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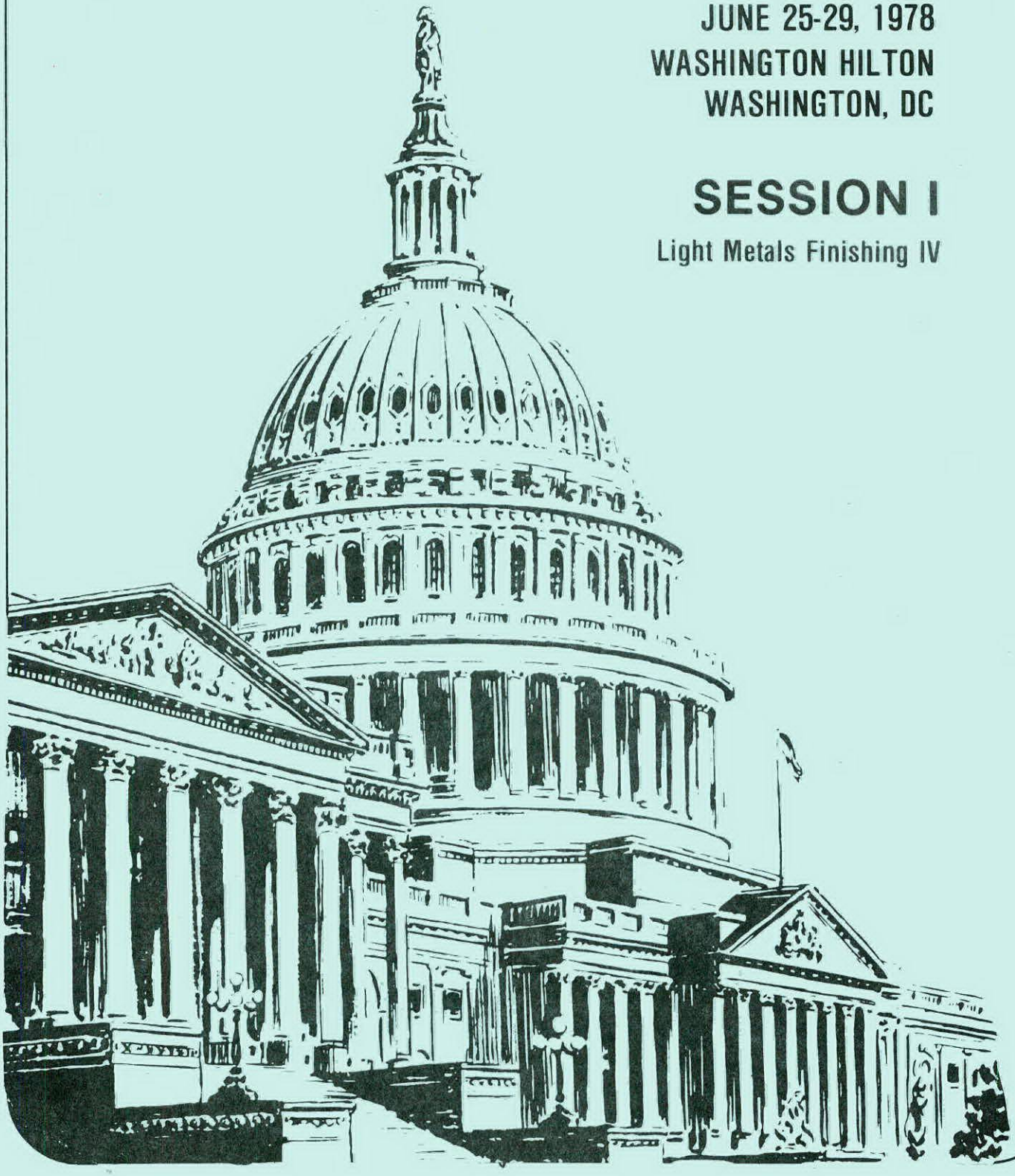
SESSION I

Light Metals Finishing IV



AMERICAN ELECTROPLATERS' SOCIETY, INC.

65TH ANNUAL TECHNICAL CONFERENCE -- WASHINGTON, D.C.

PROCEEDINGS -- SESSION I

"LIGHT METALS FINISHING IV"

Included in this proceedings:

"Bright Chrome Plating of High-Strength Bumper Alloys"

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Richmond, VA

"Electroplating on Aluminum via Controlled Dissolution of Zincate Film"

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BRIGHT CHROME PLATING OF HIGH STRENGTH BUMPER ALLOYS

By

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INTRODUCTION

The automotive industry is currently undergoing perhaps the most rapid change in its history. Faced with federally mandated requirements (Table 1) for increased fuel economy each model year until 1985, when the fleet average must equal 27.5 miles per gallon, the industry is taking every feasible means to effect a weight reduction in its entire fleet. Making such weight reductions more difficult are federal safety and emission standards, which tend to increase weight.

In addition to down-sizing, the industry has responded by expanding their use of high strength to weight ratio materials. The high strength bright anodized aluminum bumper was introduced in 1972 and its use has expanded ever since.

Table 2 lists the major reasons why aluminum bumpers are finding widespread application. In addition to the bright anodized bumper, the automotive industry is vitally interested in bright chrome-plated aluminum bumpers. Consequently, there is currently an extensive R&D effort in the aluminum industry to develop plating practices and processes for the various bumper alloys.

Figure 1 shows a bright anodized bumper on the car at the left and a chrome-plated aluminum bumper on the right. One major auto maker has predicted that by the early 80's all its bumpers will be aluminum; those on mid-size and larger cars will be chrome plated, while those on compacts and smaller sizes will be anodized.

Currently, the bright anodized X7029 alloy (Tables 3 and 4) extruded bumper is used on the Pinto, (80# less than 76 steel), Fairmont and Zephyr.

PRETREATMENT AFFECTING PLATE ADHESION

It is doubtful if anyone has ever touched an oxide-free aluminum surface or even seen one. Oxide-free aluminum surfaces do not exist except in an absolute vacuum. The aluminum surface we perceive is not aluminum but aluminum oxide. Aluminum is electrochemically a very active metal, and readily combines with any oxygen present forming a compact, continuous coating of Al_2O_3. This ever-present natural oxide film, 10-150 Å thick, is responsible for aluminum's excellent corrosion resistance, protecting the bulk aluminum from the environment with a relatively inert coating that is self-healing. However, this oxide coating is also largely responsible for the difficulty in achieving adherent electrodeposits, by preventing intimate interatomic contact between the aluminum and the first plated metal.

The electrode potential of bare aluminum with reference to a hydrogen electrode is -1.66 volts[1]. Observing this sign convention, the potential of an oxide-coated aluminum surface would be greater or more noble. Therefore, the electrode potential of an aluminum surface in an appropriate electrolyte is a measure of the oxide thickness in that electrolyte. The closer the potential to -1.66 volts, the thinner the oxide coating. Table 5 shows the peak electrode potential observed for X7029T6 alloy aluminum immersed in various electrolytes at 25°C for 5 minutes, measured with a saturated calomel electrode and corrected to hydrogen by adding +.244 volts[2].

The two best electrolytes for removing oxide are seen to contain the OH ion and the F ion. It is no coincidence that historically the best pretreatments for aluminum were based on solutions containing sodium or potassium hydroxide or hydrofluoric acid.

Any plating process for aluminum must substantially remove the oxide film or otherwise negate its normally negative effect on adhesion. Of course, other factors such as aluminum's relative position in the electromotive series with respect to the plating bath metal, their respective crystal structures, atomic diameters and mutual solubilities, also may play a roll in adhesion, but

the removal of the oxide coating is of foremost important. Pre-treatments prior to the critical oxide-removal step, such as degreasing, chemical brightening, etching and desmuting, all followed by water rinsing, have essentially no influence on adhesion other than the mechanical effect due to surface roughness. The oxide film, even if essentially removed by any of these treatments, immediately reforms upon water rinsing.

