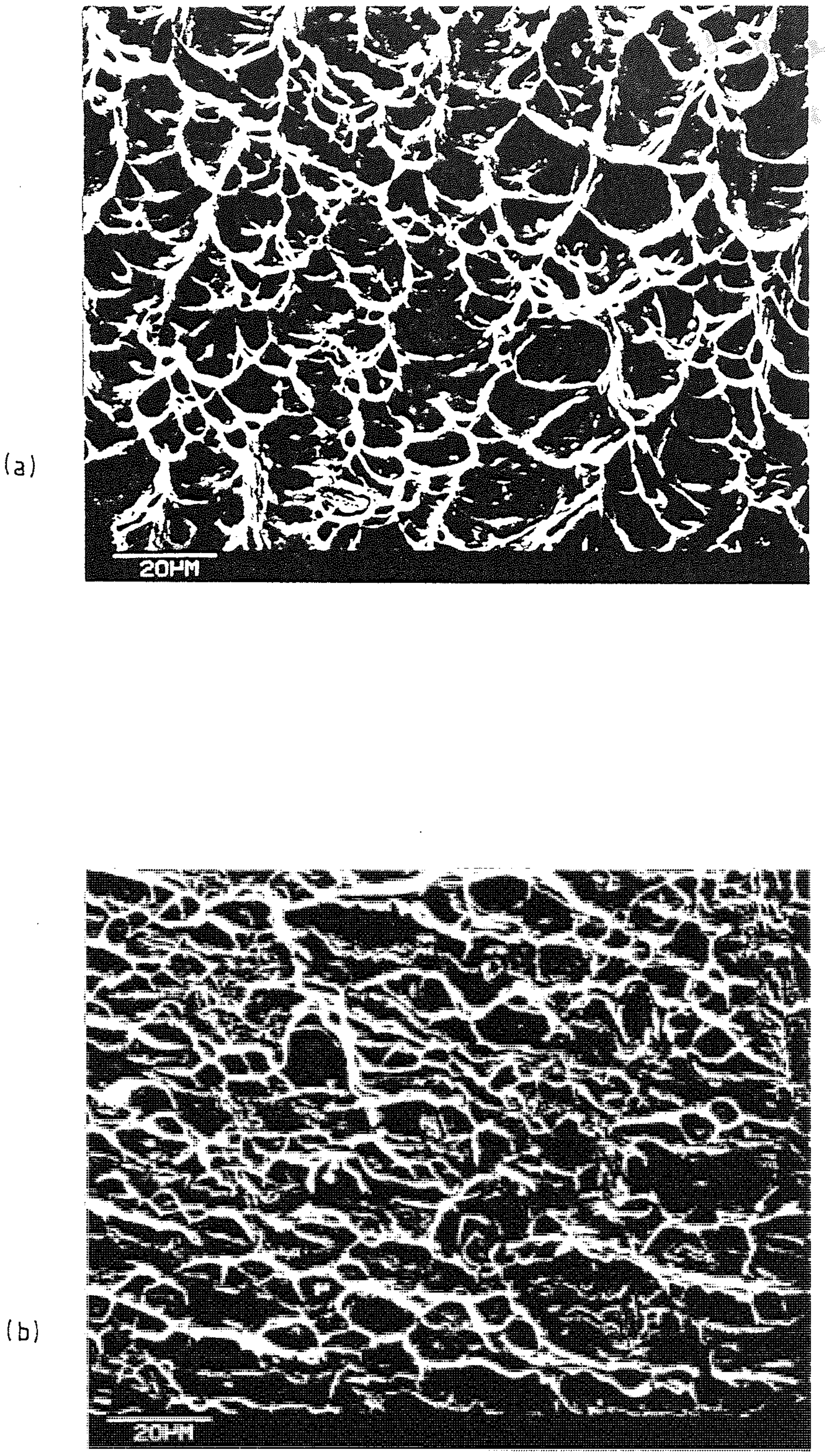


Fig.63. Scanning electron micrographs of the failure surfaces after peel adhesion testing of alloy S1C pretreated using sequence III with a 2 min conventional first immersion and 30 s 0·5 A dm^{-2} electrolytic second immersion in room temperature M.A.Z. solution : (a) the alloy surface after peeling off the nickel foil; (b) the back of the peeled nickel foil.
The peel adhesion was 21·6 KN m^{-1}.

Fig 62 should be contrasted with the completely sub-surface, ductile cup-and-cone type failure of S1C pretreated using SEQ III $\begin{matrix}\text{R.T.,2 min}\\ \text{0·5 A dm ,30 s}\end{matrix}$ shown in Fig 63. The latter was associated with an adhesion value of 21·6 KN m^{-1}. Fig 63b illustrates that a considerable amount of substrate was detached with the electroplate during peeling.

CHAPTER FOUR

4. DISCUSSION OF RESULTS

The first four sections of the discussion deal with the main areas of the work namely :

1. Effect of pretreatment prior to final M.A.Z. immersion.
2. Film growth from various zincate solutions.
3. Peel adhesion testing results.
4. Corrosion testing results.

Comparisons and relationships between the various aspects of the work are considered in the final section.

4.1. Effect of Pretreatment Prior to Final M.A.Z. Immersion

Each alloy type had a characteristic response to a specific pretreatment. This response depended upon their metallurgical state, i.e. whether alloying or impurity elements are finely dispersed in solid solution or present as intermetallic constituents. The properties of phases present at the surface of the alloys govern their chemical and electrochemical activities. With all the alloys, sequence I caused less attack of the surface than sequence II, Fig 9. The equivalent double-dip pretreatments, sequences III and IV respectively, produced even greater attack, Fig 10. This was partially due to the surface dissolution that occurred during formation of the first M.A.Z. film and partially due to the effects of etching. Hence the effect of the double-dip pretreatments was influenced by the nature of the first film deposited. The more substantial the first film, the more significant its effect on surface condition. It is claimed (104) that when the first film is removed by stripping in acid, the chemical activity of the freshly exposed surface is more uniform. Zinc immersion films having superior properties can then be deposited on this surface.

4.2. Film Growth from Various Zincate Solutions

When considering the growth of immersion deposits from S.Z. solutions, Bullough and Gardam (109) stated that the ideal zinc film is formed by the direct replacement of a monomolecular layer of aluminium atoms with a monomolecular layer of zinc atoms. Once a monomolecular or thin film of zinc has deposited further action should cease, advantage being taken of the higher hydrogen overvoltage of zinc. However, this postulated behaviour is not realized on heterogeneous alloys; features such as grain or phase boundaries and intermetallic compounds result in local differences in potential even after etching. Mechanical damage on the surface such as scratch lines and flowed layers which result in stressed regions remaining after the polishing operation, can also lead to the formation of a non-uniform zinc coating.

Typical conventional immersion M.A.Z. deposits were certainly thicker than monomolecular layers although uniform coverage was not always achieved in 2 min, particularly at the bottom of etch pits. Figs 11 and 12 show that nucleation and growth of the

M.A.Z. film was influenced by local surface variations in potential due to either compositional variations or mechanically induced stresses. The former of these effects is the more important. This confirms that mechanisms other than just a simple replacement reaction are involved in film growth. Once the oxide layer has dissolved from the aluminium surface it is likely there is an initial direct displacement of aluminium atoms by zinc atoms. The film formed at this stage would be porous and incomplete due to the surface variations discussed earlier. The establishment of anodic and cathodic areas and the resultant microcells created all over the surface provide the galvanic driving force responsible for the development of the film beyond monomolecular dimensions. The magnitude of the galvanic couple established varies from zone to zone and depends on the nature and source of the microcell established. Consequently, variations in film growth occur.

Alloy type and pretreatment influenced the growth rate, Figs 15 to 17, and morphology of the conventional immersion M.A.Z. film.

