
Masters Theses

Student Theses and Dissertations

Summer 1983

A study of the electroless plating of Sn onto a die-cast aluminum alloy

Ann-Tinn Shen

Follow this and additional works at: https://scholarsmine.mst.edu/masters_theses



Part of the [Chemistry Commons](#)

Department:

Recommended Citation

Shen, Ann-Tinn, "A study of the electroless plating of Sn onto a die-cast aluminum alloy" (1983). *Masters Theses*. 215.

https://scholarsmine.mst.edu/masters_theses/215

This thesis is brought to you by Scholars' Mine, a service of the Missouri S&T Library and Learning Resources. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Thesis
T 5136

A STUDY OF THE ELECTROLESS PLATING OF Sn
ONTO A DIE-CAST ALUMINUM ALLOY

by

ANN-TINN SHEN, 1956-

A THESIS

Presented to the Faculty of the Graduate School of the

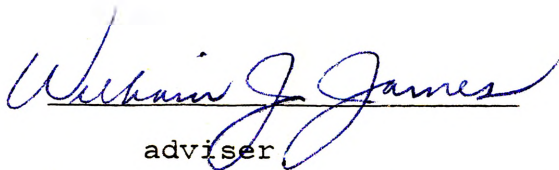
UNIVERSITY OF MISSOURI-ROLLA

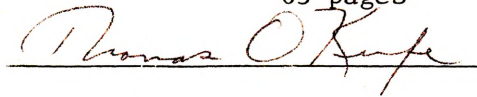
In Partial Fulfilment of the Requirements for the Degree

MASTER OF SCIENCE IN CHEMISTRY

Approved by

T5136
copy 1
63 pages


adviser





ABSTRACT

A tin layer was immersion plated onto a zinc-silicon containing aluminum alloy by using a potassium stannate solution. Conventional aluminum pretreatment was used before immersion plating.

Effects of immersion time with immersion tin thickness and Al-Sn adhesion were studied. Conditions of subsequent Sn-Pb electroplating on Sn plated aluminum samples were investigated.

SEM (scanning electron microscope) and x-ray energy dispersion studies were extensively used on samples of each stage.

ACKNOWLEDGEMENTS

I would like to express my appreciation to my husband, Lainsu Kao. Without his support, this thesis would never have been completed. I also like to thank my parents for their love and encouragement.

Many thanks to Dr. William J. James, my adviser, for his guidance, financial assistance and patience during my study, and Dr. Thomas J. O'Keefe for his many valuable suggestions throughout the course of this research.

TABLE OF CONTENTS

	page
ABSTRACT	ii
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	iv
LIST OF FIGURESvi
LIST OF TABLES	vii
I. INTRODUCTION	1
II. EXPERIMENTAL	5
A. SAMPLE PREPARATION	5
B. IMMERSION TIN PLATING PROCEDURE	5
C. ELECTROPLATING PROCEDURES	6
D. SCANNING ELECTRON MICROSCOPY	7
E. X-RAY DIFFRACTION	7
F. MECHANICAL TESTING	7
G. BURNISH AND OIL FLOW	8
III. RESULTS	10
A. SEM AND X-RAY ENERGY DISPERSION ANALYSIS	10
B. THICKNESS MEASUREMENT	19
C. HIGH SILICON CONTENT ALUMINUM ALLOY	19
D. X-RAY DIFFRACTION SPECTROSCOPY	20
E. PURE ALUMINUM AND Al-Mn ALLOY	27
F. ADHESION OF Al-Sn	27
G. ADHESION OF ELECTROPLATED SAMPLES	28

(continue)

	page
IV. DISCUSSION AND CONCLUSIONS	45
BIBLIOGRAPHY	52
VITA	54
APPENDICES	55
A. X-RAY DIFFRACTION DATA FOR ALUMINUM AND BETA-TIN	55
B. CALCULATION OF TIN THICKNESS VS. X-RAY ABSORPTION	56

LIST OF FIGURES

Figure		page
1	FAILURE MODE OF PULL TEST	9
2	SURFACE OF SAMPLE AFTER ETCH	13
3	SURFACE OF SAMPLE AFTER ACID DIP	14
4	SURFACE OF SAMPLE AFTER DIPPED IN HNO_3 -HF	15
5	SURFACE OF SAMPLE AFTER IMMERSION	16
6	SURFACE OF SAMPLE AFTER IMMERSION	17
7	SURFACE OF HIGH Si CONTENT ALLOY AFTER IMMERSION .	18
8	TIN THICKNESS VS. IMMERSION TIME FROM TABLE II . .	22
9	TIN THICKNESS VS. IMMERSION TIME FROM TABLE IV . .	25
10	TIN THICKNESS VS. IMMERSION TIME FROM TABLE VI . .	30
11	SURFACE OF PURE Al AND Mn-Al ALLOY AFTER IMMERSION	31
12	SURFACE OF SAMPLE BEFORE AND AFTER PULL TEST . .	32
13	SURFACE OF SAMPLE AFTER PULL TEST	33
14	ADHESION VS. IMMERSION TIME FROM TABLE VII-IX . .	37
15	SURFACE OF ELECTROPLATED SAMPLE	41
16	SURFACE OF SAMPLE IMMersed FOR 120 MINUTES	42

LIST OF TABLES

TABLE	page
I	X-RAY ENERGY DISPERSION DATA
	BEFORE AND AFTER ETCH 12
II	TIN THICKNESS CALCULATED FROM DISSOLVED TIN . . . 21
III	COMPOSITION OF HIGH Si CONTENT ALLOY 23
IV	WEIGHT CHANGES AND TIN THICKNESS
	OF HIGH Si CONTENT ALLOY 24
V	X-RAY DIFFRACTION DATA 26
VI	X-RAY DIFFRACTION PEAKS INTENSITIES
	AND THICKNESS 29
VII	ADHESION OF SAMPLES IMMERSSED FOR 3 MINUTES . . . 34
VIII	ADHESION OF SAMPLES IMMERSSED
	FROM 1 TO 10 MINUTES 35
IX	ADHESION OF SAMPLES IMMERSSED
	FOR 3, 6, 7 AND 8 MINUTES 36
X	ADHESION OF ELECTROPLATED SAMPLES 40
XI	SURFACE COMPOSITION OF SAMPLE
	AFTER EACH TREATMENT 43
XII	COMPOSITION OF ELECTROPLATE VS.
	ELECTROPLATING CURRENT 44

I. INTRODUCTION

Aluminum is the most widely used, non-ferrous structural metal, because of its light weight, relatively high strength, excellent heat and electrical conductivity, and good corrosion resistance. Sometimes aluminum and its alloys are plated so as to obtain other desirable surface properties for a specific end use. The electroplated coatings are usually Cu, Cr, Ni, Sn, Pb, Zn, Au, Ag, or combinations thereof. However, such plating of aluminum and its alloys is often difficult [1,2,3] due to the presence of a protective oxide film which is detrimental to the adherence of the metal films. To solve the problem, the aluminum is immersion plated, a process which simultaneously removes the oxide film and deposit a more noble metal by a simple displacement reaction. The immersion layer can then be plated using more conventional electrodeposition techniques, but the adherence of the total deposit to the aluminum is dependent upon the original bond between the immersion layer and the aluminum. The zincate process [4,5,6,7] which puts an immersion deposit of zinc on the aluminum by using a caustic zinc solution is the most widely used pretreatment. Ordinarily, a cyanide copper strike or a neutral nickel strike is applied after the zinc immersion treatment, and before further electroplating [8,9,10].

More recently, a process using a potassium or sodium stannate solution as the immersion plating solution has been used when the part to be plated is to be subjected to a corrosive environment [11,12,13,14,15]. Lateral undercutting corrosion does not occur. The stannate process, although similar to the zincate process, differs in that the aluminum surface is not rinsed following immersion in the stannate bath and is placed directly into a bronze strike bath where voltage is applied. According to a study [11], a continuous layer of tin is not formed, the subsequent bronze strike is directly on the aluminum surface. It seems that the function of the stannate immersion is to first remove the oxide layer covering the surface (to activate the surface) and then to protect the exposed metal as the sample is transferred into the bronze bath. However, reports [11,15,16] indicate the stannate process is sensitive to alloy type, and experience with die-cast aluminum alloys is very limited.

The fact that there are numerous aluminum alloys which behave quite differently from each other makes it difficult to find a plating process that is universally acceptable. For example, when elements are added for alloying purposes, solid solution alloying elements behave differently than those forming intermetallic compounds. The surface of the alloy becomes non-homogeneous during treatment since the various regions show different reactivities in solutions. As a consequence the deposit may have regions with varying

degrees of adherence which can result in a final coating containing surface defects such as blisters. To alleviate this problem, a double zincate process is used [16], in which the first zinc layer is stripped and the zinc immersion steps are repeated. During the first zincate dip, the most active areas are attacked and more metal is removed at these sites. Thus the difference in the surface activities decreases and the second zinc deposit forms more uniformly over the resulting surface. The modified double process can be used on most of the commercial alloys with one major drawback: the zincate process is inherently sensitive to lateral corrosion attack which results in a mass of blisters and eventually a complete detachment of the electrodeposit. It is this lateral corrosion encountered in the zincate process which has restricted the wider use of plated aluminum.

For this study, a steel-backed, die-cast Zn-Si aluminum alloy was used. This alloy is used for bearings and has a Sn-Pb electrodeposit on the surface to improve the conformability, embeddability, and lubrication of the bearings. Nickel is used as the intermediate layer between the aluminum and the Sn-Pb overlayer, so as to improve the adhesion of the Sn-Pb layer to the aluminum alloy. Another aluminum alloy is also used commercially for steel-backed aluminum bearings [17,18,19]. The alloying elements are mainly copper, nickel and cadmium. The zincate process is used followed by a nickel or copper strike. A sulfuric acid

mixture is used for the acid dip. A Pb-Sn-Cu overlay is electroplated from a fluoroborate bath. However, when the overlayer is worn off after the bearing has been used extensively, the hard nickel interlayer is exposed which damages the shaft.

The object of this study was to determine the feasibility of using a stannate bath for the initial immersion coating, and directly electroplating a Sn-Pb overlayer in order to eliminate the often undesirable nickel strike. It was also desired to gain some additional insight into the nature and properties of the initial Sn coating on the aluminum. Of particular importance were the structure and morphology of the Sn deposit and the relationship between its adherence to the aluminum and the processing parameters used in producing the Sn layer.

II. EXPERIMENTAL

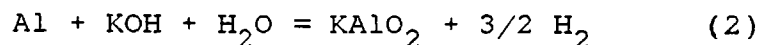
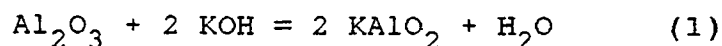
A. SAMPLE PREPARATION

The steel-backed, aluminum alloy samples, provided by Caterpillar Tractor Co. were cut into 3/4 x 3/4 inch pieces. The sides and edges of the samples were polished with #120 grit paper and masked with tape to prevent exposure of the steel to the chemical reagents. The aluminum surface was polished using #600 grit paper.