Table 6 outlines the more significant events in the historical development of plating on aluminum. These processes, except those based upon anodizing, rely on the removal of the oxide film by chemical dissolution and the protection of the aluminum surface from re-oxidation by a chemically deposited coating of zinc or tin. In the case of tin, additional protection is gained by proceeding to an electrolytic strike without rinsing. The anodizing processes rely on building a relatively thick and porous aluminum-oxide coating which anchors or "keys" a subsequent electrodeposit. The first attempts to achieve a metallurgical bond between the atoms of the substrate and the deposit while the latter relies on mechanical bonding through the relatively large anodic pores.

Three of the processes mentioned above are still being investigated for plating aluminum bumpers. Table 7 outlines some of the advantages and disadvantages of each process. The phosphoric anodizing process, as normally practiced, proved inadequate for 7XXX alloys, and inconsistent results were obtained.

The zincate process, the most widely used process for plating aluminum, proved to have a corrosion problem, in corrosive environments, once the top plate had been cracked or penetrated. The zinc film behaves anodically and lateral corrosion of the zinc layer occurs resulting in lifting of large areas of the top plate. A modification of this process to combat this problem has been introduced by a major aluminum company.

The stannate process, currently the most promising due to its good corrosion resistance, utilizes a deoxidation or "activation" treatment in an alkaline tin solution either with or without current and then proceeds to a cyanide-bronze strike solution without an intermediate rinse.

Stannate Pretreatment

Table 8 gives the processing sequence used for stannate preplate conditioning. Early in our evaluation of this process, a so-called "pitting" problem developed. What appeared to be fine pitting became visible after nickel plating. On closer inspection, the problem turned out to be fine roughness. Metallographic and microprobe analysis showed the roughness to be due to nodules of bronze, from the strike, on the surface. The visibility of these nodules was magnified by subsequent plating.

The source of the problem was traced to the alkaline etch-desmut operations. Substitution of a mild alkaline etch followed by a fluoride-free desmut completely solved the problem. Table 9 gives our recommended desmut formulation which is now included as standard practice by the propriatary product supplier[3].

As shown in Table 8, the transfer between the tin activation step and the bronze strike is carried out without an intermediate rinse. This guards against re-oxidation during the rinse, but can cause a problem if the transfer time exceeds 10-15 seconds. In some plating lines, the transfer from one tank to another can take as long as 45 seconds. This has resulted in a serious problem. The upper areas of the plated work developed non-adherent dark deposits of tin during transfer, resulting in blistered deposits of bronze. Figure 2 illustrates the problem encountered after a 45-second transfer on alloy X7029T6.

A further development, by the supplier of the commercial product, was introduced to alleviate this problem. It does increase the acceptable transfer time for most alloys; however, 7029 alloy still exhibited the problem for transfer times above 15-20 seconds. Our work, concentrating on X7029 alloy, has resulted in a further modification of the stannate formulation called the DS-35 process[4], which allows at least a one minute transfer for X7029T6, without problems. Transfer times as long as two minutes have been accomplished in the lab. Figures 3 and 4 show a X7029T6 panel after one minute transfer and bronze strike.

Figures 5 and 6 show SEM micrographs (1000X and 5000X) of the tin deposit made by Dr. Lashmore during his work on AES

Project 41. This is a joint program with the Aluminum Association, to study the fundamental aspects of plating on aluminum[5]. He has shown that extremely fine grained (10-80 Å) tin completely covers the surface. Another problem common to all electroplating processes and alloys, is shown in Figure 7. The closed-in-box design of most aluminum bumpers results in poor or non-existant plating on the back side of the bumper. There are two adverse effects of this; contamination of the plating baths with dissolved aluminum and potential corrosion problems in service on the back side. This problem is being attacked from a masking standpoint. Current efforts in all affected industries, are to mask the back side before plating with an organic coating for protection both during plating and in service.

PHOSPHORIC-ACID ANODIZING

As mentioned previously, initial attempts to plate 7XXX alloy bumper material following a phosphoric-acid anodize, resulted in inconsistent adhesion.

Anodizing, as a pretreatment for plating, relies on producing a thick and porous oxide coating which serves to lock the electrodeposit within the anodic pores. A successful anodic pretreatment, then, must meet two criteria; a measureably thick-oxide coating must be produced and a consistently large pore volume obtained.

Our work to date indicates that the inconsistent results obtained over the years with phosphoric-acid anodizing, is due to one or the other of these criteria not being met. Anodizing, in general, and phosphoric-acid anodizing, in particular, is alloy sensitive. Therefore those anodizing conditions suitable for say 6061 are not necessarily suitable for 7029 or 7046. The electrolyte concentration, temperature, current density, and anodize time must be adjusted so that the two criteria are met for a particular alloy.

Our work indicates that with the concentration and temperature suitably adjusted, the current density and anodize time must be such that a limiting film thickness is achieved. Figure 8 depicts the relationship between limiting film thickness (LFT) and increasing current density (CD) and time. Consistently good adhesion has been obtained with alloys 7029 and 7046 after a watts-nickel plate, i t

anodizing is allowed to proceed to a limiting film thickness plateau.

Table 10 shows typical anodizing conditions seen in the literature and the modified conditions used in our investigation. Phosphoric concentration and temperature are kept low to reduce the dissolution action of the electrolyte on the 7XXX alloys and allow a measurably thick coating to develop. Current density and time are adjusted to insure that a limiting film thickness has been reached.

Figure 9 is a metallographic cross section at 1500X showing the substrate at the top and watts nickel at the bottom. The anodic film is seen to be permeated by nickel. Figure 10 is a scanning electron microscope image of nickel in the film at 10000X. Again the aluminum substrate is at the top (dark area). Figure 11 is the same film at 20000X. Figure 12 shows an analytical trace for nickel (top) and oxygen, proceeding from the aluminum substrate at left, through the anodic film into bulk nickel. The relativity high saturation of nickel in the anodic film is evident both from the increasing nickel content and decreasing oxygen content.

It appears good adhesion is possible for 7XXX alloys using phosphoric-acid anodizing and this process is a viable non-cyanide alternative for plating aluminum bumpers.

TYPICAL TOP PLATE

A typical plating sequence for aluminum bumpers is illustrated in Table 11. A cyanide copper strike following the bronze strike is perhaps not essential; however, it will prevent the formation of chemical displacement films deposited from more concentrated copper solutions and enhance and protect the bronze strike from attack in subsequent acid-plating solutions.

Bright acid copper is useful in two respects. First, it offers excellent leveling and fills surface pores and inside corners (Figure 13)*. Secondly, when damaged, the crack tends to proceed through the nickel layer but is stopped by the ductile copper, thus offering corrosion protection to the substrate (Figure 14)*.

*AES Slide

The combination of copper, duplex nickel, and chromium exhibits better ductility than copper, bright nickel and chromium. Due to its higher purity, semibright nickel is more resistant to corrosion than bright nickel.

Microdiscontinuous chrome is usually preferred because of its corrosion resistance. The total top plate is depicted in Figure 15*.

CONCLUSION

The aluminum industry has responded to the automakers need for strong, light-weight, corrosion-resistant aluminum alloys for bumpers. Work currently underway, in the several affected industries, seems certain to answer the need for a multitude of viable plating processes for aluminum. The stannate process and its modifications seem to best answer the current needs of the auto industry, but current developments in both the zincate and phosphoric anodize processes show them to be potential alternatives.

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* AES Slide

REFERENCES

1. Handbook of Chemistry and Physics, The Chemical Rubber Company, 43rd Edit., p. 1740.
2. The Encyclopedia of Electrochemicstry, C. A. Hampel, Reinhold Publishing Corporation, 1964, p. 1014.
3. Tentative Technical Data Sheet, Alstan XP-231 Process, M&T Chemicals Inc.
4. DS-35 Stannate Pretreatment, Reynolds Metals Company.
5. D. S. Lashmore, "Microstructural Investigations of Immersion Deposits on Aluminum and Preliminary Peel Test Results", Progress Report No. 2, February 21, 1978.