Single dip pretreatments resulted in coarse grained M.A.Z. deposits which exhibited relatively slow coverage though grew rapidly on all the alloys except X-7046. These films developed by the formation of certain rounded growth centres which probably grew from nuclei already present in the monomolecular layer, Fig 11. It is also evident that preferred sites for nucleation, such as around etch pits, exist on any surface. Fig 11a illustrates this effect on S1C after 5 s immersion; obviously the galvanic driving force varies in intensity across the surface. After prolonged immersion, growths develop over the remainder of the surface, Fig 13a. Larger galvanic couples can be formed on LM25 due to the presence of relatively large silicon platelets in the eutectic regions of the microstructure. These platelets represent significantly more cathodic zones than, for example, the centres of dendrites. The effect of this couple is reduced with distance so that preferential formation of growth centres occurred near the silicon platelets at an early stage, Fig 13b. Conversely, at regions more remote from the silicon platelets growth was concentrated on fewer sites and resulted in a coarser deposit. More uniform growth occurred on fully heat-treated LM25 which had a more homogeneous microstructure, Fig 26a. The mechanisms responsible for the type of film growth described are dynamic in nature, whereby sites which had previously been involved in the anodic reaction could become sites for the cathodic reaction later in the immersion period. This effect of microcells moving around on the surface provides an explanation of why growth forms do not appear simultaneously over the whole surface but initially at preferred sites. There will normally be a slight delay before the film starts to grow since a finite time is necessary for oxide dissolution. Even after pretreatment, it is unlikely that the oxide will be removed from all over the whole surface at the same instant, and so this effect may also have a slight influence on film growth. The growth centres do not develop to a definite size and then stop. After rapid initial growth they continue to grow at a slower rate so that eventually they spread and coalesce as illustrated in Figs 13a to 13c. The original growths tended to loose their individual identity as a more continuous deposit formed.

The M.A.Z. films formed following a double-dip pretreatment were finer grained and grew more slowly on all the alloys except X-7046. Films obtained on this alloy were coarse, slow growing and exhibited poor coverage, irrespective of pretreatment. Sequence IV caused excessive pitting of the other alloys and therefore film coverage was non-uniform, Figs 13d to 13e. The sequence III deposits were superior and apart from on LM25, rapidly covered the surface and were so thin, fine grained and uniform that they were almost featureless, Fig 14. This is consistent with film formation on a more uniform and less reactive surface as suggested by Korpium.(104) The M.A.Z. deposits achieved on LM25 using sequence III were not as satisfactory because due to the alloys extreme inhomogeneity, the pretreatment did not modify its surface condition to a sufficient extent.

Potential-time measurements also show the two different modes of M.A.Z. film formation outlined previously, namely,
(i) fast growing, coarse grained and providing poor coverage, and
(ii) slower growing, fine grained but giving rapid coverage.
The rate of change of surface potential appeared to be primarily determined by the rate of surface coverage with film. For example, the influence of the contrasting film coverage rates associated with S1C pretreated using sequences I and III is shown in Fig 18.

Potential measurements also illustrated why the tendency for M.A.Z. film growth was minimal on X-7046. The solution potential characteristics of aluminium are significantly affected by small additions of zinc. The potential of an oxide free X-7046 surface in M.A.Z. solution was much nearer to the potential of pure zinc than was the surface of S1C or LM25. The relatively high percentage of zinc present in X-7046 causes a significant reduction in the galvanic driving force between the alloy surface and zinc ions present in solution and therefore limited film growth occurs.

Table XVI illustrates the error of using potential data obtained in sodium chloride solution to explain the behaviour of aluminium alloys in M.A.Z. solution where different reactions take place.

The formulation of the zincate solution was also important. Both the D.S.Z. and C.S.Z. solutions yielded heavier deposits than the M.A.Z. solution, Fig 42. S.Z. film growth was also affected by alloy type and pretreatment, Figs 43 and 44. However when using a single dip sequence, S.Z. films were unlike M.A.Z. deposits in that they were prone to rapid non-uniform vertical dendritic growth at certain more active sites, Figs 40 and 41 respectively. The C.S.Z. solution was the most successful when the only aim was to produce a generally fine grained deposit using the simplest pretreatment. The film weight-immersion time curves for the C.S.Z. and M.A.Z. solutions were similar in shape. Both exhibited a considerable reduction in growth rate with time although actual film weights were different. However, the explanation of the characteristic levelling out of the curves was not the same for each solution. M.A.Z. solution is a complexed, modified version of a dilute solution in which restriction of film growth is achieved by the incorporation of copper and nickel into the growing surface. As the film developed, its composition changed which suggests that once a critical level of one or both of the above elements is reached, further growth is inhibited owing to the reduction in its potential with respect to the zinc in solution. This agrees with the work of Such and Wyszynski.(105,115) In contrast, the reduction of film growth rate in C.S.Z. solution is a diffusion controlled mechanism. Because of the concentrated nature of the C.S.Z. solution, during the early stages of immersion growth was very rapid due to the high concentration of zincate ions available. However, diffusion was severely limited by its high viscosity. Once the immersion solution adjacent to the aluminium surface became depleted of zinc ions (also enriched in dissolved aluminium) replenishment of zinc could only take place by slow diffusion from the bulk solution and this resulted in a slower rate of film growth. The D.S.Z. solution gave the coarsest grained deposits, the growth of which did not reduce with time. This was indicative of a very thick, porous type deposit which confirmed earlier work.(110,113-115)

Film growth from heated M.A.Z. solution had similar characteristics to that achieved using conventional immersion. The main objective of warming the M.A.Z. solution was to increase and improve film growth on X-7046. Unfortunately on this alloy the 50°C M.A.Z. deposits were unsatisfactory because they were coarse grained, grew relatively slowly, and gave poor coverage, Fig 49, irrespective of pretreatment. In contrast, film growth on S1C and LM25 was increased significantly by raising the temperature of the M.A.Z. solution and was sensitive to changes in pretreatment, Figs 50 and 51. On these two alloys, during the early stages of immersion the morphology of the 50°C M.A.Z. deposits was similar to that of films produced using an equivalent pretreatment but conventional

M.A.Z. immersion. However, as the growth rate of films from heated M.A.Z. solution did not slow down very much with time, thick, coarse grained deposits developed, Fig 46.

Formation of an M.A.Z. deposit involves dissolution of the aluminium substrate. This is illustrated in Fig 48, where development of a 2 min 50°C M.A.Z. deposit is shown to have caused extensive attack of an S1C surface.

The problems that can arise when operating an M.A.Z. bath without thermostatic temperature control are emphasised by Fig 53. It is feasible that seasonal temperature fluctuations can result in a variation of solution temperature over the range of 4°C to 20°C. Such a variation in solution temperature would be of little consequence when processing S1C and X-7046. If however LM25 was pretreated using sequence I, this same difference in temperature could result in over a one hundred percent change in film weight. In Fig 53, the shift to the right of the sequence III curve for S1C is another benefit of the double-dip technique. This is especially significant as it moves the most temperature sensitive portion of the curve out of the influence of any fluctuations in ambient temperature.

In spite of applying an external current, growth of the electrolytic M.A.Z. deposits was still influenced by the galvanic effect of the substrate which is responsible for film growth under conventional immersion conditions, Figs 54 and 55. For the solution operated at a particular current density, differences in shape of the film weight curves of the various alloys, Figs 58 to 60, are primarily due to variations of this galvanic driving force. It can also be seen there was a limiting maximum deposition rate from the M.A.Z. solution. Fig 57 shows the change in weight with time of M.A.Z. films deposited on S1C and brass at 1 A dm^{-2}. The latter has a negligible driving force for conventional film growth and therefore film deposition was solely due to the impressed external current. However, S1C has a significant inherent driving force and so the film weight curve represents the cumulative effect of deposition resulting from natural galvanic action and the superimposed current. As the deposit develops, the contribution to growth due to the effect of the S1C substrate reduces and eventually deposition is only due to the applied current.