B. IMMERSION TIN PLATING PROCEDURE

The samples were first etched in a 45 g/l KOH solution for 30 seconds at temperatures of 20, 50, 70 or $90^{\circ}\text{C} \pm 3^{\circ}\text{C}$ to remove the oxide film. During etching, the surfaces changed from a metallic luster to a gray matte-like appearance at 50°C and room temperature, or to powdery black at higher temperatures. After etching, the samples were rinsed several times with distilled water, with a total rinse time of about 20 seconds.

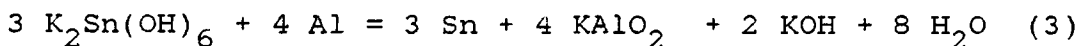
The reactions of aluminum with the KOH solution are as follows:



The etched samples were then dipped in an appropriate acid

of 3 parts concentrate HNO_3 and 1 part 50% HF, or a mixture of 300 g/l H_2SO_4 and 34 g/l CrO_3 , or 50% by volume HNO_3 at room temperature for 15 seconds to remove the layer formed during etching, thought to be a mixture of hydrated aluminum oxide and finely dispersed aluminum metal. The surfaces were quite shiny following the acid dip, and were then rinsed in distilled water.

The etched samples were immediately immersed into the stannate plating solution for the desired time, usually three minutes, washed in distilled water and air dried. The composition of the plating solution is 70 g/l $\text{K}_2\text{Sn}(\text{OH})_6$, 4 g/l KOH and 0.02 mole/l potassium gluconate. The plating reaction is as follows:



C. ELECTROPLATING PROCEDURES

After immersion plating, the samples were electroplated in 200 ml of a Sn/Pb proprietary solution designed to give a 60/40 weight % Sn/Pb electroplate. The exact Sn/Pb ratio obtained varied with current density. A 60/40 weight % Sn/Pb anode was used in all experiments. A Hewlett-Packard 6020B DC power supply was used. When electroplating, a 20 or 60 mA/cm^2 initial current density was maintained for 2 minutes, then a 20 mA/cm^2 current density was maintained for 8 minutes by controlling the applied voltage.

D. SCANNING ELECTRON MICROSCOPY

The morphologies of the sample surfaces were observed under a JEOLCO JSM-35CF scanning electron microscope. The compositions of the samples were determined by X-Ray energy dispersion analysis using a Kevex EDS System 7077. Usually a 25 KeV electron beam and a magnification of 10,000 were used, but an electron beam of 10 KeV and other magnifications were also used. The first number at the bottom of the SEM micrographs is the electron beam energy, the second number is the magnification. The elements were identified using their known spectral energies (wave lengths).

E. X-RAY DIFFRACTION

X-Ray diffraction spectra were obtained using a Siemens Crystalloflex IV diffractometer to determine the crystalline structure of the samples. The diffractometer was operated at 30 KeV and 10 mA using Cu K α radiation. The detecting range was set at 500 cps (counts per second) or 1,000 cps.

F. MECHANICAL TESTING

In order to determine the tensile adhesion of the tin deposits to the aluminum substrate, pull tests were made using an Instron Test Unit [20].

Each sample was aligned in a jig plate between the faces of two 3/8" diameter steel rods. A very thin and even

layer of a two phase epoxy (CHEMLOCK) was applied to both sides of each sample and then contacted with rods on each side with a slight pressure while in the jig plate. The assembly was then baked in an oven at 50°C for 24 hours to cure the epoxy. Following the cure, pull tests were made on the Instron Unit, and the force required to detach the tin from the surface of aluminum was recorded. The various failure modes are illustrated in Fig. 1.

G. BURNISH AND OIL FLOW

Some samples were modified after the immersion tin plating by "oil flow" and "burnish". "Oil flow" means the sample was placed in a hot oil bath (well above the Sn melting point 232°C) for a short time, usually 10 seconds. "Burnish" means the surface was repeatedly compressed using an air driven tool (Condensaire of Densco).

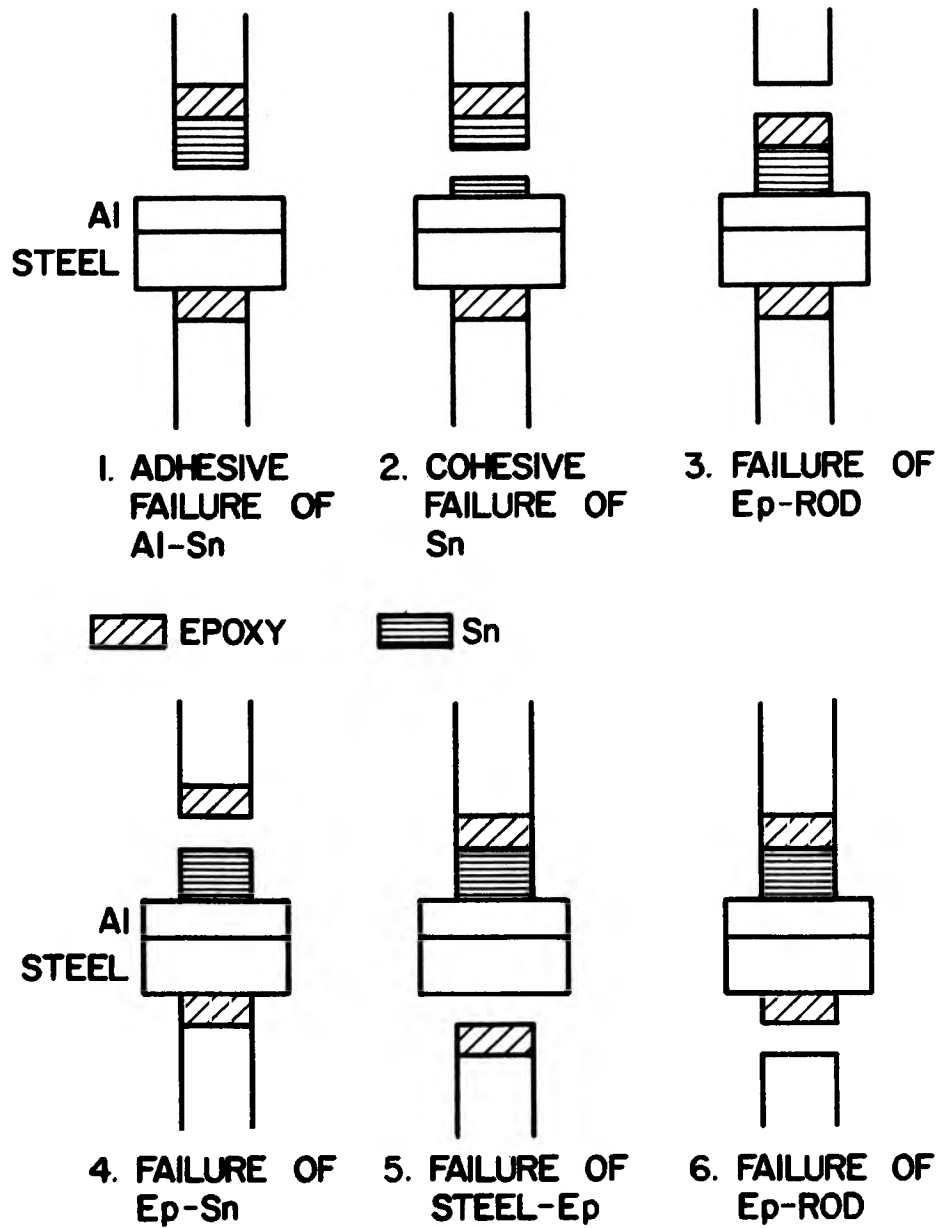


FIG. 1. FAILURE MODE OF PULL TEST.

III. RESULTS

A. SEM AND X-RAY ENERGY DISPERSION ANALYSIS

The original samples, when examined by scanning electron microscopy (SEM) and X-Ray energy dispersion analysis, showed the presence of small amounts of Zn and Cu. Silicon was not observed until after plating was attempted along with small amounts of lead and iron, see Table 1.

When samples are etched in the KOH solution for 30 seconds, some Al_2O_3 and Al is dissolved whereas other constituents, Zn, Cu, Si, Fe, and Pb are only slightly or not attacked. The x-ray dispersion analysis shows increasing amounts of Zn, Si, Cu, Fe, and Pb with increasing temperature from room temperature to 90°C , see Table I. At room temperature and 50°C , the SEM micrographs indicate the surface to be only mildly etched whereas at 70 and 90°C , several holes (pits) and residue particles which appear as bright areas are evident, see Fig. 2.

For samples etched at 70°C and then dipped in a 50% by volume HNO_3 solution or the H_2SO_4 - CrO_3 solution for 15 seconds at room temperature, the SEM micrographs reveal the presence of a substantial number of residue particles. An analysis of these particles using the x-ray dispersive unit indicates a high silicon content, Fig. 3.

If the samples were immersed in the HNO_3 -HF mixture under the same conditions, the sample surface appeared

similar to the eye, but in contrast to Fig. 3, the SEM micrographs reveal a pitted surface with very few bright particles. This was expected as a consequence of the solubility of Si in HF. When dipped in the HNO_3 -HF mixture, the roughness of the pitted surface increases with increasing temperature up to 70°C . When etched at 90°C the alkaline attack is much more uniform and sufficiently extensive to remove the abrasion caused initially by the grit paper and the pits are larger and shallower, see Fig. 4.

In order to observe the growth of the tin deposit, the samples were etched at 70°C , dipped into the HNO_3 -HF mixture, rinsed in distilled water and then immersed in the stannate plating solution for varying times of 30 seconds, 1, 2, and 3 minutes. The SEM micrographs are shown in Fig. 5. For samples immersed for 30 seconds, no tin particles are observed using a 25 KeV electron beam. At 10 KeV, a large number of white spots is evident but the 10 KeV electron beam is too low to allow an accurate X-Ray energy dispersion analysis. For samples immersed for 1 or more minutes, a tin layer is observed to uniformly cover the surface, and the particle size increases with immersion time. The tin deposits are the same whether the samples are etched at 70°C or room temperature, see Figs. 5 and 6. The surface roughness is similar to those of samples following the acid dip, compare Figs. 4, 5d and 6a. When samples

TABLE I.

X-RAY ENERGY DISPERSION DATA BEFORE AND AFTER ETCH.