TABLE 1

CAFE

1978 - 18 MPG	1982 - 23 MPG
1979 - 19 MPG	1983 - 24.5 MPG
1980 - 20 MPG	1984 - 26 MPG
1981 - 21.5 MPG	1985 - 27.5 MPG

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TABLE 2

ADVANTAGES OF ALUMINUM BUMPERS

. Weight Reduction (1# Al. = 2.25# saved)

. Fuel Economy

. Hi Strength/Weight for impact

. Formability

. Corrosion Resistance

TABLE 3

X7029 ALLOY

COMMERCIAL COMPOSITION

0.10% Max. Si	0.5-0.9% Cu
0.12% Max. Fe	1.3-2.0% Mg
0.03% Max. Mn	4.2-5.2% Zn
0.03% Max. Ti	0.03% Max. others ea.
	0.10% Max. others tot.

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TABLE 4

X7029 ALLOY

Commercial Forms - Ext. - Sheet

Thickness Range - .100" - .250"

Corrosion Resistance - Mild Pit.

Brinnel Hardness - 127 Avg.

UTS (T6) - 62 KSI

YS (T6) - 55 KSI

TABLE 5

PEAK ELECTRODE POTENTIALS

Sol'n	Volts	Sol'n	Volts
.1M KOH	- 1.48	.1M H_3PO_4	- .28
.1M NH_4OH	- 1.28	.1M H_2SO_4	- .26
.1M HF	- .99	3% $(NH_4)_2C_4H_4O_6$	- .23
.1M KF	- .98	Hot Water	- .13
.1M HCl	- .55	CrO_3/H_3PO_4	- .12
CrO_3/F	- .30	.1M HNO_3	- .12

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TABLE 6

PLATING PROCESSES FOR ALUMINUM

. First Patent - 1896 - England
. Immersion Tin - 1903 - England
. Immersion Tin - 1904 - France
. Immersion Tin - 1915 - U.S.
. Zincate - 1927 - U.S. Pat. 1,627,000
. Phosphoric Anodize - 1934 - Fisher Process
. Oxalic Anodize - 1934 Krome Alum Process
. Dbl. Zincate - 1939 U.S. Pat. 2,142,564
. Stannate - 1965 - Alstan Process

TABLE 7

CANDIDATE PROCESSES FOR

PLATING ALUMINUM BUMPERS

PROCESS	ADVANTAGES	DISADVANTAGES
Stannate	Corrosion Resistance	Cyanide
	Commercial	Propriatary
Zincate	Simple	Poor Corr. Res.
	Non-Propriatary	Cyanide
Phos. Anod.	Non-Cyanide	Inconsistant Adh.
	Non-Propriatary	Addit. Equip.

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TABLE 8

PRE-PLATE CONDITIONING

- Buff
- Alkaline Degrease
- Mild Alkaline Etch
- Desmut
- Tin Activate
- Transfer Without Rinse
- Bronze Strike - Hot Entry
- Acid Rinse
- Plate

TABLE 9

ACID DESMUT

Standard	Recommended
60% HNO_3	20% H_2SO_4
30 g/l NH_4HF_2	10% Vol. H_2O_2

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TABLE 10

PHOSPHORIC-ACID ANODIZING

7XXX ALLOYS

	Typical	Recommended
H_3PO_4 Conc.	25-50% Vol.	25% Vol.
Temperature	75-100°F	70-80°F
Current Density	10-30 ASF	10-20 ASF
Time	5-15 Min.	10-20 Min.

TABLE 11

BUMPER PLATING PROCESS

. Stannate Pretreatment

. Cyanide Copper Strike

. Acid Rinse

. Bright Acid Copper - .6 mil. min.

. Semi-Bright Nickel

. Bright Nickel - 2.0 Mil. Min. total Ni

. Microdiscontinuous Chrome - .01 Mil. Min.