For a specific alloy, if conventional film growth were affected by pretreatment the same would be true of the electrolytic M.A.Z. deposits. The nature of the substrate also influenced the morphology of the electrolytic M.A.Z. films. Using conventional immersion, limited film growth occurred on X-7046. This alloy had little effect on the growth characteristics of M.A.Z. films deposited electrolytically and fine grained, uniform deposits giving good coverage were achieved irrespective of pretreatment, Fig 56. This was the first technique developed that produced M.A.Z. films of satisfactory appearance on X-7046. In contrast, even after pretreatment using sequence III, LM25 retained such a strong tendency towards formation of a coarse grained deposit giving poor coverage that a relatively high imposed current density of 2·0 A dm^{-2} was needed to obtain a film exhibiting the preferred characteristics.

4.3. Peel Adhesion Tests

The adhesion between two different materials is determined by the extent of chemical bonding; (which involves the same molecular forces responsible for cohesion) and mechanical bonding due to interlocking, keying action.

Because of differences in the mechanical strengths of the alloys, it would be expected that differing percentages of 'perfect' adhesion between substrate and coating would be required to obtain the same overall measured level of adhesion. Where the force or bond between the electrodeposit and substrate is greater than the cohesive forces between the atoms of the substrate, the adhesion value would only depend on the mechanical properties of the substrate provided that the coating could withstand the peeling load involved. This corresponds to the 'ultimate' adhesion attainable.

Mathematical analysis of the peel test when used for determining the adhesion of electrodeposits to plastics (163) indicated that the resulting numerical reading was not a true measure of adhesion. It was claimed to be a measure of a complex of factors including the Young's modulus and tensile strength of the substrate and coating. Using the limited evidence available, it was believed that this study also applied to the peeling of electrodeposits from metal substrates.

As with all methods of measuring adhesion, the peel test has limitations and in the present work there was quite a scatter of peel results recorded even though precautions were taken to standardize test conditions. There were also problems encountered in reproducing peel results when changing from one batch of an alloy to another. This was however, due to subtle variations in the substrate material rather than being a problem associated with the peel test. A ductile Watts nickel coating was employed for the peel test while commercially a bright or semi-bright nickel layer would be applied for most decorative applications.(105) Therefore, as in the case of plated plastics,(164) it is a controversial matter whether the peel test is a realistic measure of adhesion in relation to service performance.

In this study a peel adhesion value $< 7{\cdot}5$ KN m^{-1} was deemed unsatisfactory. Adhesion levels quoted are specific to the method of peel testing used. Such and Wyszynski (105,115) obtained higher adhesion values using a spring balance and peeling by hand, although this would involve a much higher and also uncontrolled rate of peel. However using similar apparatus, Wittrock (33) claimed that an adhesion value of $5{\cdot}0$ KN m^{-1} was adequate.

Peel results obtained using the conventional M.A.Z. pretreatments are reported in Table XVII. A zinc-alloy immersion deposit was produced on the alloys even where zero adhesion resulted. This shows that the mere presence of an M.A.Z. deposit does not guarantee adhesion. The level of adhesion was affected by alloy type and pretreatment, single dip pretreatments giving satisfactory adhesion only on S1C. The advantage that can be obtained using the double-dip technique is demonstrated by sequence III since the same formulation alloy zincate solution was used in all instances. Sequence III proved the most flexible pretreatment route, resulting in the highest adhesion for all the alloys except X-7046. It should be emphasised that the results in Table XVII relate to a standard 2 min immersion time, since following a specific pretreatment, each alloy is likely to have a characteristic critical M.A.Z. immersion time for optimum adhesion. However sequence III also proved to be the pretreatment least sensitive to the effects of variation in final immersion time. S1C was clearly the easiest alloy to pretreat for successful plating while none of the four standard pretreatments resulted in adhesion to X-7046. X-7046 was also attacked by the plating solution if insufficiently protected by the immersion film. It is also apparent that the benefits of the double-dip technique may be negated if they are achieved at the expense of severe surface attack as associated with sequence IV.

While excessive etching is undesirable, a limited amount is useful since it removes surface layers weakened by polishing and furthermore pitting can improve adhesion due to increased mechanical keying. A certain minimum level of attack appears to be necessary if the immersion film produced is to have the characteristics required to result in acceptable adhesion. This is typified in Table XVII by sequences I and II which resulted in significant adhesion only on S1C and NS4, these being the two alloys most etched by these pretreatments prior to M.A.Z. immersion.

It was surprising that sequences II and IV, which incorporated the HF containing etch, did not give better results for LM25 as most sources (138,139) recommend the use of HF-containing etches for the pretreatment of aluminium-silicon casting alloys. The present results indicate that the double-dip version of the pretreatment utilizing the 50% HNO_3 etch (sequence III) was most successful. It may be that the use of a lower concentration of HF, resulting in a less aggressive etchant, would give improved results as it seems reasonable to assume that some attack of the silicon plates would be desirable.

Post-plating heat-treatment improved adhesion where pretreatment alone had not resulted in the ultimate value, Table XVIII. In most circumstances however, the extra cost involved in this operation would prohibit its utilization. Excessive heat-treatment can result in the formation of a thick, weak intermetallic layer that would have a detrimental effect on adhesion.

The heat-treated condition of LM25 had a considerable effect on the peel adhesion adhieved using a specific pretreatment, Table XX. Much higher adhesion was obtained on LM25 in the fully heat-treated and therefore microstructurally more homogeneous condition, than in the as-cast state.

When the alloys were processed using D.S.Z. and C.S.Z. solutions, zero electrodeposit adhesion was obtained irrespective of pretreatment route. This emphasises the superiority of the M.A.Z. type pretreatment and agrees with the work of Such and Wyszynski.(105,116)

A protective copper or brass strike is usually electrodeposited over S.Z. deposits before final plating, but this is normally unnecessary with M.A.Z. deposits. In this investigation the Watts nickel electroplate was always applied directly on to the immersion layer.

The M.A.Z. solution was used at 50°C and also operated electrolytically in an attempt to obtain adhesion on X-7046. The appropriate peel adhesion values are shown in Tables XXI to XXV. Immersion times were adjusted to allow for the increased rates of film formation. As with conventional M.A.Z. immersion, the double-dip technique proved most advantageous. Only the double-dip versions of both electrolytic and elevated temperature M.A.Z. pretreatments produced adhesion on the alloys considered. The use of either of these variations of M.A.Z. pretreatment is only justifiable when the improvements in adhesion attained are essential or when it provides the only means of achieving adhesion on a specific alloy. Therefore although sequence III in conjunction with both electrolytic and 50°C M.A.Z. films gave adhesion on S1C of the same order as achieved using conventional immersion, Tables XXI and XXIII, this is of no commercial advantage. However for LM25, use of sequence III in conjunction with 50°C M.A.Z. deposits resulted in an improvement in adhesion, Table XXI.

Although the levels of adhesion achieved using sequence IV in conjunction with 50°C M.A.Z. immersion were not of an acceptable standard, this procedure resulted in the first example of adhesion on X-7046, Table XXII. Slightly higher adhesion was achieved on this alloy using 0·5 A dm^{-2} M.A.Z. deposition and sequence IV, Table XXIV. Table XXV indicates that when the duration of the first dip was increased from the usual 2 min to 6 min, sequence IV in conjunction with 0·5 A dm^{-2} M.A.Z. deposits produced adhesion in excess of 7·5 KN m^{-1} on X-7046. Extending the duration of the first dip ensured the formation of a more substantial first film which had a significant influence on the overall effectiveness of the pretreatment. This is also an example of a situation where the nature of the pretreatment required to achieve satisfactory adhesion causes excessive attack and surface weakening and therefore limits the maximum adhesion attainable. For the other alloys, sequence IV was always avoided.