	Al	Si	Zn	Cu	Fe	Pb
original	93.6	-----	5.29	1.07	-----	-----
etch at Rm. temp.	86.7	3.92	6.31	3.11	-----	-----
etch at 50°C	82.8	6.48	7.42	3.29	-----	-----
etch at 70°C	78.6	4.88	11.2	3.49	0.53	1.22
etch at 90°C	67.2	6.28	21.7	1.62	1.00	2.27

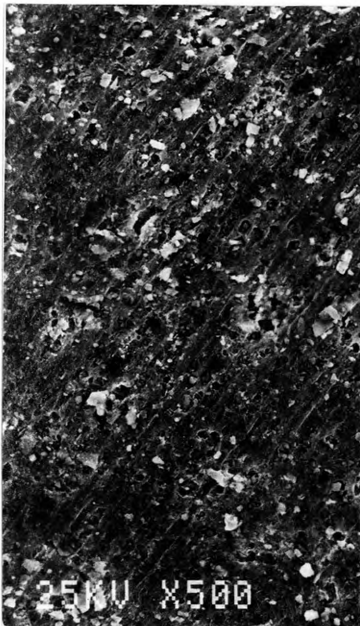
a. room temperature



b. 50°C



c. 70°C



d. 90°C



FIG. 2. SURFACE OF SAMPLE AFTER ETCH.

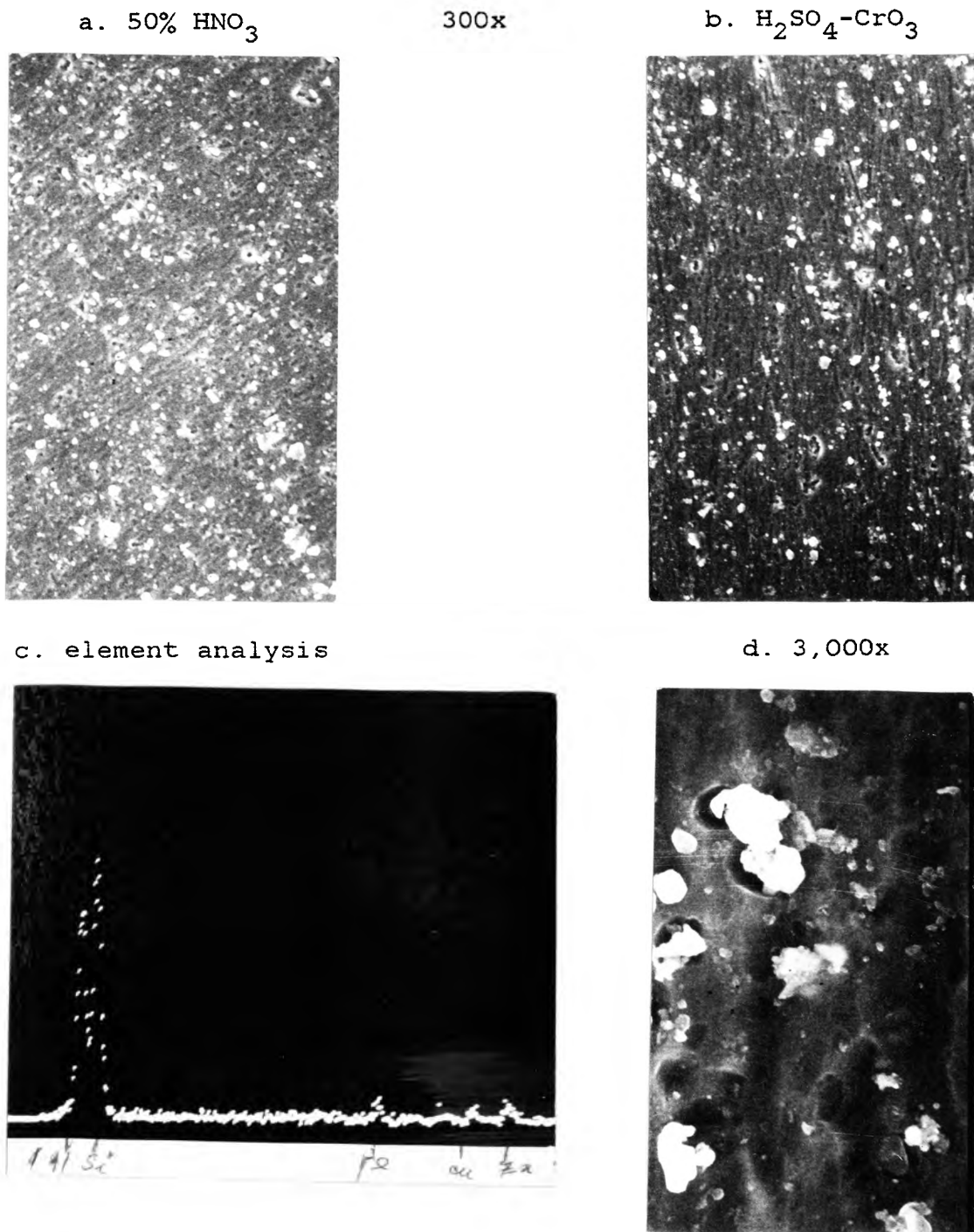
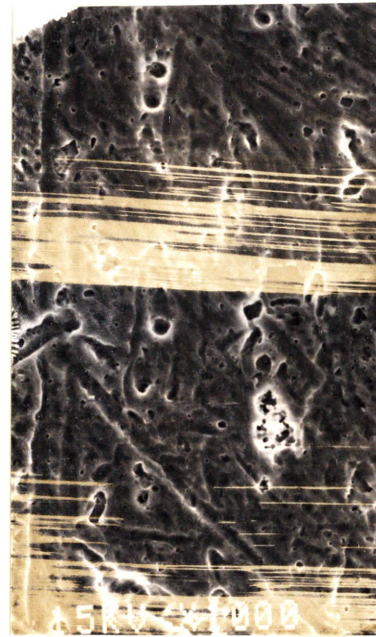


FIG. 3. SURFACE OF SAMPLE AFTER ACID DIP.

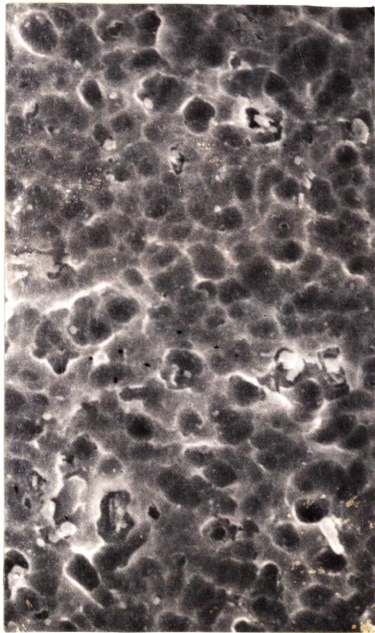
a. room temperature



b. 50°C



c. 70°C



d. 90°C

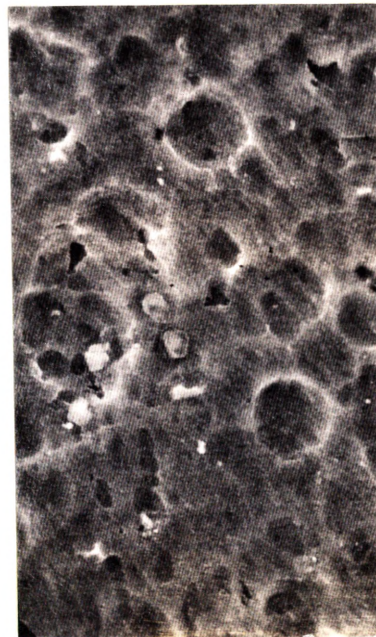
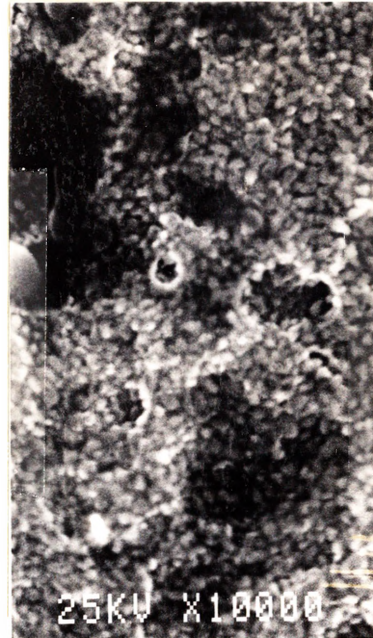


FIG. 4. SURFACE OF SAMPLE AFTER DIPPED IN HNO₃-HF.

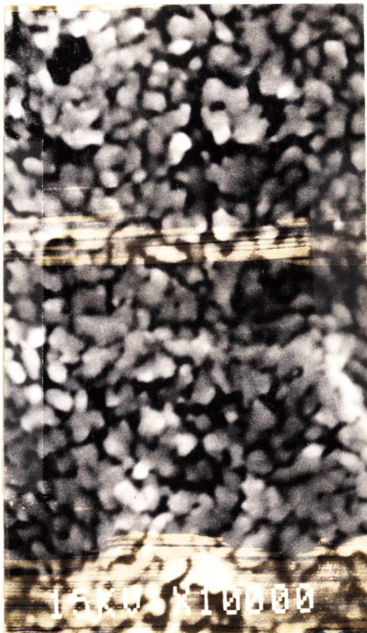
a. 30 seconds



b. 1 minute



c. 2 minutes



d. 3 minutes

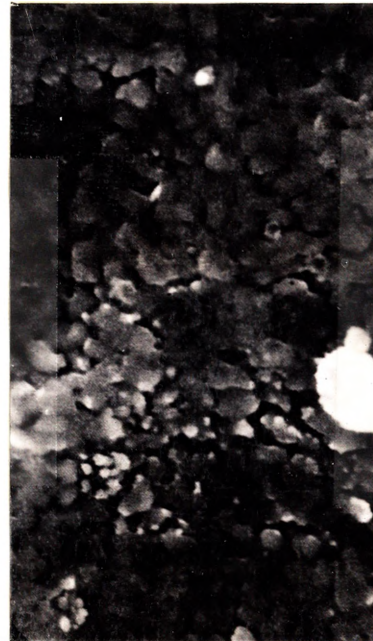


FIG. 5. SURFACE OF SAMPLE AFTER IMMERSION.