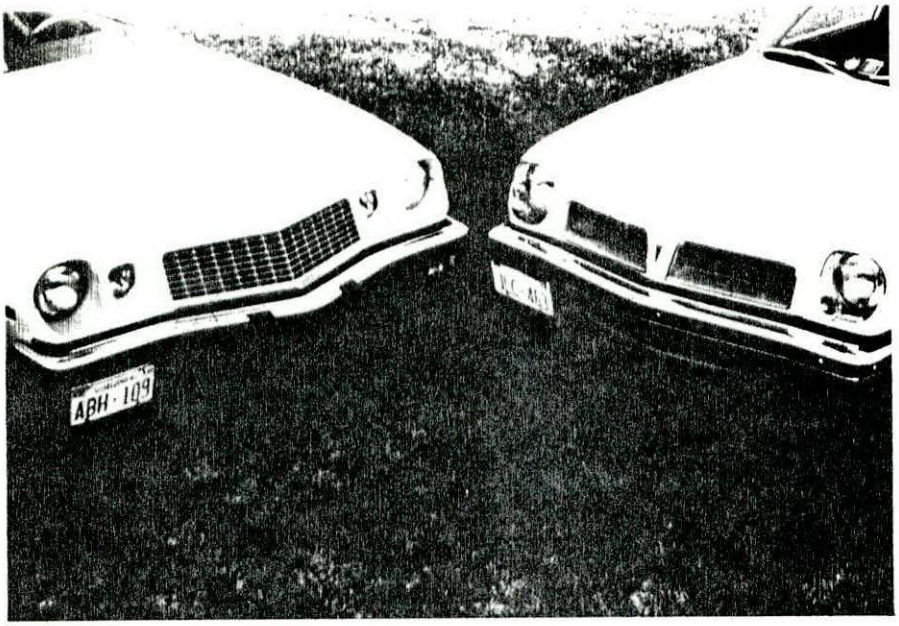


FIGURE 1

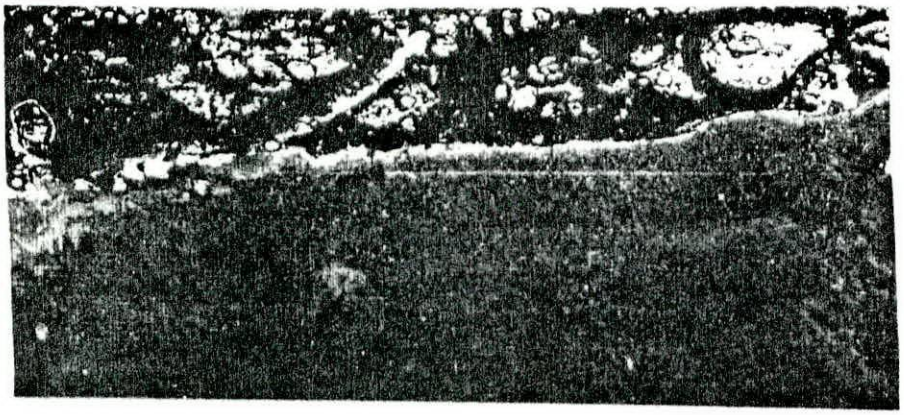


FIGURE 2

FIGURE 3

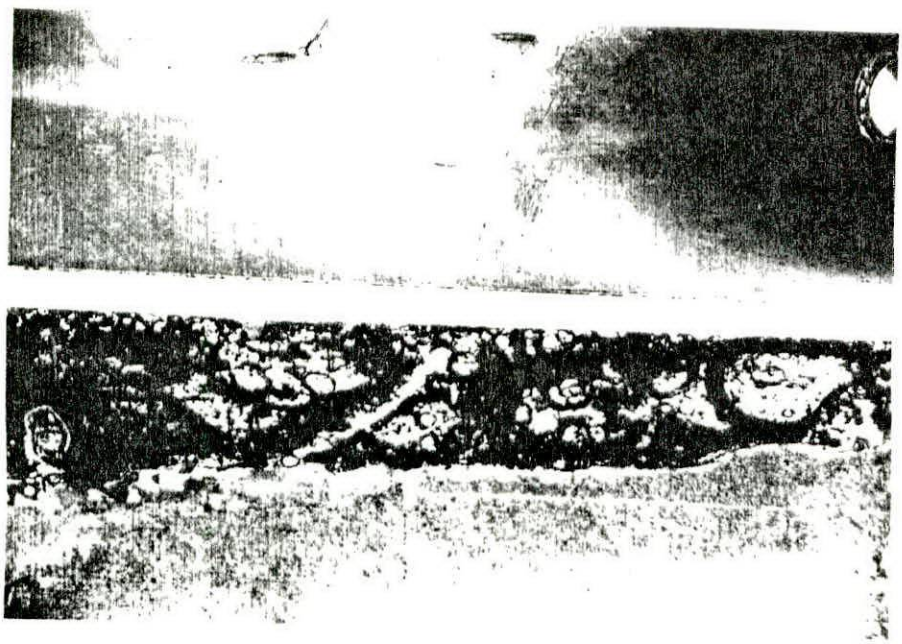


FIGURE 4

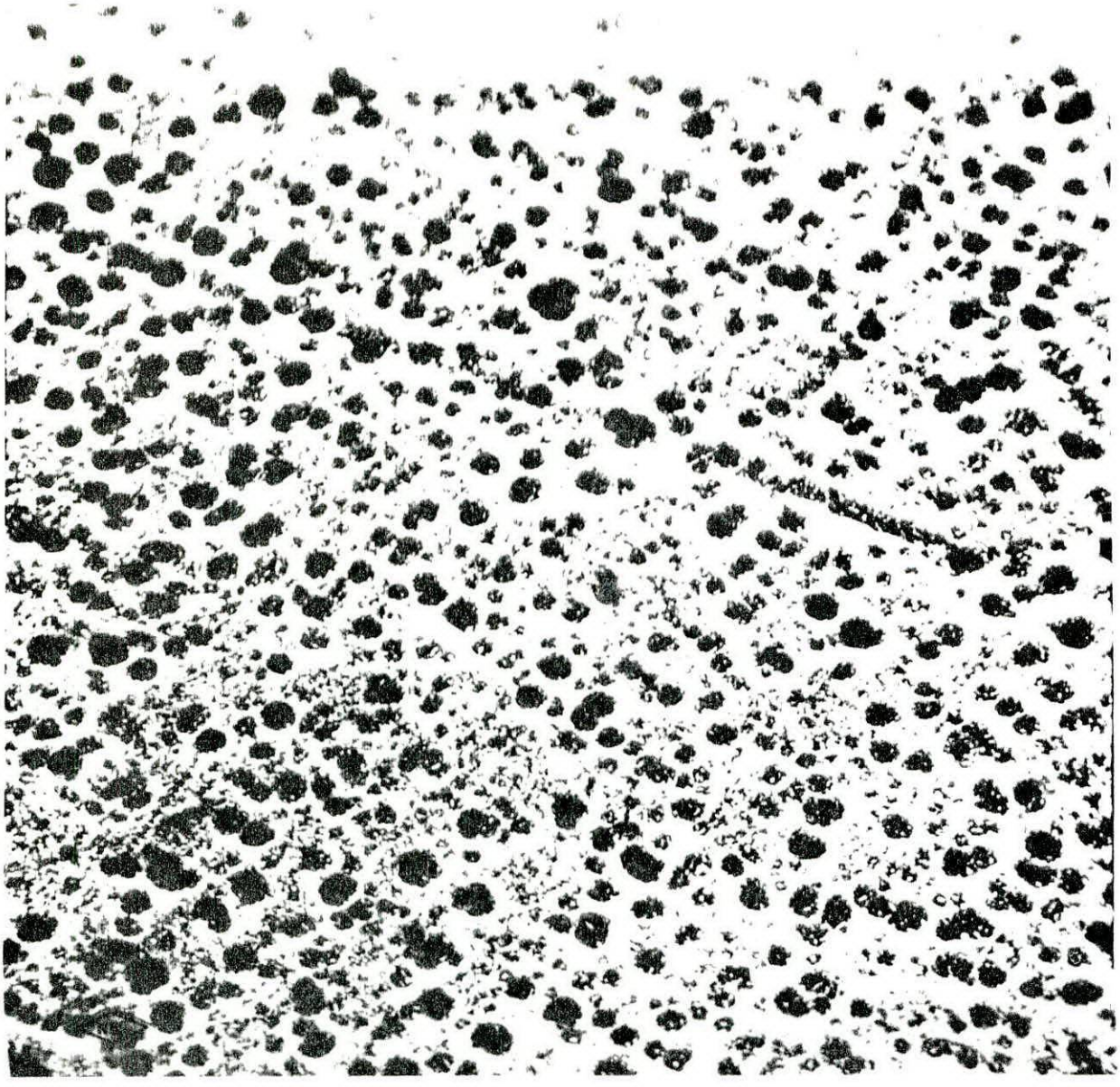