Visual examination of the failure surfaces following peel testing illustrated that peel adhesion values cannot always be considered in isolation. This is illustrated in Tables XXI and XXIII which relate to sequence III used in conjunction with 50°C and 1·0 A dm^{-2} M.A.Z. immersion. Satisfactory mean peel adhesion values were obtained for S1C even when the failure surfaces were non-uniform and unacceptable. For the 50°C M.A.Z. sequence III pretreatment, this was due to the effect of using non-optimum immersion times. For the 1·0 A dm^{-2} M.A.Z. sequence III pretreatment, this phenomenon was independent of immersion time, referred to as the 'snake-skin adhesion effect' and did not occur when the M.A.Z. solution was operated at 0·5 A dm^{-2}. When the M.A.Z. solution was used conventionally no such complications were encountered.

S.E.M. examination revealed that failure surface characteristics are influenced by adhesion level, alloy type and pretreatment. Even when adhesion was very low, Fig 23, a slight amount of substrate was pulled off with the electroplate during peeling. For a specific alloy, an improvement in adhesion was associated with an increase in the amount of substrate detached on the peeled foil. For example, the post-plating heat-treatment for 1·5 h at 230°C of HE9, pretreated using sequence III and conventional M.A.Z. immersion, resulted in an improvement in adhesion, Table XVIII. This was accompanied by a transition from failure at the substrate surface to failure within the substrate. The mechanism of failure also depends on the nature of the alloy substrate. For example, the cup-and-cone type failure exhibited by S1C is indicative of a ductile substrate, Fig 21. LM25 is considerably less ductile and consequently failed in a manner characteristic of a more brittle material, Fig 22. Additionally the silicon platelets present on the LM25 surface also influence the maximum adhesion attainable since the electroplate will not bond as well in such regions.

Although it might be anticipated that higher peel adhesion levels would be associated with the higher strength alloys, this was not found to be so. It is assumed that maximum adhesion was achieved on alloys S1C and HE9, giving values of approximately 24 KN m^{-1} and 19 KN m^{-1} respectively, since in both cases failure occurred entirely within the alloy substrate. However, the minimum tensile strength of HE9 is more than twice that of S1C, Table XI. Although it has the lowest mechanical strength of all the alloys plated, the highest adhesion recorded during this investigation was that achieved on S1C. This corresponded to the ultimate peel adhesion on S1C and agrees with the value quoted by Wittrock and Swanson.(141)

4.4. Corrosion Tests

The results of C.A.S.S. testing, Figs 27 to 29, show that the corrosion resistance of the plated aluminium alloys, pretreated using conventional M.A.Z. immersion deposits, depended upon the particular pretreatment sequence employed. For the three alloys and three coating systems considered; the single dip pretreatment, sequence I, was associated with the worst corrosion behaviour while the double-dip pretreatments, sequences III and IV, resulted in improved corrosion performance. For instance, the requirements of service condition 3 given in B.S. 1224 : 1970 (146) were only satisfied for all the alloys and coating systems tested, when sequences III and IV were utilized. C.A.S.S. test results indicate that providing a suitable M.A.Z. pretreatment was used, the plated aluminium alloys exhibited good corrosion performance. Many of the plated panels shown in Figs 30 to 32, still had a rating of 8 or above even after 5 C.A.S.S. cycles.

Previous investigations (111,142,143) have indicated that plated aluminium alloys pretreated using S.Z. immersion films performed badly in corrosion tests. This was claimed to be due to preferential attack of the S.Z. layer. It is most significant that this study revealed that no preferential attack of the M.A.Z. layer occurred. For example, in Fig 34 although extensive undercutting and attack of the aluminium alloy substrate is evident, there is no sign of lateral corrosion of the M.A.Z. interply. Where an alloy was not satisfactorily pretreated and the coating had no adhesion, once the plated layer was penetrated there was rapid attack along the substrate-electroplate interface, Fig 37. It is possible that previous investigations have mistakenly interpreted this as preferential attack of the immersion layer.

Earlier studies (105,115) suggested that alloy type had little influence on the corrosion resistance of plated aluminium. This was not confirmed by the results presented here. For any pretreatment or coating system, S1C exhibited the best corrosion behaviour while plated LM25 generally appeared more susceptible to corrosive attack.

The coating system employed also proved to have an important effect on corrosion performance. The two microporous chromium systems gave better corrosion protection than the decorative chromium coating. The decorative chromium plated panels suffered from the formation of catastrophic corrosion sites at the earliest stage in corrosion testing. The use of microdiscontinuous chromium overlays and their influence on corrosion has been discussed by several authors.(165-167) Penetration through to the substrate and onset of severe pitting were delayed longest by the thicker microporous chromium coating. The high level of reflectivity of the chromium layer was also retained longest by the thicker microporous chromium which agrees with the work of Carter.(168) The two different thicknesses of microporous chromium also exhibited differing corrosion morphology. With the thin 0·25 µm microporous chromium, corrosion occurred at micropore sites and resulted in the formation of characteristic 'crows-foot' type cracks, Fig 35, which had a typical crack length of between 25 µm and 100 µm. However, samples plated with the thicker 0·5 µm microporous chromium failed by a different mechanism. Corrosion products were visible along crack patterns in the chromium, Fig 38, and only very few, much smaller micropore corrosion sites of the order of 10 µm diameter developed, Fig 39. The higher levels of stress in the thicker microporous chromium deposit were the most likely cause of the cracking. Hence the thick microporous chromium had characteristics similar to that of a microcracked deposit but with some of the properties of a microporous coating. The combined effect of the two types of discontinuity may be the reason why this system afforded slightly better corrosion protection than the thinner microporous chromium system.

4.5. General Considerations

With conventional immersion, the tendency for film growth from M.A.Z. solution is governed by the magnitude of the inherent galvanic driving force of the aluminium alloy surface following pretreatment. Dependent on metallurgical condition, each alloy had its own individual response to any specific pretreatment. Aluminium dissolution occurs during M.A.Z. film formation.

Using the M.A.Z. solution warm or operated electrolytically, permitted the rate of film formation to be increased. The extent of this increase depended on operating conditions, solution characteristics determined by the formulation, and also alloy type and pretreatment employed. When using only mild agitation it was found that for satisfactory results, the M.A.Z. solution should not be operated much above 0·5 A dm^{-2}. Departure from conventional M.A.Z. pretreatment would only be undertaken when essential.

This investigation indicates that the growth tendencies and characteristics of conventional immersion, elevated temperature and electrolytic M.A.Z. deposits are determined by alloy type and pretreatment sequence employed.

Satisfactory peel adhesion exceeding 7·5 KN m^{-1} was attained on all the alloys studied using one or other variation of the M.A.Z. type pretreatment. While S1C proved the easiest alloy to pretreat for successful plating, X-7046 was most difficult.

Although a single universally applicable pretreatment for all the alloys would be preferred, because of the different responses exhibited by the various alloys to identical pretreatments it seems unlikely that such a process sequence will be found. The modifications to the conventional M.A.Z. pretreatment technique discussed here are practical and could easily be utilized by a commercial plater already using the ordinary immersion process. Electrolytic operation of the M.A.Z. solution is a significant departure from conventional immersion but was essential for X-7046 due to the nature of this alloy. This is because when only simply immersed in M.A.Z. solution, the conditions which are established on the X-7046 surface do not favour satisfactory film growth.