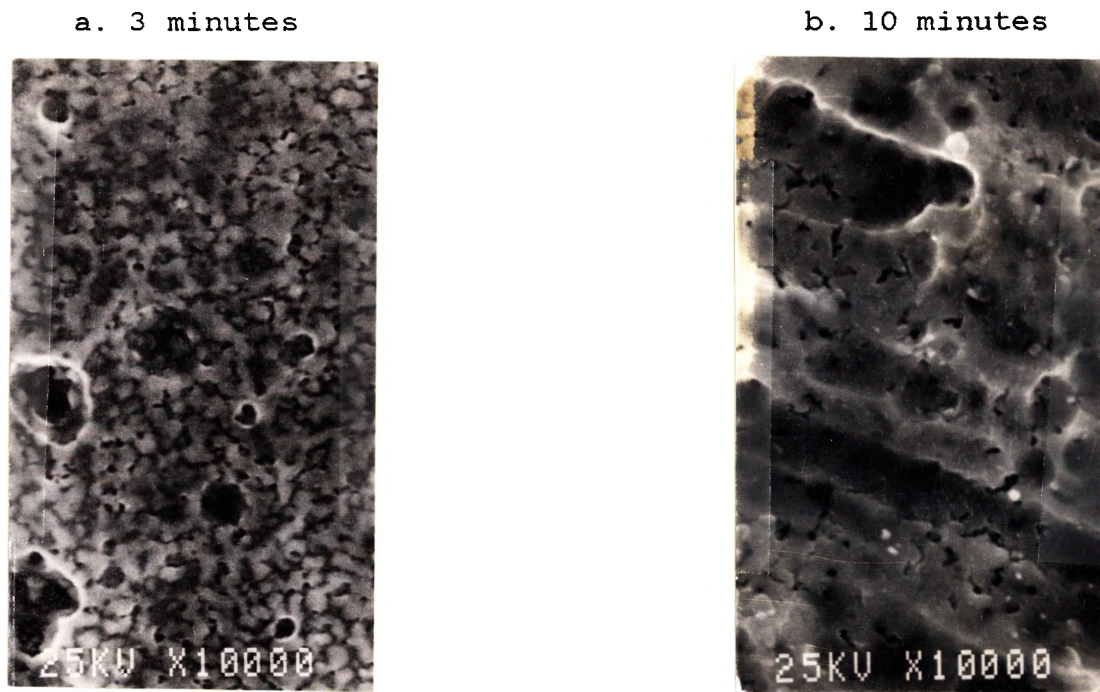
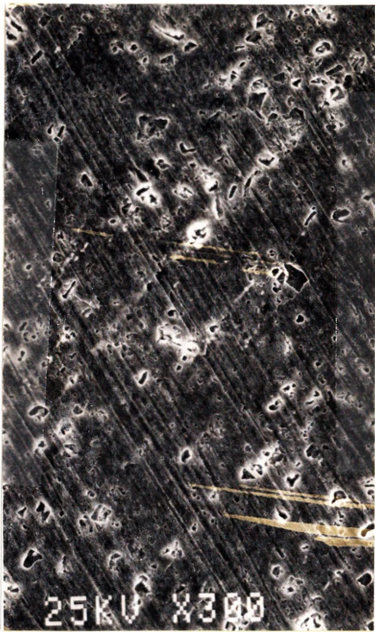


FIG. 6. SURFACE OF SAMPLE AFTER IMMERSION.

a. 3 minutes



b. 13 minutes



FIG. 7. SURFACE OF HIGH Si CONTENT ALLOY AFTER IMMERSION.

were immersed for more than 2 minutes, gas bubbles slowly appeared and accumulated on the surfaces.

B. THICKNESS MEASUREMENT

The thickness of the tin deposit was determined by dissolving tin in a 50% by volume HNO_3 acid solution, diluting to 25 ml, and measuring the concentration of tin on a Perkin-Elmer Atomic Absorption Spectrometer. The thicknesses were determined as follows:

$$\text{tin deposited (g)} = \text{tin concentration (g/c.c.)} \times 25 \text{ (c.c.)}$$

$$\text{thickness (cm)} = \frac{\text{tin deposited (g)}}{\text{tin density (g/c.c.)}} \times \frac{1}{\text{area (cm}^2\text{)}}$$

The theoretical tin density of 7.29 g/c.c. was used assuming a pore-free deposit. The thickness of tin deposits on samples immersed in potassium stannate solution for different periods of time was measured. Results show that, except for the first 2 to 3 minutes, the tin thickness is nearly proportional to immersion time, 490 $\overset{\circ}{\text{A}}/\text{min}$, see Table II and Fig. 8.

C. HIGH SILICON CONTENT ALUMINUM ALLOY

An alloy with a higher silicon content was also studied (see Table III for exact composition). The tin deposits

appeared very similar, however the etched surface had more and larger Si particles which resulted in large holes on the surface after the HNO_3 -HF mixture dip. The tin thickness growth, $200 \text{ \AA}/\text{min}$, is smaller than that for the low silicon alloy, see Table IV and Figs. 7,9.

D. X-RAY DIFFRACTION SPECTROSCOPY

X-Ray diffraction spectra show that prior to plating, only the aluminum structure is detected; after plating, peaks of beta-tin are also present. As would be expected, the relative intensities of the tin peaks increase as the deposit thickens, see Table V and Appendix A. The thickness and peak intensities can be related by the following equation [21]:

$$G = 1 - \exp(-2\mu x / \sin\theta) \quad (4)$$

where

G is the ratio of absorption compared to the absorption of infinite thickness.

μ = absorption coefficient

x = tin thickness

θ = diffraction angle

in which G is between 0 and 1, μ is 1847 cm^{-1} for Cu $K\alpha$ radiation. A glass slide with a 1200 \AA plasma coated β -tin layer whose thickness was measured by optical diffractometry was used as the standard, see Appendix B for detailed calculations. Samples of different immersion time

TABLE II.

TIN THICKNESS CALCULATED FROM DISSOLVED TIN.

immersion time (min)	area (cm ²)	conc. (ppm)	w (x10 ⁻⁵ g)	w/A (x10 ⁻⁵ g/cm ²)	thickness (A)
2	1.69	6.2	15.50	9.17	1,300
3	1.15	6.1	15.25	13.20	1,800
4	1.69	7.5	18.75	11.10	1,500
5	1.69	9.1	22.75	13.46	1,800
6	1.56	9.1	22.75	14.58	2,000
7	1.75	14.4	36.00	20.51	2,800
8	1.56	13.2	33.70	21.54	3,000
9	1.50	16.0	40.00	26.67	3,700
10	1.69	24.3	60.75	35.95	4,900
30	1.62	71.1	177.75	109.39	15,000
50	1.98	136.0	340.00	171.03	23,500
60	1.44	117.0	293.67	203.94	28,000
70 [*]	1.56	72.4	362.00	232.05	31,800
80 [*]	2.02	94.5	472.50	233.33	32,000
100 [*]	1.50	80.6	403.00	268.67	36,900
120 [*]	1.44	90.5	452.50	314.24	43,100

* Solution was diluted to 50 ml instead of 25 ml

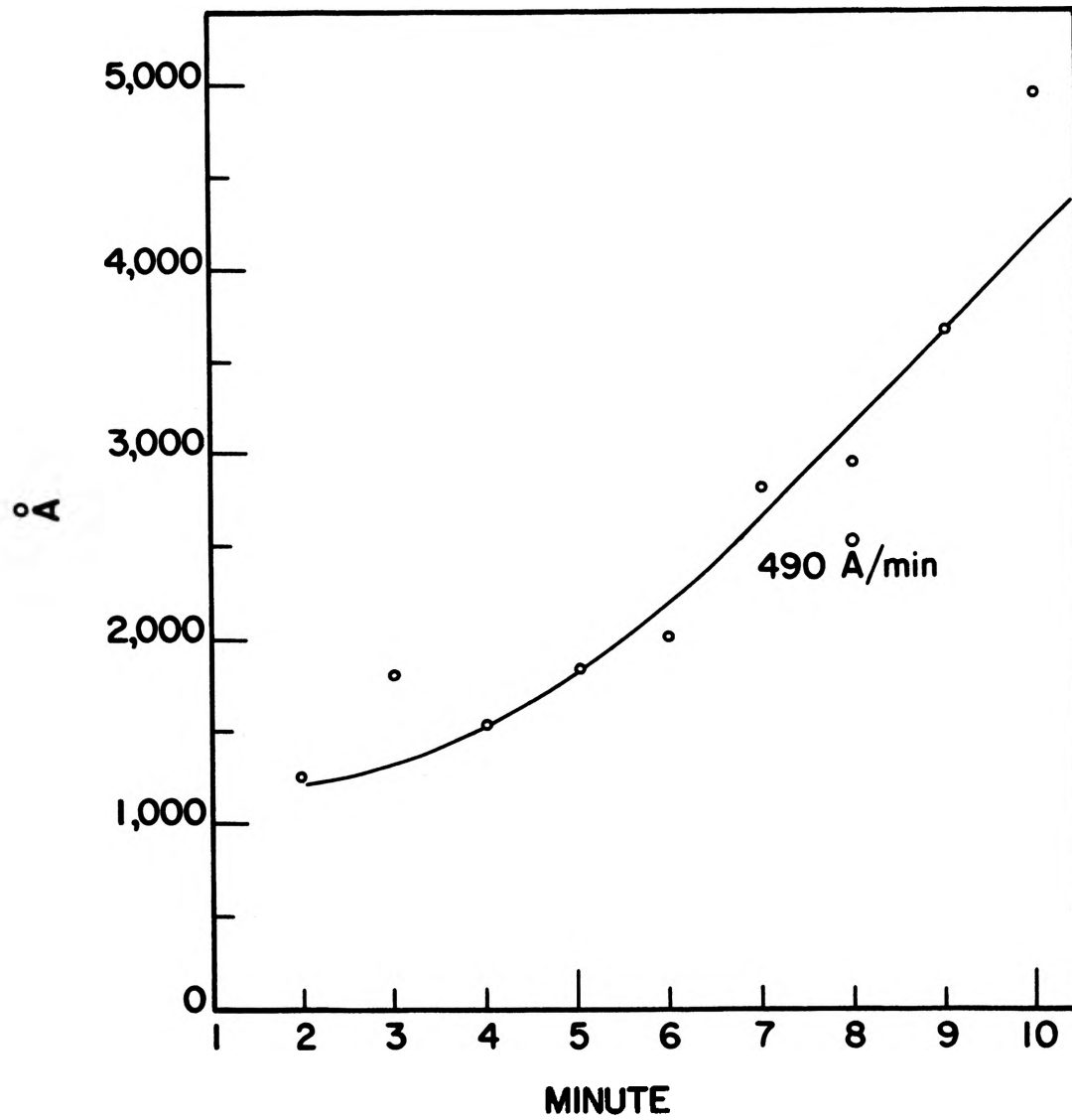


FIG. 8. TIN THICKNESS VS. IMMERSION TIME FROM TABLE II.

TABLE III.

COMPOSITION OF HIGH Si CONTENT ALLOY.

element	Zn	Si	Fe	Pb	Cu	Al
percent (%)	3.5	11.5	---	1.0	---	84.0

TABLE IV.