FIGURE 5

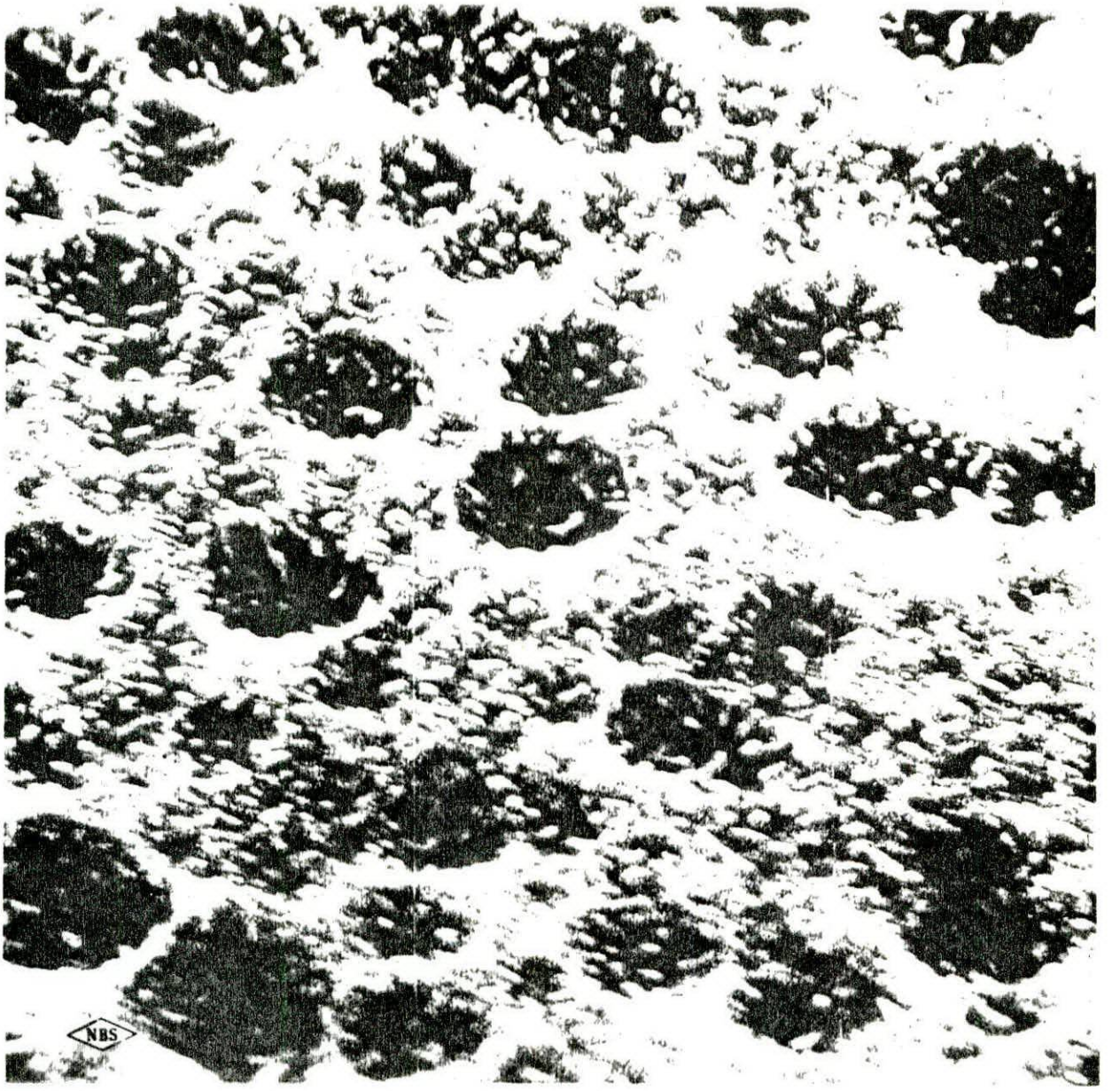


FIGURE 6

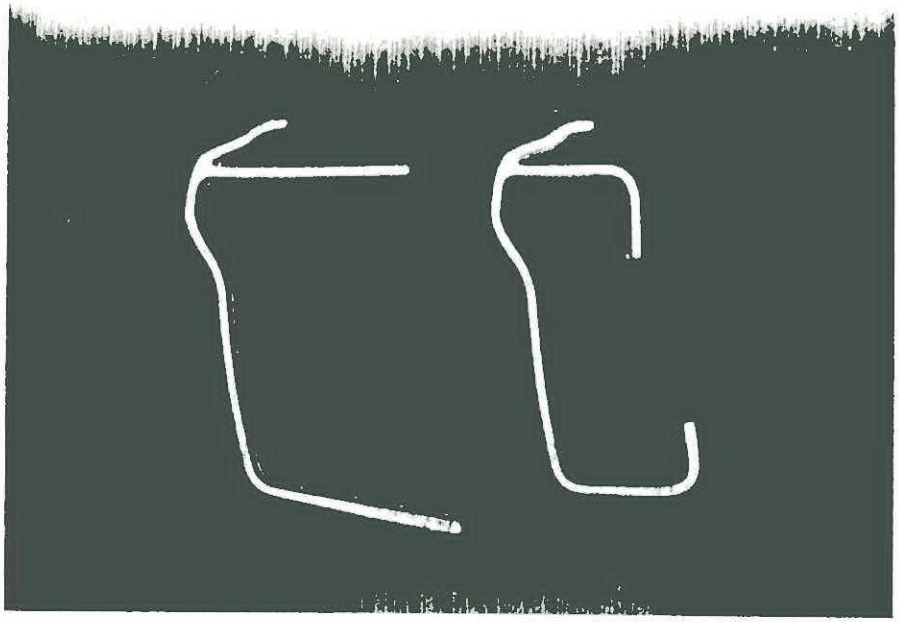


FIGURE 7

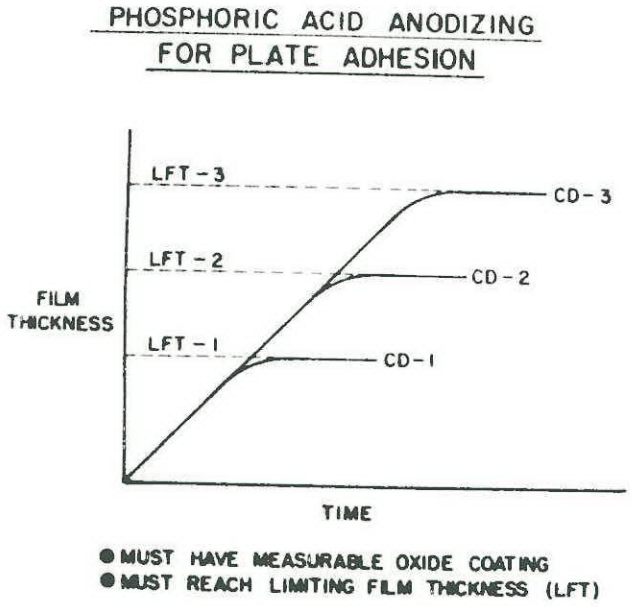
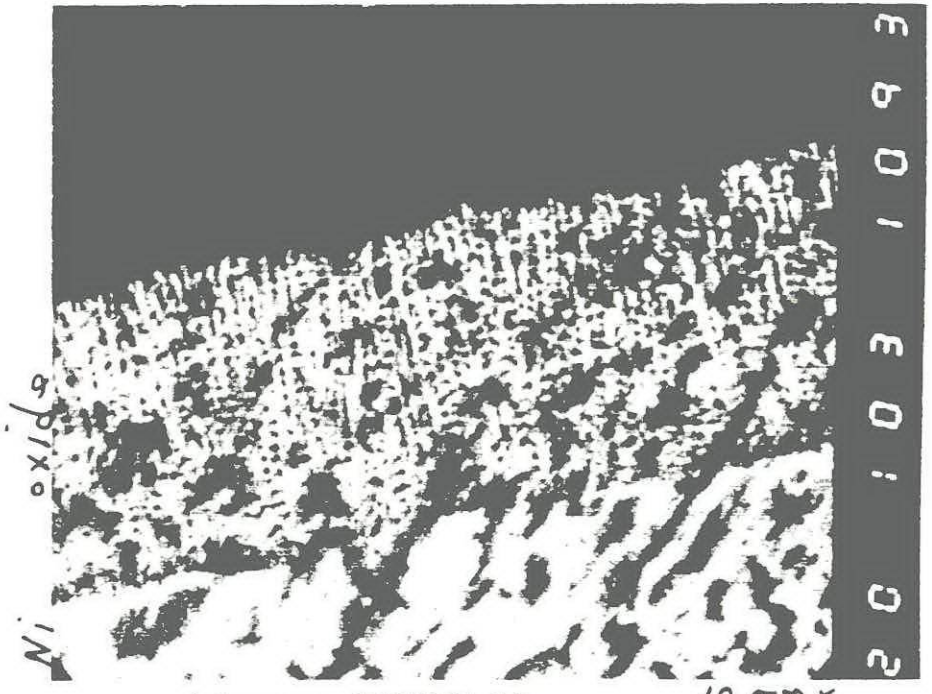