Superior adhesion is associated with a uniform, thin, fine grained type M.A.Z. deposit which exhibits rapid coverage. The presence of a film is certainly not the only criterion to promote good adhesion of electrodeposited coatings. For example, where the chemical bonding between the film and substrate is poor, the film is too thick and mechanically weak or does not exhibit effective surface coverage, low adhesion results. The latter is especially relevant with X-7046 which if not sufficiently protected by the M.A.Z. deposit, is attacked by Watts nickel plating solution. Adhesion is also influenced by properties of the M.A.Z. film such as degree of epitaxy with the substrate,(109) structure, composition, nucleation characteristics and suitability for overplating with a particular electrodeposit. Although Lashmore(130,131) established that S.Z. immersion films grow epitaxially on aluminium alloy substrates, the levels of electroplate adhesion associated with such deposits were not determined. In contrast to the zinc-alloy M.A.Z. deposits, in the present work direct plating on to the pure zinc S.Z. deposits always resulted in zero adhesion. Using conventional immersion, the S.Z. solutions yielded thicker, faster growing films than M.A.Z. solution. The apparent advantages of the finer type of growth achieved with the C.S.Z. solution are negated by other characteristics of the deposit which were less satisfactory than those produced using M.A.Z. solution.

The advantages of the double-dip technique were confirmed. The highest levels of adhesion were obtained using double-dip type pretreatments and for all the alloys except S1C and NS4, provided the only means of achieving satisfactory adhesion. It was found that the formation of the first film causes a selective 'conditioning' or 'etching' of the surface which influences the overall effectiveness of the pretreatment. This effect could not be simulated by simply increasing the duration of the acid etch. For example, when using sequence III in conjunction with conventional immersion in M.A.Z. solution, removal of the first film exposed a more uniform and less reactive surface upon which a subsequent film exhibiting improved characteristics grew. The only exception to this was X-7046, because the effect of the first immersion was so slight. On X-7046, conventional immersion M.A.Z. deposits were slow growing and unsatisfactory irrespective of pretreatment sequence employed.

Even if the M.A.Z. film is of the preferred type, it is important that the surface on which it develops is sufficiently etched. For instance, preferred type deposits were only produced on X-7046, irrespective of pretreatment sequence employed, when the M.A.Z. solution was operated electrolytically. However, adhesion was only achieved when the pretreatment which caused the greatest degree of etching, namely sequence IV, was utilized.

Over-etching is also undesirable. When using conventional immersion, elevated temperature or electrolytic M.A.Z. deposits, of the double-dip type pretreatments, sequence III rather than sequence IV was preferred for all the alloys except X-7046 because of the excessive attack associated with the latter.

For any combination of alloy and suitable pretreatment an optimum film weight per unit area and actual film thickness will exist. For practical reasons, the former of these is the most useful term and also easiest to evaluate. The maximum adhesion recorded on any of the alloys was achieved on S1C pretreated using sequence III and conventional M.A.Z. immersion. A preferred type film was produced and a film weight of $0{\cdot}060 \pm 0{\cdot}010$ mg cm^{-2}, which corresponded to an immersion time of 100 ± 30 s, resulted in ultimate adhesion. It can be postulated that if these characteristics were reproduced on other alloys by altering the pretreatment route or more simply the immersion time, superior adhesion values should be attained. However, in practice, with alloys metallurgically dissimilar from S1C it was often found that poor adhesion occurred even when the conditions specified above were achieved. Consequently, there was a fundamental error in this supposition. Curves of film weight versus immersion time do not directly relate to film thickness because of the significance of growth type and actual rate of surface coverage. In addition the 'true surface area' after pretreatment can be much greater than the simple geometric area, depending on the alloy and pretreatment sequence employed; for example the 'true surface area' of S1C pretreated using sequence III is much less than when pretreated using sequence IV. Therefore, film weight versus immersion time curves should be interpreted with caution and allowances made when selecting immersion times to give the preferred film thickness in order to achieve good adhesion. A pretreatment that involves immersion times either of very short duration or critical to within a few seconds would however be of little use in practical terms.

Alloy type and pretreatment influenced the level of peel adhesion, and these all affected the nature of the associated failure surfaces. Ultimate adhesion, which corresponded to rupture within the alloy substrate during peeling was achieved on the alloys S1C, NS4 and HE9. However the highest of these values, approximately 24 KN m^{-1}, was that for S1C, the alloy having the lowest rather than highest tensile strength. This is a surprising phenomenon and an indication of the complex factors involved in the peeling operation and adhesion mechanisms.

The results of C.A.S.S. testing show that the corrosion resistance of plated aluminium depends on the alloy type and the pretreatment sequence and coating system employed.

Using conventional M.A.Z. immersion , the double-dip pretreatments, sequences III and IV, resulted in superior corrosion results. The single dip pretreatments were generally associated with poor corrosion performance, sequence I being worse than sequence II in this respect.

Comparison of peel adhesion and corrosion testing results indicates that a certain threshold value of adhesion exists, above which the rate of corrosion is considerably reduced. This threshold value corresponded to a Watts nickel peel adhesion value of the order of 1 KN m^{-1}, very low considering the high levels of adhesion possible on some of the alloys. Although adhesion in excess of this value does not result in a dramatic improvement in corrosion performance, it is certainly likely that a component would require high levels of adhesion to withstand the deformation experienced in service environments.

The use of microporous chromium overlays resulted in superior corrosion resistance to decorative chromium. Decorative chromium overlays on any substrate would be expected to exhibit unsatisfactory performance in outdoor service as they are not listed for severe conditions in B.S. 1224 : 1970.(146) Increasing the thickness of the microporous chromium layer from 0·25 μm to 0·5 μm delayed surface dulling and penetration through to the substrate. The excellent corrosion resistance afforded by the microporous chromium deposits was not unexpected, since the virtues of this type of coating are well known. By providing numerous potential sites for corrosion, the corrosion current is effectively reduced and the intensity of attack at each site is less severe. Hence penetration to the underlying layers and substrate is retarded. However severe corrosion results, irrespective of which chromium coating system is employed, if the pretreatment does not produce adhesion above the threshold value. In such instances, once the plated coating is penetrated it is rapidly undermined and the voluminous aluminium corrosion products formed cause blistering and lifting of the plating from the substrate.

The corrosion behaviour of the plated aluminium alloys, satisfactorily M.A.Z. pretreated, was excellent. Even with the thicker films obtained using single dip pretreatments, there was no preferential attack of the M.A.Z. layer. This indicates that any scepticism concerning limitations in corrosion performance associated with the M.A.Z. process are unwarranted.

CHAPTER FIVE

5. CONCLUSIONS

1. The advantages of the modified alloy zincate (M.A.Z.) type solution in comparison with dilute and concentrated simple zincate formulations were confirmed, particularly with respect to peel adhesion.

2. Satisfactory peel adhesion in excess of 7·5 KN m^{-1} was attained on all the aluminium alloys using pretreatments which utilized either conventional immersion, elevated temperature or electrolytic M.A.Z. deposits. Each alloy had an individual response to a particular pretreatment. S1C was the easiest alloy on which to achieve high bond strength. Elevated temperature M.A.Z. deposits proved to be of no advantage except for LM25. For the 'difficult' alloy X-7046, acceptable levels of adhesion were only achieved when the M.A.Z. solution was operated electrolytically. The highest mean peel adhesion value obtained on X-7046 was 12·4 KN m^{-1}. This was achieved using pretreatment sequence IV with a 6 min 0·5 A dm^{-2} electrolytic first immersion and 1 min 0·5 A dm^{-2} electrolytic second immersion in room temperature M.A.Z. solution.

3. The growth characteristics of the various types of M.A.Z. deposit were influenced by the alloy type and pretreatment sequence used. Superior adhesion was associated with a uniform,

thin, fine grained type M.A.Z. film which exhibited rapid and complete surface coverage. The presence of this type of deposit did not always ensure good adhesion. A certain degree of surface dissolution was also important although over-etching was undesirable.

4. The advantages of the double-dip technique have been confirmed. Using either conventional immersion, elevated temperature or electrolytic M.A.Z. deposits, sequence III was the most versatile pretreatment route. Sequence III resulted in the highest levels of peel adhesion achieved on all the alloys except X-7046, where zero adhesion was attained. Double-dip pretreatments were not always necessary and may even give lower adhesion than the single dip equivalents, e.g. using conventional M.A.Z. immersion, sequence IV gave lower adhesion than sequence II for S1C and NS4.