WEIGHT CHANGES AND TIN THICKNESS OF HIGH Si CONTENT ALLOY.

immersion time (min.)	w (g)	$w^n - w^{n-1}$ (g)	$w^n - w^0$ (g)	w/A (g/cm ²)	thickness (A)
10	7.70400	3×10^{-5}	3×10^{-5}	1.9×10^{-5}	300
20	7.70425	25	28	17.2	2,400
30	7.70450	25	53	32.6	4,500
40	7.70460	10	63	38.8	5,300
50	7.70550	90	153	94.2	12,100
60	7.70520	-30	123	75.7	10,400
70	7.70520	0	123	75.7	10,400
80	7.70520	0	123	75.7	10,400

$$w^0 = 7.70377 \text{ gram} \quad \text{Area} = 1.3 \times 1.25 = 1.625 \text{ cm}^2$$

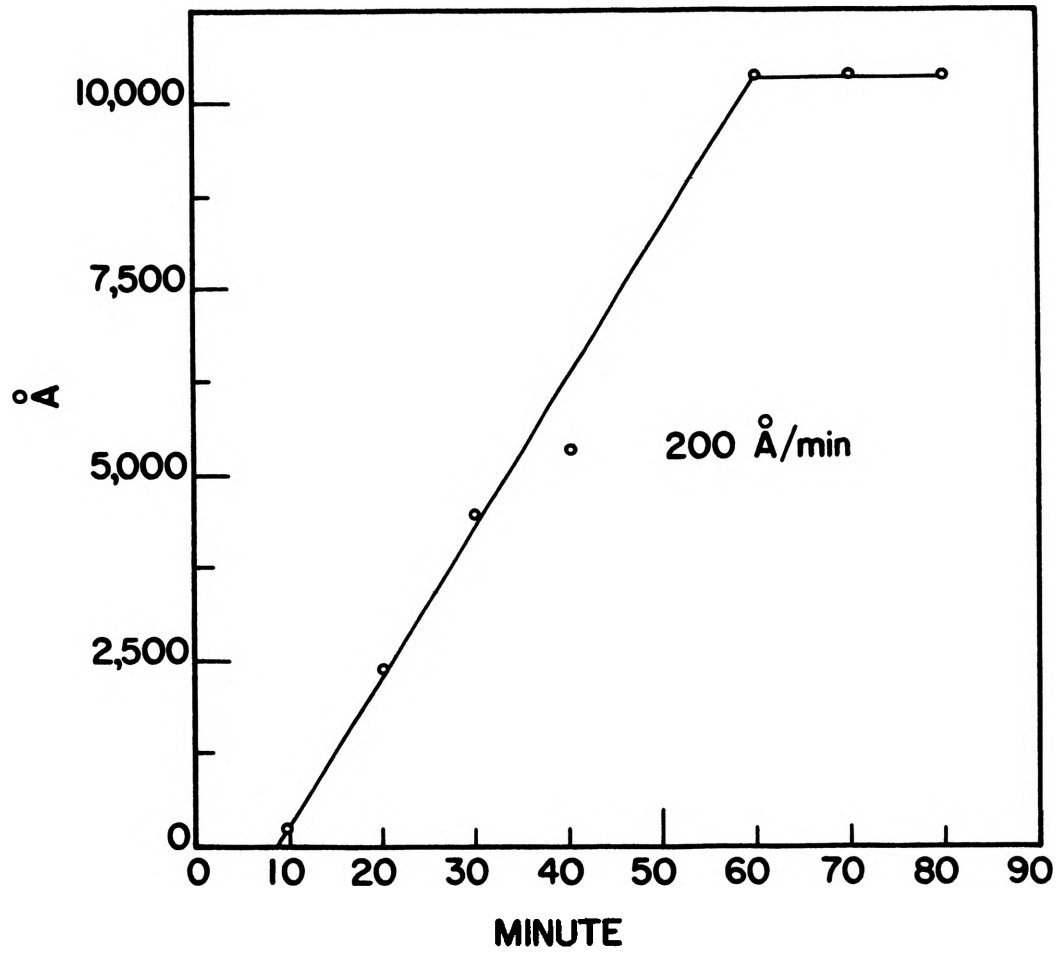


FIG. 9. TIN THICKNESS VS. IMMERSION TIME FROM TABLE IV.

TABLE V.

X-RAY DIFFRACTION DATA.

<u>d</u>	<u>I</u>	<u>hkl</u>	<u>d</u>	<u>I</u>	<u>hkl</u>
2.34	S	111 _{Al}	2.92	W	200 _{Sn}
2.03	MS	200 _{Al}	2.79	W	101 _{Sn}
1.43	MS	220 _{Al}	2.34	S	111 _{Al}
1.22	MS	311 _{Al}	2.03	S	200 _{Al}
sample after polish			1.43	M	220 _{Al}
			1.22	MS	311 _{Al}

sample plated at room temp.

<u>d</u>	<u>I</u>	<u>hkl</u>	
2.92	MS	200 _{Sn}	S = strong
2.79	VS	101 _{Sn}	M = medium
2.35	M	111 _{Al}	W = weak
2.07	W	220 _{Sn}	V = very
2.02	S	211 _{Sn} 200 _{Al}	
1.48	M	112 _{Sn}	
1.43	M	321 _{Sn} 220 _{Al}	
1.22	M	311 _{Sn}	
1.21	W	312 _{Sn}	

sample plated at 60°C

were x-rayed and the thicknesses calculated. The results are in reasonable agreement with those obtained in part B, except the tin thickness growth is $1080 \text{ \AA}/\text{min}$, see Table VI and Fig. 10.

E. PURE ALUMINUM AND Al-Mn ALLOY

Pure aluminum and a wrought Al-Mn alloy (Fisher A-552) were also treated by the stannate process described in the experimental section. The SEM micrographs were quite different from the Zn-Si-Al die-cast alloy, see Fig. 11. Only a few Sn particles scatter on the surface, most of the aluminum surface is uncovered.

F. ADHESION OF Al-Sn

Results discussed in this section were all obtained with samples of low silicon content. Table VII shows results of samples etched at room temperature, or 70°C , dipped in HNO_3 -HF mixture, immersed for 3 minutes. Table VIII shows results of samples etched at room temperature, dipped in HNO_3 -HF, immersed from 1 to 10 minutes. Table IX shows results of samples etched at 70°C , dipped in HNO_3 -HF, immersed for 3, 6, 7, and 8 minutes. The adhesion between tin and aluminum is very good for samples immersed 2 or 3 minutes; results show cohesive failures occurred which mean that the adhesive strength must be higher than the

value measured, see Fig. 12 and Table VII. When samples were immersed for longer time, and the tin deposits grew thicker, the pull strength gradually decreased, and adhesive failure occurred. For samples immersed for 10 minutes, adhesive failure occurred at a considerably lower pull strength of 2750 psi, see Table VIII and Fig. 13. When the sample was immersed for 120 minutes, the thick tin layer was easily peeled off by Scotch tape, see Fig. 13. In part B, the SEM micrograph shows the surface to be rougher when the samples are etched at 70°C instead of room temperature, and the pull tests do reveal better adhesion. However, as the deposits become thicker, the difference between samples etched at 70°C or room temperature decreases, see Table IX and Fig. 14.

G. ADHESION OF ELECTROPLATED SAMPLES

The results of the electroplating on the aluminum alloy preceded by the stannate process are limited and not entirely satisfying, results are shown in Table X. Most of the results are samples of high Si content. During electroplating, gas bubbles are produced and the surface usually has blisters. When electroplated samples were pulled to test the adhesion, failure always occurred between the Al-Sn interface or within the immersion tin layer; the Sn/Pb electroplate adheres to the immersion tin layer firmly.

TABLE VI.

X-RAY DIFFRACTION PEAKS INTENSITIES AND THICKNESS.

immersion time	sample width(cm)	peak area at 30.6°	thickness (A)	peak area at 31.8°	thickness (A)
standard	1.75	464	1,200	335	1,200
30 sec.	1.35	32	100	34	100
45 sec.	1.30	112	400	78	400
1 min.	1.35	162	500	142	600
2 min.	1.30	177	600	161	800
4 min.	1.17	622	2,600	444	2,500
5 min.	1.20	721	3,100	657	4,100
6 min. (500 cps)	1.25	971	4,300	951	6,700
6 min. (1,000 cps)	1.25	476	4,300	465	6,700
7 min.	1.40	499	3,900	452	5,400
8 min.	1.30	625	6,100	704	14,800
9 min.	1.30	713	7,600	702	14,600
10 min.	1.30	771	8,700	843	----

Standard sample is a glass slice with a 1200 A plasma coated B-tin layer.

Samples less than 6 minutes were measured at 500 counts per sec.(cps), while samples more than 10 minutes were measured at 1000 cps.

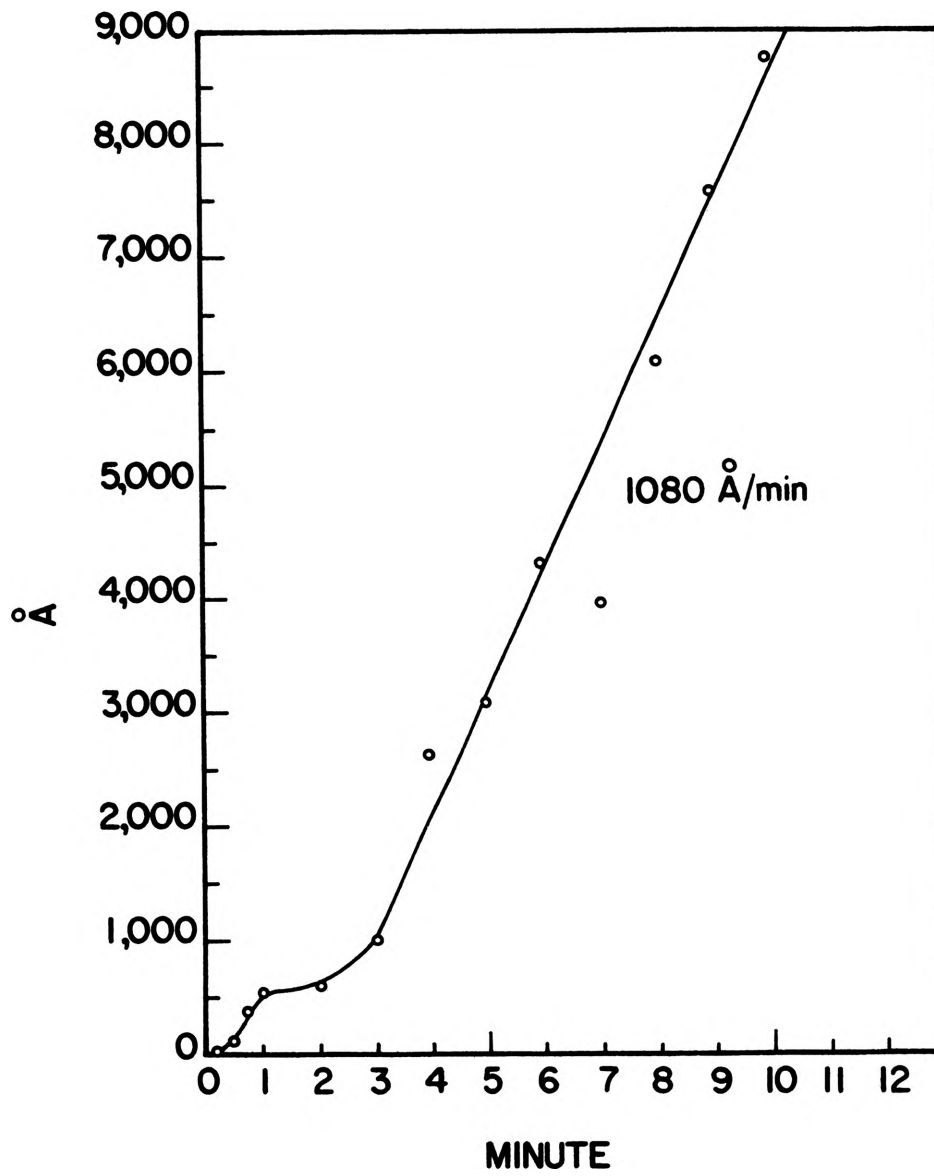
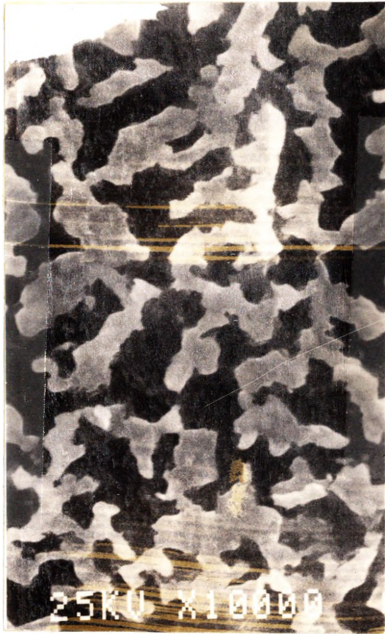