FIGURE 8

1500x

FIGURE 9

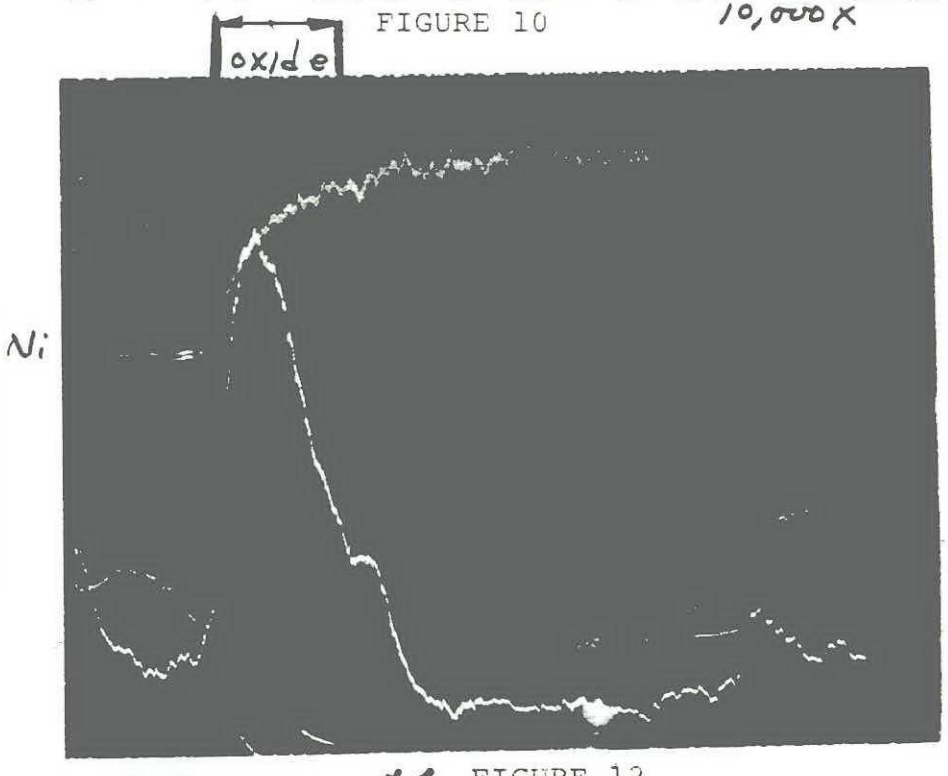


10,000x

FIGURE 10

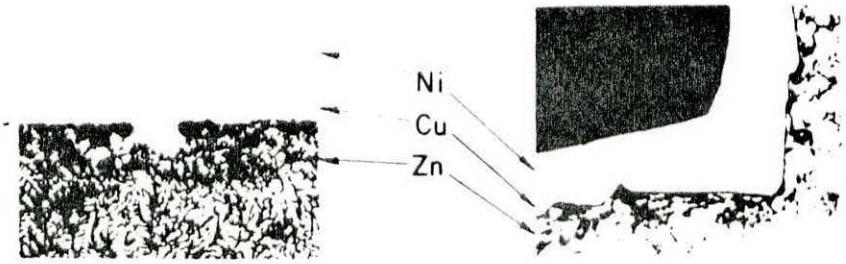
20,000x

FIGURE 11



5000x

#1 FIGURE 12



BRIGHT LEVELING COPPER PLATED IN ACID COPPER SULFATE BATH FILLS SURFACE PURES AND INSIDE CORNERS

FIGURE 13

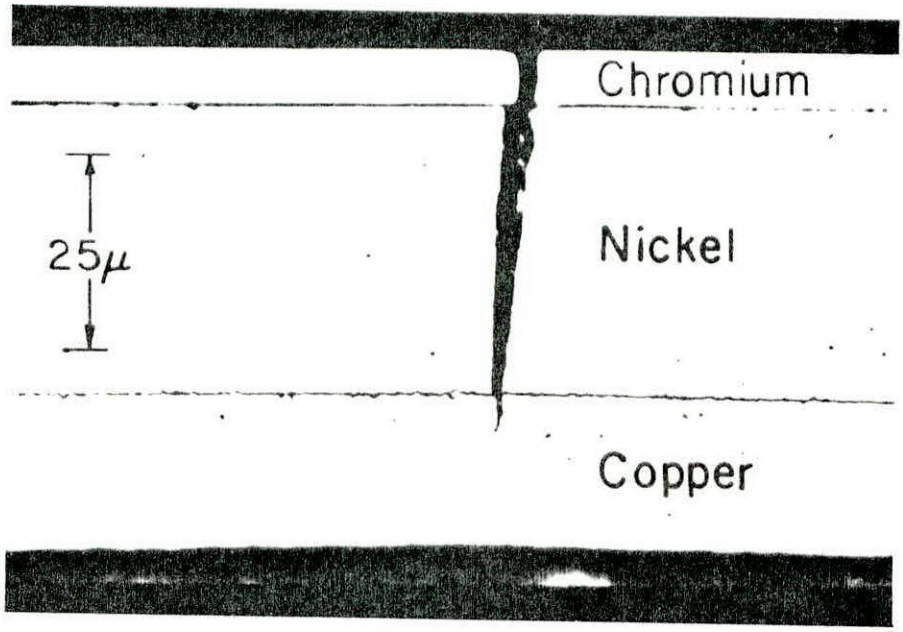


FIGURE 14

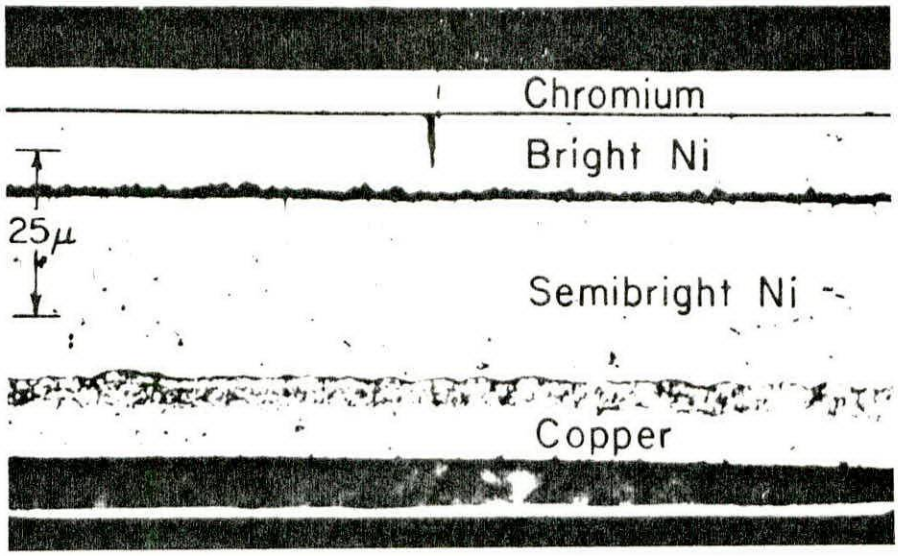


FIGURE 15

ELECTROPLATING ON ALUMINUM VIA CONTROLLED DISSOLUTION OF ZINCATE FILM*

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ABSTRACT

An improved pre-electroplating process[1] for aluminum results in good adhesion and protective qualities of electrodeposits on a wide range of aluminum alloys. Cyanide solutions are not required and use of an intermediate copper layer is optional. Potential curves and surface analyses show that an initial zinc alloy immersion film is displaced by nickel in a low chloride strike bath. Corrosion tests predict adequate performance of decorative nickel/chromium plate on automotive bumper alloys.

PRE-ELECTROPLATING PROCESSES

The current interest in using aluminum automobile bumpers for weight reduction has spurred renewed interest in procedures for decorative nickel/chromium electroplating on aluminum alloys. Direct electroplating of metals on aluminum is hindered by its great affinity for oxygen, resulting in an ever-present "natural" oxide film that usually precludes adequate plate adhesion. To overcome this problem, various pre-electroplating processes were developed over the years. Zinc immersion, one of the earliest processes, has predominated and

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continues to find wide application due to its good performance with a wide variety of aluminum alloys. The alkaline zincate bath dissolves the oxide film on aluminum while simultaneously depositing in its place a thin layer of zinc that provides for good adhesion of subsequent electrodeposits. Several variations of the zinc immersion treatment were developed--concentrated and dilute zincate baths, modified baths, e.g., the addition of iron and Rochelle salt, and the double zinc immersion treatment in which a first zinc deposit is dissolved, followed by application of a second immersion deposit to give a more uniform zinc layer[2]. Proprietary zincate bath formulations have been available for many years and are currently in use.

Anodic oxide coatings formed in phosphoric acid containing electrolytes have been advocated as a pre-electroplating treatment for aluminum[3] and still are being investigated as a potential commercial procedure. Electrodeposited metal is anchored in the highly porous anodic coating.

The Alstan Process[4], tin activation followed by a cyanide bronze strike, gives good results in commercial production. It provides improved performance, compared with the conventional zincate processes, in corrosive environments where the nickel/chromium electrodeposit is intentionally damaged to substrate metal[5]. The first commercially produced-plated aluminum bumpers employ the Alstan pre-electroplating process, which is currently a preferred process for such applications.