5. For any combination of alloy and suitable M.A.Z. pretreatment there was an optimum film weight per unit area. On S1C, using conventional M.A.Z. immersion, a film weight of $0{\cdot}06 \pm 0{\cdot}01$ mg cm^{-2} (obtained using sequence III, immersion time 100 ± 30 s) gave maximum adhesion. However, this film weight per unit area was not successful on all the alloys. Allowance must be made for 'true surface area', which was dependent upon the degree of etching resulting from the pretreatment sequence employed.

6. In view of results published previously,(138,139) the HF-containing etch did not give such high adhesion levels as expected on LM25, the silicon-containing casting alloy.

7. The level of peel adhesion was influenced by alloy type and pretreatment. Peel adhesion was not directly related to tensile strength, e.g. the highest ultimate adhesion value, approximately 24 KN m^{-1}, was achieved on S1C, the lowest strength alloy studied. The type of alloy, pretreatment and the adhesion level attained affected the appearance of the failure surfaces after peeling.

8. The corrosion resistance of the plated aluminium alloys, when suitably pretreated, was excellent and there was no preferential attack of the M.A.Z. layer. Corrosion resistance depended on alloy type, pretreatment and coating system. As on other basis metals, the best corrosion results were obtained when using a microporous chromium rather than decorative chromium overlay.

9. Peel strength much less than ultimate was adequate for good corrosion performance. There was no direct correlation between corrosion resistance and peel adhesion, although a certain minimum amount of adhesion was required. This threshold value of peel adhesion, below which corrosion performance was unsatisfactory, was approximately 1 KN m^{-1}.

10. The present work illustrates the reasons why it has not been possible for commercial electroplaters to develop a 'universal process schedule' for the plating of all aluminium alloys. Each alloy type was shown to have a characteristic response to a specific pretreatment and the importance of

selecting the correct processing sequence was demonstrated. The choice of alloy, pretreatment and electrodeposited coating must all be considered in relation to the service environment to be encountered by the plated component.

SUGGESTIONS FOR FURTHER WORK

1. In view of the results obtained on the various aluminium alloys chosen, it would be worthwhile studying the behaviour of other alloys, in particular those containing copper.

2. To achieve a more universally applicable pretreatment, other acid etch solutions should be evaluated. Since the 5% HF-containing etch employed was too aggressive for some alloys, it could prove useful to investigate the effect of lower HF-concentrations.

3. Operating the modified alloy zincate (M.A.Z.) solution electrolytically provided the only means of attaining good adhesion on X-7046. However, because this solution was only formulated for use as a conventional immersion bath, further work should be undertaken to develop a solution specifically for electrolytic operation.

4. Although much work has been carried out using the peel test and the associated failure surfaces examined, it is still difficult to completely understand the fundamental mechanisms connected with good peel adhesion. Therefore a much more detailed investigation concerning the various aspects of the peel test is required.

5. In view of the inconsistencies and limitations of the peel test, it is questionable whether peel results give a good indication of behaviour in service. Other tests should be evaluated, e.g. thermal cycling, to determine the method of testing which gives the best correlation with actual service performance.

6. The peel testing reported here involved using a Watts nickel deposit. It would be interesting to investigate the corrosion performance of various chromium coating systems in conjunction with a Watts nickel layer applied directly on to the M.A.Z. layer. This would give a more direct indication of the relationship between corrosion performance and the results of peel testing. However, this would not be of great significance since coating systems incorporating Watts nickel are not used commercially.

7. Conclusions concerning corrosion performance given in this study were derived from the results of C.A.S.S. testing. However, accelerated corrosion tests do not always give a realistic indication of service performance. A programme of static and mobile atmospheric exposure tests should be initiated.

8. Using transmission electron microscopy and electron diffraction techniques, Lashmore (130,131) found that simple zincate (S.Z.) deposits grew epitaxially on aluminium alloy substrates. However, while Lashmore did not perform adhesion tests, the

present work indicates that S.Z. pretreatments consistently resulted in zero adhesion. Therefore the work carried out by Lashmore should be repeated for both S.Z. and M.A.Z. deposits, in conjunction with an adhesion testing programme, to investigate the relationship between epitaxial film growth and subsequent adhesion of electrodeposits.

9. The initial stages of growth of the M.A.Z. deposit could be studied by Auger Spectroscopy. This would show how the composition of the film changes as it develops and whether it varies on different aluminium alloys.

10. The performance of plated aluminium alloys, pretreated using the M.A.Z. and stannate processes, could be compared. The latter is the most important alternative processing technique and is claimed to be used extensively in the U.S.A. It would be interesting to study the stannate type pretreatment since it is claimed (3) that the tin immersion film produced is discontinuous and exhibits only limited growth.

ACKNOWLEDGMENTS

The author wishes to thank his supervisor Dr.J.K.Dennis for his help and guidance throughout the course of this research work. The author also wishes to acknowledge the financial support provided by the Science and Engineering Research Council (C.A.S.E. award) and to thank W.Canning Materials Ltd., and in particular Mr.A.E.Wyszynski and Mr.T.E.Such, for supporting this research. The author is also grateful to Dr.E.Silverstone and the other members of the academic and technical staff of the Department of Metallurgy and Materials Engineering of the University of Aston in Birmingham, for their constant support throughout this project. Finally, thanks must also go to Miss Susan Lewnes for typing this thesis.

REFERENCES

1. Q.Marino, Brass World, 1913, 9, 29.
2. E.G.West, J.Electrodep. Tech. Soc., 1946, 21, 211.
3. J.C.Jongkind, Trans. Inst. Met. Fin., 1967, 45, 155.
4. H.K.Work, Trans. Electrochem. Soc., 1931, 60, 117.
5. R.Fyfe, Metal Industry, 1950, 77, 300.
6. A.W.Wallbank, J.Electrodep. Tech. Soc., 1952, 28, 209.
7. R.Ore, Bull. Inst. Met. Fin., 1953, 3, No 3, 163.
8. Gauduin, Fignon and Rouart, French Pat. 97,030 (1872).
9. J.T.N.Atkinson, J.Electrochem. Soc., 1958, 105, No 1, 27.
10. Y.Lukomskii, S.Lamina and I.Grigoreva, Zashchita Metallov., 1968, 4, No 3, 326.
11. N.A.Solov'ev, U.S.S.R. Pat. 252,806 (10.1.1966) (22.9.1969).
12. J.T.N.Atkinson, Canadian Pat. 590,840 (1960), U.S.Pat. 3,003,933 (1961).
13. J.T.N.Atkinson, Plating, 1960, 47, No 5, 509.
14. H.K.Work and C.J.Slunder, Trans. Electrochem. Soc., 1931, 59, 429.
15. Y.R.Schaer, W.D.MacLean, C.L.Faust, K.C.Graham and J.G.Beach, French Pats. 1,260,250 and 1,260,256 (1961), Brit.Pats. 877,385-6 (1961).
16. C.L.Faust, G.R.Schaer and D.E.Semones, Plating, 1961, 48, No 6, 605.
17. Eisen-u, Metalldienst. (Vienna), 1959, No 25, 8.
18. R.Ore, J.Electrodep. Tech. Soc., 1953, 29, 97.
19. J.Edwards and C.J.Swanson, Trans. Inst. Met. Fin., 1953, 29, 190.
20. B.C.Schwartz and J.B.Newkirk, Plating 1972, 59, No 5, 431.
21. W.Hume-Rothery, 'Electrons, atoms, metals and alloys', 3rd Ed., Dover Publications, U.K., 1963.
22. D.S.Lashmore, Plat. and Surf. Fin., 1978, 65, No 4, 44.
23. Brit. Pat. 290,903.