FIG. 10. TIN THICKNESS VS. IMMERSION TIME FROM TABLE VI.

a. pure Al



b. Al-Mn alloy



FIG. 11. SURFACE OF PURE Al AND Mn-Al ALLOY AFTER IMMERSION.

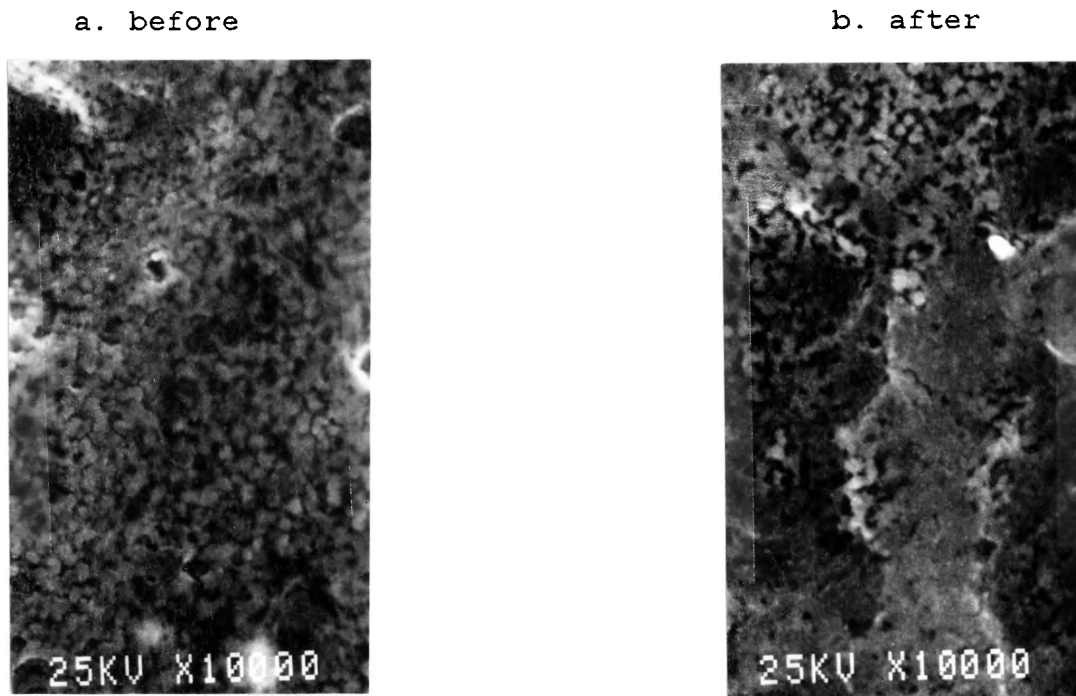


FIG. 12. SURFACE OF SAMPLE BEFORE AND AFTER PULL TEST.

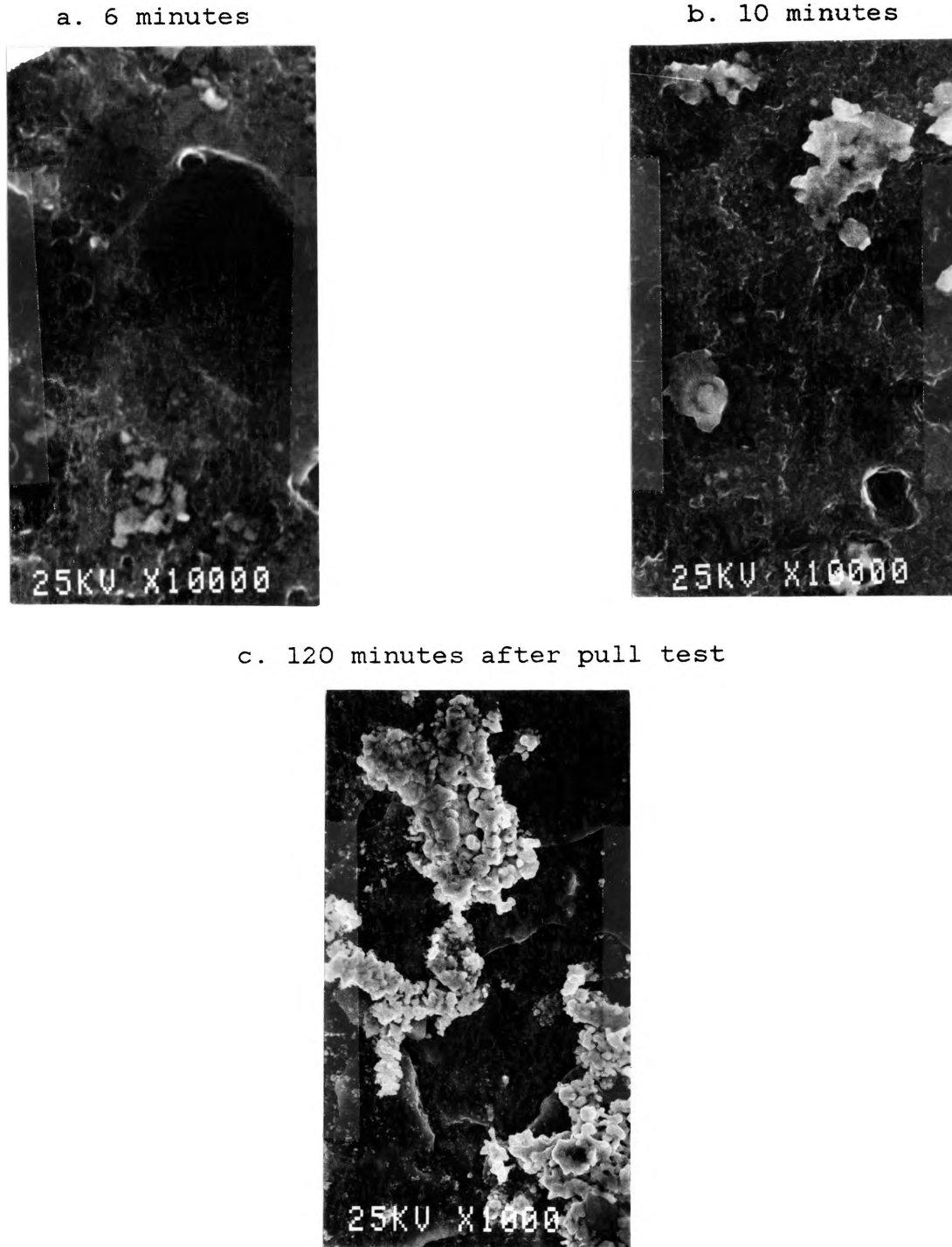


FIG. 13. SURFACE OF SAMPLE AFTER PULL TEST.

TABLE VII.

ADHESIONS OF SAMPLES IMMERSSED FOR 3 MINUTES.

KOH temp.	sample 1 force psi	sample 2 force psi	average psi	Std. Dev.	% of Dev.
70°C	5,712 ²	5,904 ²	5,808	+ 136	2.3
room temp.	4,920 ²	4,758 ²	4,839	+ 115	2.4

Superscript is failure mode; 1 is Al-Sn adhesive failure, 2 is Sn cohesive failure, 3 is Ep-rod failure, see Fig. 1.

$$1 \text{ psi} = 7.03 \times 10 \text{ g/cm}^2$$

TABLE VIII.

ADHESION OF SAMPLES IMMERSSED FROM 1 TO 10 MINUTES.

deposition time	high range force psi	low range force psi	average force psi	Std. Dev.	% of Dev.
2	6,072 ³	3,840 ³	4,986	<u>+1,000</u>	20.1
3	5,544 ³	3,742 ³	4,464	<u>+ 830</u>	18.6
4	4,200 ^{1,2}	3,800 ^{1,2}	4,016	<u>+ 182</u>	4.5
5	4,032 ^{1,2}	3,648 ^{1,2}	3,786	<u>+ 169</u>	4.5
6	4,440 ¹	3,672 ¹	3,979	<u>+ 327</u>	8.2
7	5,073 ¹	3,057 ¹	4,042	<u>+ 944</u>	23.3
8	4,728 ¹	2,544 ¹	3,654	<u>+1,227</u>	33.6
9	3,552 ¹	2,880 ¹	3,186	<u>+ 290</u>	9.1
10	2,928 ¹	2,554 ¹	2,705	<u>+ 184</u>	6.8

Superscript is failure mode; 1 is Al-Sn adhesive failure, 2 is Sn cohesive failure, 3 is Ep-rod failure, see Fig. 1.

Each condition has been done on four samples.

TABLE IX.