CONTROLLED DISSOLUTION OF ZINC FILM (ALCOA 661 PROCESS)

A potential disadvantage of the zincate process is that in many environments, zinc is anodic to both the electrodeposited overplate and the aluminum alloy substrate. Consequently, when the electroplate is ruptured to basis metal, undermining type corrosion can occur, resulting from sacrificial dissolution of the zinc layer. This produces localized lifting or blistering of plate adjacent the damage site. The effect tends to be more pronounced as the thickness of the zinc layer is increased. It was shown that when the zinc film is kept thin and compact, the undermining effect is minimal[6].

Since the zinc immersion process has shown good applicability to a wide range of aluminum alloys, work was undertaken to avoid the undermining corrosion effect of the zinc film. This work led to development of the Alcoa 661 Process whereby an initial zinc immersion deposit is substantially replaced by a nickel layer upon which well-adhering deposits of other metals can be electroplated. A further incentive in developing this process was to provide electroplaters with the option of a cyanide-free plating process. With the Alcoa 661 Process, a cyanide copper strike or other cyanide solutions are not required.

The process (Table I) is carried out employing conventional precleaning, etching and zinc immersion treatments. After rinsing the zincated work, it is immersed in a nickel sulfate-boric acid electrolyte for a specified period of time to start

dissolution of the zinc layer and its replacement with nickel. The immersion dwell time depends on the nickel bath temperature and pH. It is typically from 15 to 45 seconds. When the potential difference between the zinc coated aluminum and the nickel electrode falls approximately 200 mV below the initial value, the external plating circuit is activated to electrodeposit nickel on the aluminum cathode. The zincated aluminum must not be allowed to remain too long in the bath before commencing electrodeposition of nickel. Otherwise, a passivation reaction occurs which interferes with the formation of a good metal-to-metal bond. During application of the external potential, galvanic displacement of nickel from solution by zinc continues until the zinc deposit substantially disappears. Typically, this is accomplished within about 2 minutes of applied potential, during which time approximately 1 μm of nickel is deposited. The surface of the work is now essentially a nickel electrode, ready for further electrodeposition of the desired, total plate system. Figure 1 shows a fracture cross-section of the Alcoa 661 nickel strike layer on an aluminum bumper sheet alloy. The fractured cross-section of the nickel layer and its nodular-appearing top surface are apparent.

VERIFICATION OF CONTROLLED DISSOLUTION OF ZINC

The replacement of the zinc deposit with nickel was investigated by making microprobe surface analyses of test specimens removed after various times of immersion in the nickel strike bath (Table II). Also, the potential difference between

the specimen, which behaves initially as a zinc electrode, and the nickel electrode in the strike bath was monitored. The results are plotted in Figure 2. Weight percent values shown are relative, not absolute, owing to the penetrating effect of the microprobe beam into the aluminum substrate. As immersion time is increased, the surface zinc decreases rapidly at first then levels off to a minimum value. Nickel, on the other hand, increases with immersion times up to about 45 seconds, showing that nickel is replacing zinc on the surface.

The cell voltage versus time curve shows an initial potential difference of nearly 500 mV between the zinc coated aluminum and the nickel electrode. After a few seconds, the cell voltage represents the potential difference between a mixed electrode (Zn + Ni) versus nickel. The potential difference then decreases at a slightly greater rate with time as the electrode becomes richer in nickel. Once the aluminum substrate becomes covered with nickel at about 2 min. immersion time, the potential difference drops to zero. The slight positive potential of the curve, followed by its reversion to slightly negative may be due to nonequilibrium conditions from development of a passive Ni-NiO-Al_2O_3 film composition. The immersion has been carried too far at this point to obtain a good metal-to-metal bond.

Dissolution of the zinc film and its replacement with nickel was further studied by Auger Electron Spectroscopy analyses. Depth profiles were made by sputtering with argon ions into the surfaces of test specimens representing different

stages in the Alcoa 661 Process (Figure 3). High purity aluminum sheet was employed as the substrate to eliminate alloying elements. The sputtering depths indicated in nm are hypothetical, based upon a calibrated sputtering rate for aluminum oxide. The actual depths may be about one third those shown. Figures 3a and 3b show depth profiles made from the surface into the aluminum substrate. Both zinc and iron were deposited from the modified zincate bath. Figures 3c and 3d show portions of the profile in the vicinity of the deposit/substrate interface. The portions of the profiles from the outer surface of the nickel deposit, through most of the nickel are not shown. Figures 3a and 3b support the observations from the microprobe results that during the initial immersion period of zincated work in the nickel strike bath, zinc is dissolving and being replaced by nickel. Figure 3c shows that shortly after applying the external potential, zinc and iron continue to dissolve while nickel is being electrodeposited. Figure 3d indicates that after 2 min. of applied potential, zinc and iron are substantially absent leaving a nickel/aluminum interface. Some oxide is present at the aluminum interface during the nickel strike and appears to peak with the iron (fig. 3c), but is substantially gone upon completion of the strike (fig. 3d). Interestingly, these profiles show that the iron deposited from the modified zincate bath lays down ahead of the zinc, i.e., the iron concentration peaks at a greater depth than the zinc. The role played by iron in the process is unclear at this time. Tests demonstrate that to obtain good electroplate adhesion when

employing the Alcoa 661 Process with decorative nickel/chromium deposits, a modified zincate bath containing iron must be used. Poor adhesion results when the iron is omitted.

ADHESION OF ELECTRODEPOSITS

Tests such as the grind-saw, file, bend and impact tests of ASTM Method B571 made on both laboratory samples and full-size bumpers with decorative nickel chromium plate over the Alcoa 661 pretreatment show that excellent adhesion is obtained. Although such tests are highly subjective they do show that failure produced (with difficulty) by tearing off the plate is by fracture of the aluminum alloy substrate and not by failure of the metal-to-metal bond. Evidence for this mode of failure is shown in Figure 4. Scanning electron micrographs of the aluminum alloy substrate and of the underside of the detached electroplate show that ductile fracture of the substrate has occurred in the short transverse direction. Torn, fractured aluminum can be seen adhering to the underside of the detached electroplate. In a Jacquet type peel test, nickel plate over the Alcoa 661 pretreatment on alloy X7146-T63 showed a peel strength of 140 N/cm.

RESISTANCE TO CORROSION

Performance of decorative nickel/chromium electroplated aluminum alloys having the Alcoa 661 Process pretreatment upon exposure to the CASS Test for 44 hrs. is good, provided that the total electroplate thickness is at least 38 μm (duplex nickel plus microdiscontinuous chromium). No corrosion of the substrate

alloy (X7146, 7021, 6010) occurs and undercutting of the plate at scribe damaged sites is less than 1.6 mm. In contrast, specimens having a conventional zincate pretreatment tended to show an unacceptable degree of undercutting. The test results with the Alcoa 661 Process were obtained on full size bumpers plated in pilot lines, as well as on laboratory prepared specimens. Mobile tests of plated specimens and bumpers mounted on automobiles are showing good performance of the electroplate and practically no corrosion of the substrate after two winters' exposure.

CONCLUSION

The Alcoa 661 Process offers the potential of a cyanide-free electroplating process by which decorative nickel/chromium plate can be applied to aluminum alloys with good adhesion and protection against corrosion. Pilot plant tests using full size bumpers demonstrate the practicality of the process. Outdoor exposure testing, both static and mobile, shows good performance of plated parts after two years' exposure. Although not detailed in this paper, the Alcoa 661 Process has been found to be applicable to most of the common aluminum alloys, suggesting its use in a variety of applications.

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TABLE I

ALCOA 661 PROCESS STEPS

Step		Bath Type
1.	Soak clean	Inhibited alkaline cleaner
2.	Acid or alkaline etch	Phosphoric acid or sodium hydroxide base
3.	Desmut	Nitric acid-ammonium bifluoride
4.	First zinc immersion	Concentrated, modified zincate solution*
5.	Strip zinc deposit	Nitric acid, 50 vol. %
6.	Second zinc immersion	Concentrated, modified zincate solution*
7.a)	Immersion-dwell in nickel strike bath	Nickel sulfate + boric acid, < 300 ppm chloride
b)	Nickel strike	Remove with hot lead
	Electroplate	

NOTE: Water rinse after steps 1-7.