24. Siemens and Halske A.G., Brit. Pat. 385,067 (1933).

25. Siemens and Halske A.G., Brit. Pat. 404,251 (1934).

26. Siemens and Halske A.G., Brit. Pat. 394,637 (1933).

27. W.J.Travers, U.S. Pat. 971,761 (1934).

28. Siemens and Halske A.G., U.S. Pat. 1,036,962 (1936).

29. Bell Telephone Laboratories Inc., U.S. Pat. 2,430,468 (1947).

30. Anon. Aluminium, 1937, <u>19</u>, No 6, 381.

31. W.J.Travers, Trans. Amer. Electrochem. Soc., 1939, <u>75</u>, 201.

32. W.J.Travers, Proc. Amer. Electroplaters Soc., 1942, <u>29</u>, 119.

33. H.J.Wittrock, Tech. Proc. Amer. Electroplaters Soc., 1961, <u>48</u>, 52.

34. H.J.Wittrock, 'Finishing of Aluminium', Reinhold Publ. Corp., New York, U.S.A., 1963.

35. H.J.Wittrock, Kaiser Aluminium Co., U.S. Pat. 3,098,804 (28.3.1960) (23.7.1963).

36. Aluminium, 1937, <u>19</u>, No 6, 381.

37. B.E.Bunce, Electroplating and Met. Fin., 1953, <u>6</u>, No 9, 317.

38. H.Bengston, Trans. Electrochem. Soc., 1945, <u>88</u>, 307.

39. Aluminium Co. of America, 'Electroplating of Aluminium and its Alloys ', 1946.

40. R.C.Spooner and D.Seraphim, Trans. Inst. Met. Fin., 1954, <u>31</u>, 29.

41. Ya.I.Aleksandrov, F.A.Azovskii, D.D.Evseeva and A.I.Sverdlov, Zashchita Metallov., 1969, <u>5</u>, No 3, 281.

42. D.W.Levinson and L.F.Mondolfo, Plating 1966, <u>53</u>, No 8, 986.

43. G.Eckert, Metallwaren Industrie und Galvano Technik, 1932, <u>30</u>, 81.

44. B.K.Braund and H.Sutton, J.Electrodep. Tech. Soc., 1936, <u>11</u>, 57.

45. H.J.Work, J.Electrodep. Tech. Soc., 1933, <u>8</u>, No 7, 1.

46. T.C.DuMond, Materials and Methods, 1950, <u>32</u>, 56.

47. E.Meyer-Rassler, Metall, 1952, <u>6</u>, No 17/18, 504.

48. H.K.Work, Trans. Electrochem. Soc., 1928, <u>53</u>, 361.

49. J.M.Bryan, Metal Industry, 1953, 83, No 23, 461 and No 25, 302.

50. General Development Corp. D.A.S. 1,226,392 (6.10.1966).

51. J.Nat. Metall. Lab. Jamshedpur, 1961, 1, No 3, 37.

52. D.S.Tandem and J.Banerjee, Indian Inst. Met. Dec., 1957; Indian Pats 51,524 and 53,358 (1956).

53. Dr.Finkh GmbH, Brit. Pat. 465,078 (1937).

54. K.Gebauer, Korrosion u. Metallschutz, 1941, 17, 276.

55. A.Beerwald, Aluminium, 1941, 23, 148.

56. T.C.Withers and P.E.Ritt, Metal Finishing, 1958, 56, No 1, 53.

57. M.Kishi, J.Metal Finishing Soc. Japan, 1959, 10, No 6, 215; No 8, 293; No 11, 408 and No 12, 450.

58. M.P.Melkov, V.A.Babenko and A.M.Pashennykh, U.S.S.R. Pat. 165,627 (20.4.1963)

59. L.J.V.Lobo, P.S.Kinnerkar, G.M.Ganu and W.L.Roy, Electroplating and Met. Fin., 1969, 22, No 9, 21.

60. S.Heiman, J.Electrochem. Soc., 1949, 95, 205.

61. L.Perner, U.S.Pat. 2,297,241 (1942).

62. 'ALCOA 661 Process Electroplating Pretreatment for Aluminium' , Alcoa internal report (6.22.1976).