ADHESION OF SAMPLES IMMERSSED FOR 3, 6, 7, AND 8 MINUTES.

deposition time	high range force psi	low range force psi	average force psi	Std. Dev.	% of Dev.
3 min.	5,720 ³	4,440 ³	5,093	+ 533	10.5
6 min.	4,752 ¹	3,744 ³	4,320	+ 431	10.0
7 min.	3,537 ¹	3,072 ¹	3,227	+ 269	8.3
8 min.	3,750 ¹	2,975 ¹	3,282	+ 412	12.6

Superscript is failure mode; 1 is Al-Sn adhesive failure,
2 is Sn cohesive failure, 3 is Ep-rod failure, see Fig. 1.

Of 3 and 6 minutes, four samples have been done respectively.
Of 7 and 8 minutes, three samples have been done respectively.

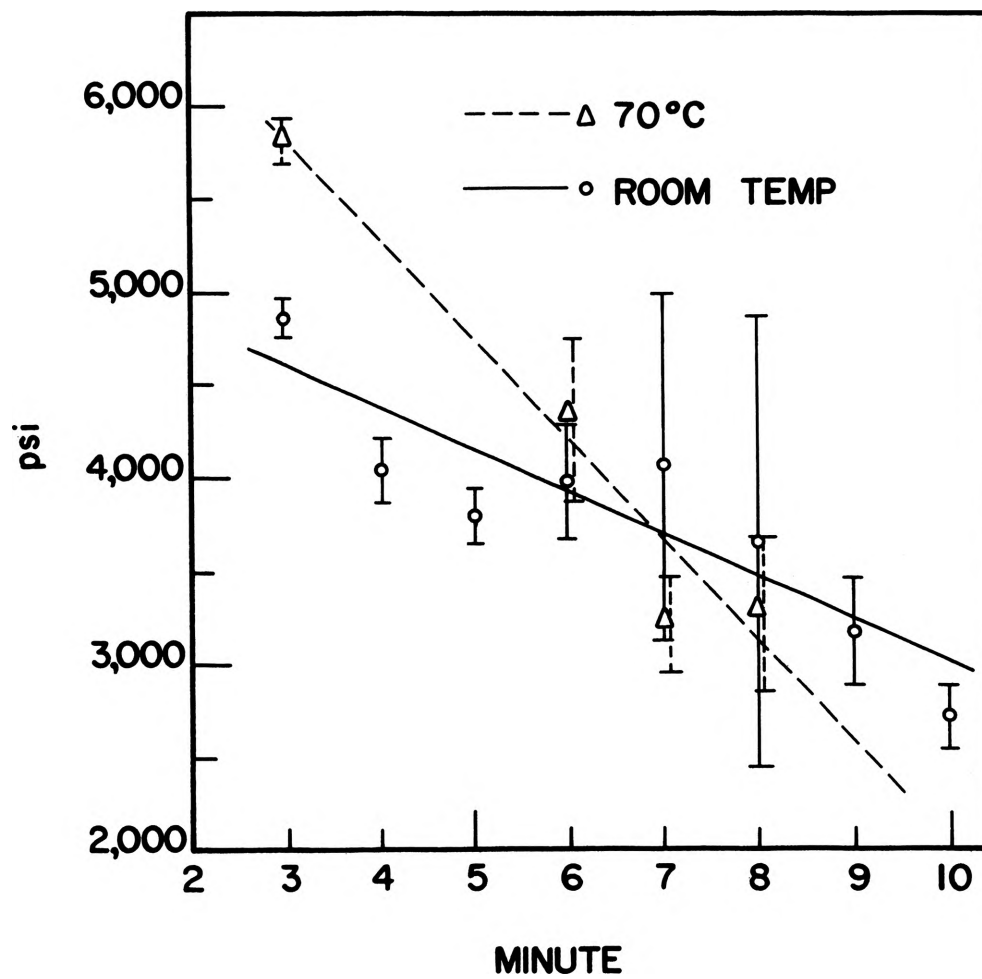


FIG. 14. ADHESION VS. IMMERSION TIME FROM TABLE VII-IX.

When electroplating, samples prepared by using the previously mentioned optimized tin immersion conditions, mainly immersion in a solution of 70 g/l potassium stannate for 3 minutes after being dipped in a HNO_3 -HF mixture for 15 seconds, exhibit many blisters on the surface, and the deposit is loosely attached to the substrate. In order to prevent this blistering and improve the adhesion, some changes were made both with the stannate process and with the electroplating conditions. The stannate concentration was increased to 140 g/l, and the immersion time was increased to 5 minutes. As for the electroplating conditions, the initial current density was increased to 60 mA/cm^2 for 2 minutes. The electroplated sample prepared by using these conditions still shows a few blisters, and the result of the pull test (219 psi) indicates adhesive failure at the Al-Sn interface. Reducing the acid dip time to 5 seconds was tried, and the electroplated sample shows only a few blisters, but the pull strength decreases to 139 psi. If the sample was dipped in 50% by volume HNO_3 for 15 seconds, the electroplated sample shows no signs of blistering, but the pull strength decreases to 61 psi with failure again occurring at the Al-Sn interface.

For samples of low silicon content, the surface usually has fewer blisters, but the pull strength is essentially the same as that of the high silicon content sample within the limits of error for samples dipped in HNO_3 -HF, e.g., 194 psi compared to 219 psi. However when for a sample dipped

in 50% by volume HNO_3 , the pull strength improves from 61 to 155 psi, see Table X.

When the sample is immersed at room temperature for 120 minutes, or at 70° for 3 minutes, and modified by "oil flow" and "burnish", the surface is free of blisters and an adhesion of 600 psi is obtained. It should be noted that when samples immersed for 120 minutes or at 70°C were pulled, only the area attached to the pulling rod was pulled away, and failure occurred within the tin layer, as shown in Fig. 16 and Table XI. But when samples with an immersion time of 5 minutes at room temperature were pulled, the entire deposit was pulled away from the surface, and the failure occurred between the Al-Sn interface see Fig. 15. When calculating the adhesion, the detaching force was divided by the total electroplated area instead of the contacting rod area when failure occurred on the entire electroplated area.

When an initial current density of 60 mA/cm^2 was employed during the electroplating, the adhesion is superior to that obtained at an initial current density of 20 mA/cm^2 , see Tables X. The ratio of tin increases from 52 % to 74 % when the initial current density is increased from 20 to 60 mA/cm^2 , but the appearance and SEM micrographs are very similar, see Table XII.

TABLE X.

ADHESION OF ELECTROPLATED SAMPLES.

stannate conc. (g/l)	time min.	acid	modify	initial C. D. (mA/cm ²)	appearance blistering	adhesion psi
70	3	A		20	heavy	0
140	5	A		60	few	219
140	5	D		60	few	139
140	5	B		60	no	61
140C	5	A		60	few	194
140C	5	B		60	no	155
70	120	A	*	35	no	600
70**	3	A	*	20	no	552

A: HNO₃-HF (3 to 1 by volume) mixture was used as acid.
Samples were always dipped in acid for 15 seconds.

B: 50% by volume HNO₃ was used.

C: Low Si content alloy was used.

D: Sample was dipped in HNO₃-HF for 5 seconds.

*: Sample was modified by "oil flow" and "burnish".

** : Sample was immersed at 70°C, all the others are at room temperature.

a. before pull test



b. after pull test

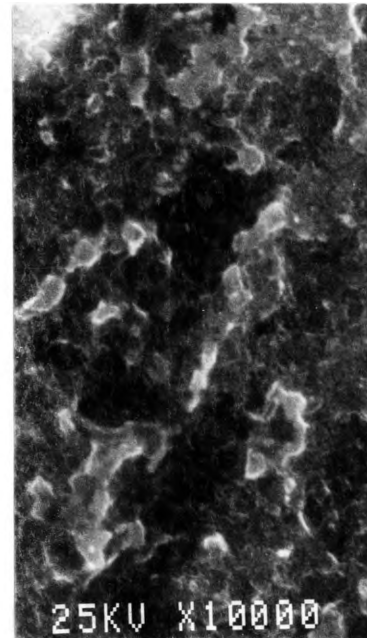


FIG. 15. SURFACE OF ELECTROPLATED SAMPLE.

a. after modify

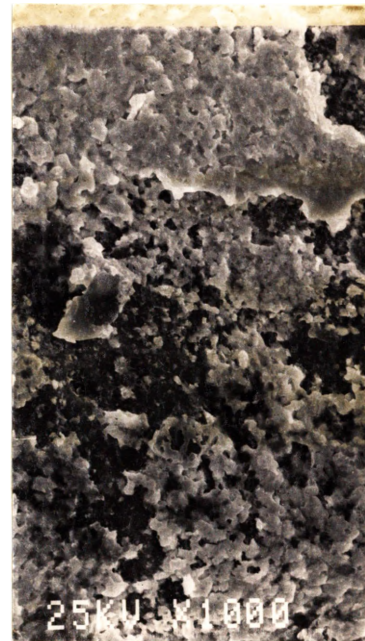
b. after electroplate
and pull test

FIG. 16. SURFACE OF SAMPLE IMMEDRSED FOR 120 MINUTES.

TABLE XI.

SURFACE COMPOSITION OF SAMPLE AFTER EACH TREATMENT.

	Al wt.%	Sn wt.%	Pb wt.%
after immersion 120 min.	2.25	97.29	0.46
after electroplate	3.02	52.18	44.80
after pull test	64.33	34.53	1.14

TABLE XII.

COMPOSITION OF ELECTROPLATE VS. ELECTROPLATING CURRENT.

current density	Sn wt.%	Pb wt.%
20 mA/cm ² 10 min.	52.1	47.8
60 mA/cm ² 2 min.		
20 mA/cm ² 8 min.	74.0	26.0

IV. DISCUSSION AND CONCLUSIONS

In the KOH etchant, the original Al_2O_3 layer dissolved to expose a fresh Al surface. Because of the high oxidation potential of Al ($E_{\text{SHE}} = +1.66 \text{ V}$), water is reduced to hydrogen and the aluminate ion is formed, see equation (2). The black appearance of the surface is typical of metals like Zn, Mg, and Al where attack by either strongly alkaline or halogen-containing solutions, produces a large number of very fine metallic particles together with hydrated oxides of the metal [22]. The black appearance is a consequence of the destructive interference of multitudes of reflections from the tiny metal crystallites which are oriented in all possible ways.

The black surface is readily removed by immersion into the HNO_3 -HF mixture which dissolves the metallic particles and the ZnO to reconstitute a new thin aluminum oxide layer. When this new surface is immersed in the plating solution, the oxide layer is removed exposing a fresh aluminum surface to the plating solution. The Sn^{4+} ions are reduced to Sn which deposits onto the aluminum surface, see equation (4).

Initially, no tin can deposit as it is necessary to expose a fresh surface through dissolution of the oxide. In this regard, after the sample is removed from the HNO_3 -HF

mixture, it should be placed in the plating solution with as little delay as possible so as to prevent a build-up of the oxide layer which would then slow up the plating process. If HF is not used to remove the bulk of the Si on the surface, the plating deposition rate is slow as expected because of the poor conducting properties of Si.