63. W.P.Kampert, U.S.Pat. 3,989,606 (1976).

64. G.H.Poll, Products Finishing, 1970, Oct, 60.

65. M.Brown, V.Schuberg and G.Dell, Automotive Ind., 1936, 75, 884.

66. E.Finnie, Product Finishing, 1942, 6, 42.

67. Aluminium Co. of America, U.S.Pat. 2,337,606 (1945).

68. C.T.Suchy, Light Metals Res., 1948, 9, 415.

69. C.T.Suchy, Brit. Pat. 601,825 (1948).

70. O.Kramer, Metal Industry, 1945, 66, 121.

71. A.E.R. (1938) Ltd., Brit. Pat. 597,443 (26.1.1948).

72. R.W.Thomas and E.D.Swann, 1950, Unpublished work.

73. H.R.Watson and A.T.Ward, Brit. Pat. 626,693 (20.7.1949).

74. W.E.Hoare, 'Immersion Tinning of Aluminium', Tin Research Institute Memorandum DF 225, 1945.

75. D.E.Weimer and J.W.Price, Trans. Inst. Met. Fin., 1954, 30, 95.

76. Yu.Yu.Matulis, Russian Pat. 265,652 (14.10.1968) (9.3.1970).

77. P.Morriset, J.W.Oswald, C.R.Draper and R.Pinner 'Chromium Plating', Robert Draper Ltd., U.K., 1954.

78. J.D.Greenwood, 'Hard Chromium Plating', Robert Draper Ltd., U.K., 1964.

79. Philadelphia Rust Proof Co., U.S. Pat. 2,624,684 (1953).

80. J.C.Jongkind, Plating and Surf. Fin., 1975, 62, No 12, 1135.

81. J.C.Jongkind and L.P.Gowman, French Pat. 1,398,605 (1965).

82. L.P.Gowman and J.C.Jongkind, Canadian Pat. 811,131 (1969).

83. J.C.Jongkind and L.P.Gowman, German Pat. 1,496,899 (1964).

84. E.J.Seyb, J.C.Jongkind and L.P.Gowman, Proc. Amer. Electroplaters Soc., 1964, 51, 133.

85. J.C.Jongkind and P.G.Kenedi, U.S.Pat. 3,274,021 (1966).

86. M and T Chemicals Ltd., U.S. Pat. 3,274,021 (20.9.1966).

87. M and T Chemicals Ltd., U.S. Pat. 3,338,725 (29.8.1967).

88. M and T Chemicals Ltd., Brit. Pat. 1,080,291 (4.8.1964).

89. M and T Chemicals Ltd., Brit. Pat. 1,087,054 (29.9.1964).

90. M and T Chemicals Ltd., Brit. Pat. 1,109,676 (7.5.1965).

91. M and T Chemicals Ltd., Brit. Pat. 1,110,412 (22.4.1965).

92. M and T Chemicals Ltd., Brit. Pat. 1,100,770 (13.5.1965).

93. S.J.Beyer, Plating, 1969, 56, 257.

94. P.Matlow, J.Electrochem. Soc., 1961, 108, No 7, 709.

95. N.S.Tsvetkov and O.S.Zarechnyuk, Zhur. Priklad. Khim., 1960, 33, No 3, 636.

96. Sperry Rand Ltd., Brit. Pat. 1,141,131 (1.5.1967) (5.2.1969).

97. R.V.Vanden Berg, Trans. Inst. Met. Fin., 1967, 45, No 4, 161.

98. Ministry of Supply, Brit. Pat. 615,925 (1949).

99. E.H.Hewitson, U.S. Pat. 1,627,900 (1927).

100. K.Altsmannsberger, Chemiker-Zeitung, 1931, 55, 709; 1932, 56, 247.

101. G.Elssner, Aluminium, 1935, 17, 376.

102. B.K.Braund and H.Sutton, Trans. Faraday Soc., 1935, 31, 1595.

103. V.I.Lainer and S.I.Orlova, Legkie Metall, 1936, 5, No 2, 22.

104. J.Korpium, U.S. Pat. 2,142,564 (1939).

105. T.E.Such and A.E.Wyszynski, Plating, 1965, 52, 1027.

106. W.R.Meyer, Proc. Amer. Electroplaters Soc., 1946, 33, 269.

107. W.R.Meyer and S.H.Brown, Proc. Amer. Electroplaters Soc., 1949, 36, 163.

108. R.A.Ehrhardt and J.M.Guthrie, Proc. Amer. Electroplaters Soc., 1946, 33, 269; 1947, 34, 421.

109. W.Bullough and G.E.Gardam, J.Electrodep. Tech. Soc., 1947, 22, 169.

110. F.Keller and W.G.Zelley, J.Electrochem. Soc., 1950, 96, 143.

111. F.Keller and W.G.Zelley, Proc. Amer. Electroplaters Soc., 1949, 36, 149.

112. W.G.Zelley, J.Electrochem. Soc., 1953, 100, 328.

113. G.L.J.Bailey, J.Electrodep. Tech. Soc., 1951, 27, 233.

114. E.B.Saubestre and J.L.Morico, Plating, 1966, 53, No 7, 899.

115. A.E.Wyszynski, Trans. Inst. Met. Fin., 1967, 45, 147.

116. A.E.Wyszynski, The Engineer, 1967, 223, 135.

117. F.Passal, U.S. Pat. 2,662,054 (1953).

118. J.Patrie, U.S. Pat. 2,745,799 (1956).

119. W.Zelley, U.S. Pat. 2,676,916 (1954).

120. J.Korpium, U.S. Pat. 2,418,265 (1947).

121. J.K.Dennis and T.E.Such, 'Nickel and Chromium Plating', Newnes-Butterworths, U.K. 1972.

122. S.Wernick and R.Pinner, 'The Surface Treatment and Finishing of Aluminium and its Alloys', Robert Draper Ltd., U.K., 1972.

123. C.A.Forbes and H.E.Ricks, Plating, 1962, 49, No 3, 279.

124. Westinghouse Electric Corp., U.S. Pat. 3,075.894 (23.1.1959) (29.1.1963).

125. M.E.Straumanis and N.J.Brakss, J.Electrochem. Soc., 1949, 96, No 1, 21; No 6, 310.

126. M.A.Streicher, J.Electrochem. Soc., 1948, 93, No 6, 285; 1949, 96, No 1, 21; 96, No 6, 310.

127. J.V.Petrocelli, J.Electrochem. Soc., 1952, 99, No 12, 513.

128. T.P.Dirkse, J.Electrochem. Soc., 1954, 101, No 6, 328.

129. D.S.Lashmore, Unpublished work.

130. D.S.Lashmore, Plating and Surf. Fin., 1980, 67, No 1, 37.

131. D.S.Lashmore, J.Electrochem. Soc., 1980, 127, No 3, 573.

132. H.Richaud, Revue de l'Aluminium, 1961, 881.

133. U.S. Pat. 2,142,564 (1939).

134. W.G.Zelley, Aluminium Co. of America, U.S. Pats. 2,650,886 (19.1.1951) (9.1.1953); 2,676,916 (23.9.1949) (27.4.1954).

135. W.Canning Materials Ltd., Brit. Pat. 1,007,252 (12.9.1961) (13.10.1965).

136. V.I.Lainer and Yu.A.Velichko, Vestnik Machinostroerya, 1957, 37, 48.

137. Ministry of Supply Specification D.T.D. 901E (1959).

138. 'Recommended Practice for Preparation of and Electroplating on Aluminium Alloys by the Zincate Process', A.S.T.M. Method B253-73.

139. A.S.M. Committee on Finishing of Aluminium, 'Cleaning and finishing of aluminium and aluminium alloys', Metals Handbook, Vol.2, 1964.

140. A.E.Wyszynski, Trans. Inst. Met. Fin., 1980, 58, 34.

141. H.J.Wittrock and L.Swanson, Plating, 1962, 49, 880.

142. R.C.Spooner and D.P.Seraphim, Metal Finishing, 1960, 58, 40.

143. R.C.Spooner and D.P.Seraphim, Metal Finishing, 1961, 59, 37.

144. W.R.Chaffin, Wire and Wire Products, 1967, 42, No 12, 2169.

145. A.S.T.M. Subcommittee B-08,03 report, Plating and Surf. Fin., 1977, 64, No 12, 18.

146. 'Specification for Electroplated Coatings of Nickel and Chromium', B.S.1224 : 1970.

147. O.J.Klingenmaier, Plating, 1974, 61, 741.

148. A.H.Beeb, B.F.Rothschild and G.J.LeBrasse, Tech. Proc. 43rd Annual Amer. Electroplaters Soc., 1956.

149. D.Davies and J.A.Whittaker, Metals and Materials, 1967, 1, No 2; Met. Rev., 12, No 112, 15.

150. H.Plog, Galvanotechnik, 1970, 61, 155.

151. B.Berdan, 'Electroplaters Process Control Handbook', Reinhold Publ. Corp., U.S.A., 1963.

152. 'Standard Test Methods for Adhesion of Metallic Coatings', A.S.T.M. Method BS71-72.

153. E.A.Ollard, Trans. Faraday Soc., 1925, 21, 81.

154. G.Gugunishvili, Indust. Lab., 1958, 24, 333.

155. B.B.Knapp, Metal Finishing, 1949, 47, No 12, 42.

156. B.F.Rothschild, Products Finishing, 1969, 33, No 9, 66.

157. E.J.Roehl, Iron Age, 1940, 146, 17.

158. A.W.Hothersall and C.J.Leadbeater, J.Electrodep. Tech. Soc., 1938, 14, 207.

159. P.A.Jaquet, Trans. Electrochem. Soc., 1934, 66, 393.

160. 'Standard Recommended Practice for Rating of Electroplated Panels Subjected to Atmospheric Exposure', A.S.T.M. Method B537-70.

161. J.K.Dennis and J.J.Fuggle, Trans. Inst. Met. Fin., 1971, 49, 54.

162. P.C.Varley, 'Technology of Aluminium and its Alloys', Butterworths, U.K., 1970.

163. E.B.Saubestre, L.J.Durney, J.Hajdu and E.Bastenbeck, Plating, 1965, 52, 982.

164. P.Tipping and J.K.Dennis, Trans. Inst. Met. Fin., 1974, 52, 133.

165. J.K.Dennis and T.E.Such, Trans. Inst. Met. Fin., 1963, 40, 60.

166. P.C.Crouch, Trans. Inst. Met. Fin., 1973, 51, 117.

167. V.E.Carter, Trans. Inst. Met. Fin., 1968, 46, 49.

168. V.E.Carter, Trans. Inst. Met. Fin., 1970, 48, 19.

TITLE Electrodeposition on
Aluminium and its alloys
AUTHOR James William Golby
DEGREE Ph.D.
DATE October 1981

Surface Technology, *12* (1981) 141 - 155

A STUDY OF THE EFFECT OF PRETREATMENT PROCEDURES ON THE PLATING OF ALUMINIUM ALLOYS

J. W. GOLBY and J. K. DENNIS
Department of Metallurgy and Materials, The University of Aston in Birmingham, Gosta Green, Birmingham (Gt. Britain)

(Received April 1, 1980)

Factors Influencing the Growth of Zinc Immersion Deposits on Aluminium Alloys

J. W. Golby, J. K. Dennis* and A. E. Wyszynski*†

*University of Aston in Birmingham, Dept of Metallurgy and Materials Engineering

†W. Canning Materials Ltd

MS received 20 January 1981