As the surface is gradually covered by a tin deposit, the deposition rate decreases and should eventually cease when the surface is totally covered by tin. The results show that after an initial 15 to 30 seconds needed to dissolve the oxide film and initiate nucleation, the surface is quickly covered by a tin deposit in one to two minutes. However, probably another redox reaction takes place, some aluminum areas continue to be exposed to the solution and tin continues to deposit on the surface, see Tables II, III and V and Figs. 8, 9 and 10.

After samples had been immersed for about 2 minutes, hydrogen gas bubbles gradually appeared on the surface and grew larger, see equation (2). The continuous gas evolution also indicates that there is some aluminum surface which has not been covered by Sn. As the deposit grows thicker, hydrogen gas may be trapped between the tin layer and aluminum, diffuses to neighbouring areas, and lifts off the deposited tin layer. This may explain why adhesion is decreased and why the fraction of failure that occurs between aluminum and tin increases when immersion time is increased, see Tables VIII and IX and Figs. 13, 14.

When the tin thickness was measured by dissolving the deposited tin (part B results), the thickness was calculated by dividing the total amount of deposited tin with the deposited area. Since the true area cannot be measured, the geometric area was used; thus the thickness value may be larger than the true thickness. More precisely, it should be the deposited amount on the surface instead of the thickness because the thickness also depends on the density of the deposit. The assumption of a pore-free deposit is not supported by the SEM micrographs which indicate the opposite, see Figs. 6, 7. The thickness measured by x-ray diffraction (Table VI, part D), is almost twice that obtained in part B except for the first three minutes, see Fig. 8 and 10. Because the x-ray results are directly related to the thickness, equation (4), this shows that the density of the tin layer is only about half of the theoretical density (7.29 g/cm^3), and the structure on the thick tin layer is likely to be porous. This is in accordance with the SEM micrographs. The lower growth of tin on the alloy of high Si content, $200 \text{ \AA}^0/\text{min}$, as compared to that on the alloy of low silicon content can be explained. When aluminum is dissolved to reduce the Sn ions, Si particles that have been buried are exposed, hence the contact area of aluminum exposed to the stannate solution is decreased. The more Si particles on the surface, the less aluminum area that can react. However, it should be noted that though all samples were polished with #600 grit paper and underwent the

same process, the increase in hardness and number of micro-particles resulting from the increased silicon amount make the true surface area quite different from that of the low silicon alloy, and comparisons should be made with caution.

The stannate solution did not have to be changed after each use, the tin deposits were consistently good even though the solution had been used many times. It should be noted that the arbitrarily chosen amount of potassium gluconate additive was only half of the amount normally used in studies by other researchers (0.01-0.25 mole/liter). When the stannate concentration is increased to 140 g/l, the useful life time of the bath is greatly shortened which indicates that the amount of potassium gluconate added may be too small. The amount of the potassium additive should be increased, especially when the stannate concentration is high. However, the relation between the amount of potassium gluconate needed and the potassium stannate concentration needs further investigation.

Since a tin layer forms on the die-cast alloy surface, aluminum is prevented from forming an oxide; the bronze strike can be eliminated, and direct Sn-Pb electroplating is possible. The blisters on the electroplated surface are caused by trapped hydrogen gas. When samples are put in the acidic Sn-Pb electroplating solution, the uncovered aluminum areas reduce the hydrogen ions to hydrogen gas which in part may be trapped within the porous tin layer and beneath the subsequent Sn-Pb electroplate. Thus the hydrogen trapped

beneath the electroplated layer can exert sufficient pressure to detach the electroplate layer, form blisters and/or rupture sites. For samples immersed in a stannate solution at an elevated temperature of 70°C, or for long periods of time, so as to produce a thick layer, the final electroplated samples are free of blisters provided that the porous tin coating is melted or "flowed" in an oil bath and "burnished". This ensures that there is no aluminum surface exposed to the acid attack of the electroplating bath. When samples are dipped in HNO₃-HF mixture, the silicon particles dissolve and leave deep pits on the surface, see Figs. 3 and 4. The results that high Si content alloys tend to have more blisters and that samples dipped in 50% by volume HNO₃ instead of the HF mixture have no blisters, suggest that the pits are most likely formed on the uncovered aluminum areas. These uncovered areas serve as cathodic sites on which the hydrogen ions are reduced so that the increase of silicon content increases the possibility of Al-hydrogen corrosion and results in more blisters.

In part F of results, the adhesion of Sn decreases as samples were immersed longer and the tin deposit grew thicker. When a sample was immersed for 120 minutes, the thickness of the tin layer is likely to be around 15,000 Å, and the porous structure breaks easily. The "oil flow" and "burnish" only smear the outer part of the tin layer, the porous structure does not change significantly, see Fig. 16.

Thus, the cohesive failure within the tin layer occurred at low pull strength, as is shown in Tables X and XI.

The adhesion between the Sn/Pb electroplate and the immersion tin layer seems quite strong. The present difficulty is to improve the properties of the immersion tin layer. The surface activity needs to be equalized to minimize the uncovered areas. A double stannate process may be useful in equalizing the different activities on areas of the surface. It is also important to avoid the porous structure of the tin layer. "Burnishing" which compresses the surface seems to be a suitable technique for this purpose. However some improvement in the technique is needed because burnishing can scratch the surface and leave some bare areas. Possibly samples immersed for less than 10 minutes at room temperature can be burnished after having been electroplated for 1 or 2 minutes, and then electroplated again.

This study shows that the stannate plating process, followed by Sn/Pb electroplating, is a promising technique. The stannate solutions have a long useful life time, and need little care. Furthermore, the resulting electroplated Sn-Pb layer is fine grained. From other experience, the common Sn-Pb fluoroborate bath [23] should give results similar to the proprietary Sn-Pb plating solution. An optimization study should be carried out to determine the best electroplating parameters and the stannate bath

compositions. Thus far an adhesion strength of about 1,000 psi has been achieved for a 60/40 weight % Sn-Pb electroplate onto an immersion tin surface. With some modifications, the adhesion should be improved, and the blisters eliminated. Based on this study, a stannate pretreatment followed by a direct electroplating from a Sn/Pb fluoroborate solution on a Zn-Si die-cast aluminum alloy is feasible.

BIBLIOGRAPHY

1. S. Heiman, J. Electrochem. Soc., 95(5), 205(1949).
2. B. A. Shenoi, Metal Finishing, 64(6), 101(1966).
3. D. S. Lashmore, Plating and Surface Finishing, 65(4)
44(1978).
4. F. Keller and W. G. Zelle, J. Electrochem. Soc., 97(4)
143(1950).
5. A. E. Wyszynski, Trans. Inst. Metal Finishing, 45(4)
147(1967).
6. L. D. Brown, Trans. Inst. Metal Finishing, 56(4)
141(1978).
7. R. Satee, Product Finishing, 43(9), 46(1979).
8. B. C. Schwartz and J. B. Newkirk, Plating, 59(5), 431
(1972).
9. D. S. Lashmore, Metal Finishing, 78(4), 21(1980).
10. M. M. Goldberg, Plating and Surface Finishing, 65(6)
42(1978).
11. J. C. Jongkind, Trans. Inst. Metal Finishing, 45(4)
155(1967).
12. E. S. Seyb, J. C. Jongkind and L. P. Gowman, Tech.
Proc., AES, 133-8 1964.
13. J. C. Jongkind and P. G. Kendi, U S Patent 3,274,021
1966.

(continue)

14. J. C. Jongkind, *Plating and Surface Finishing*, 62(12) 1135(1975).
15. G. A. DiBari, *Plating and Surface Finishing*, 64(5) 68(1977).
16. W. G. Zelle, *J. Electrochem. Soc.*, 100(7), 328(1953).
17. A. H. Beebe, Jr., B. F. Rothschild and G. J. Lebrasse, 43rd annual Tech. Proceedings, AES, 164(1956).
18. A. H. Beebe, Jr., Symposium on Plating on Difficult-to-Plate Metals, AES, 22-33 1980.
19. E. Acher, *Plating and Surface Finishing*, 68(6), 12 (1981).
20. K. Bhasin, W. J. James, et al, *Thin Solid Films* 45 195(1977).
21. B. D. Cullity, "Elements of X-Ray Diffraction," p.292 2nd. Ed., Addison-Wesley Co. Inc..
22. W. J. James, "Advances in Corrosion Science and Technology", p133, vol. 4, Plenum Press, 1974.
23. N. J. Spiliotis, *Metal Finishing Guide*, p268, 46th Ed., 1978.

VITA

Ann-Tinn Shen was born on Oct. 3, 1956 in Lowtung Taiwan. She received her primary and secondary education in Lowtung, Taichung and Taipei. She received a Bachelor of Science degree in Chemistry from National Tsing-Hua University in Hsinchu in June 1978.

She has been enrolled in the Graduate School of University of Missouri-Rolla since August 1978.

APPENDIX A

X-RAY DIFFRACTION DATA FOR ALUMINUM AND BETA-TIN.

<u>d</u>	<u>I</u>	<u>hkl</u>
2.34	100	111
2.02	47	200
1.43	22	220
1.22	24	311

Aluminum

<u>d</u>	<u>I</u>	<u>hkl</u>
2.92	100	200
2.79	90	101
2.06	34	220
2.02	74	211
1.48	23	112
1.44	20	321
1.21	20	312

Beta-tin

APPENDIX B

CALCULATION OF TIN THICKNESS VS. X-RAY ABSORPTION.

$$G = 1 - \exp(-2\mu x / \sin\theta)$$

$$\text{Absorption coefficient} = \mu/\rho \times \rho$$

For S_n of Cu K_α radiation:

$$\mu/\rho = 253.3 \text{ cm}^2/\text{g} \text{ for } \rho = 7.29 \text{ g/cm}^3$$

$$\mu = 1,847 \text{ cm}^{-1}$$

$$\text{For } 2\theta = 30.6^\circ, \sin\theta = 0.2639$$

$$\text{When } x = 1,200 \text{ \AA} = 0.12 \text{ }\mu\text{m}$$

$$G = 1 - \exp(-1847 \times 1200 \times 10^{-8} / 0.2639) = 0.155$$

$$G_{\text{sample}} = G_{\text{std}} \times \left(\frac{\text{Peak area of sample}}{\text{Width of sample}} \right) \times \left(\frac{\text{Width of std}}{\text{Peak area of std}} \right)$$

$$x_{\text{sample}} = \ln(1/1-G_{\text{sample}}) \times (\sin\theta/2\mu)$$

x(μm)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
G	0.13	0.24	0.34	0.43	0.50	0.57	0.62	0.67
x(μm)	0.9	1.0	1.2	1.5	1.75	2.0	2.25	2.5
G	0.72	0.76	0.82	0.88	0.92	0.94	0.96	0.97