*ASTM B253, Zinc Immersion Solution, Bath I, or similar proprietary bath.

TABLE II

MICROPROBE SURFACE ANALYSES OF ZINCATED ALUMINUM ALLOY 1100 AFTER VARIOUS TIMES OF IMMERSION IN NICKEL STRIKE BATH

Immersion Time sec.	Weight Per Cent		
	Zn	Ni	O
0	2.09	0.03	0.8
5	0.70	0.08	1.6
15	0.50	0.11	1.0
30	0.24	0.24	0.6
45	0.26	0.37	0.7
90	0.17	0.22	0.7
150	0.15	0.16	0.8
210	0.17	0.17	0.8
Bare Alloy (reference)	0.01	0.01	0.6

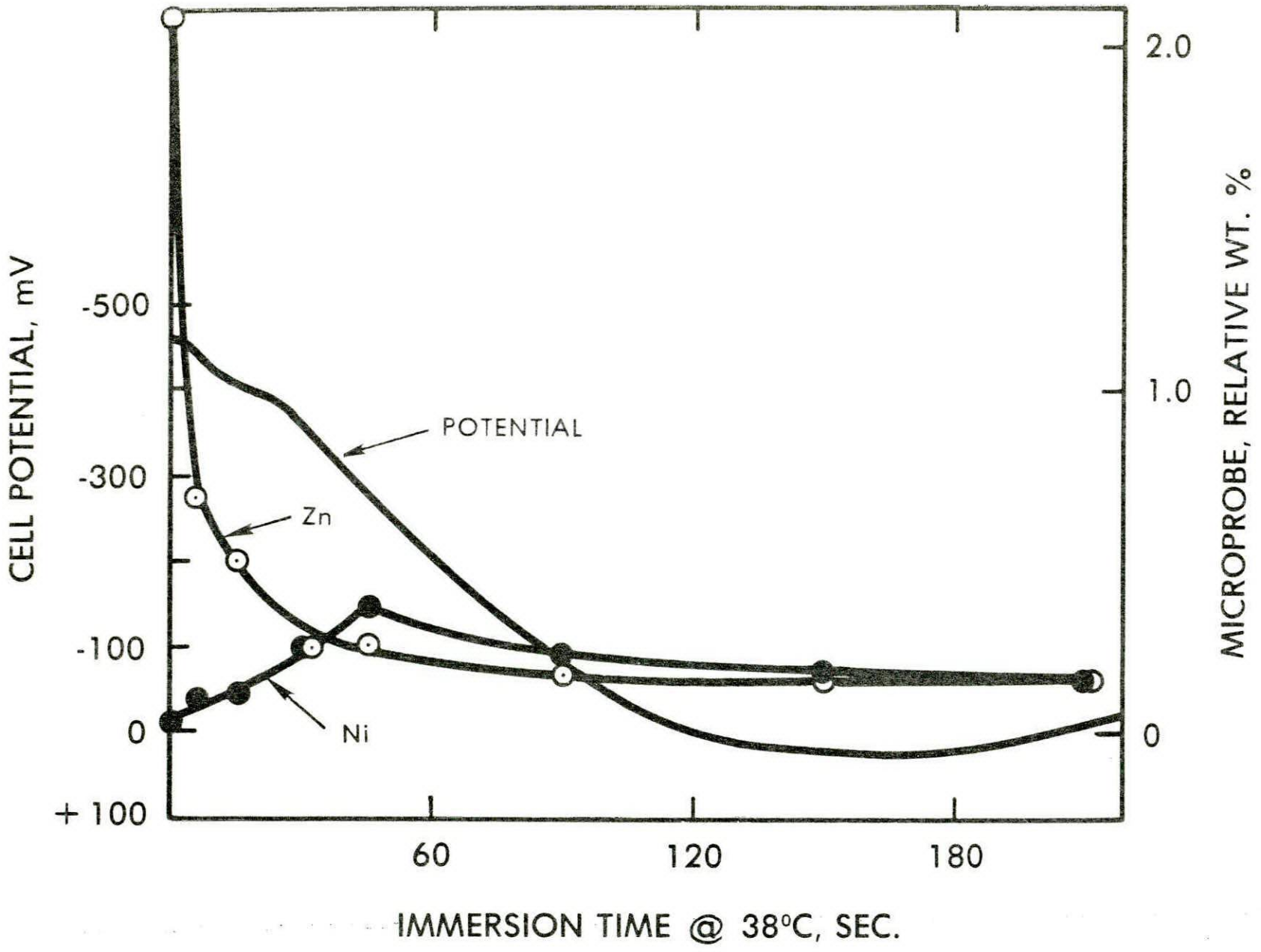


FIG. 1 TIME OF IMMERSION IN Ni STRIKE BATH VERSUS Zn AND Ni IN DEPOSIT, AND POTENTIAL BETWEEN ZINCATED Al ALLOY 1100 AND NICKEL ELECTRODE.

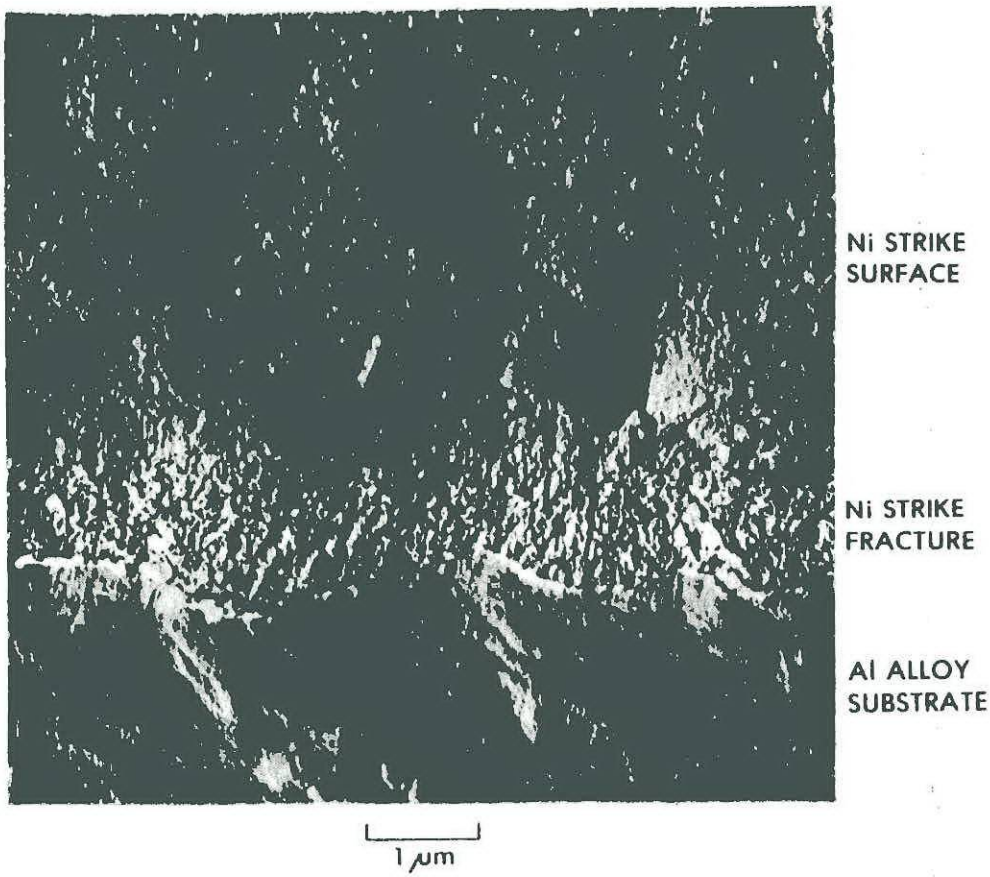
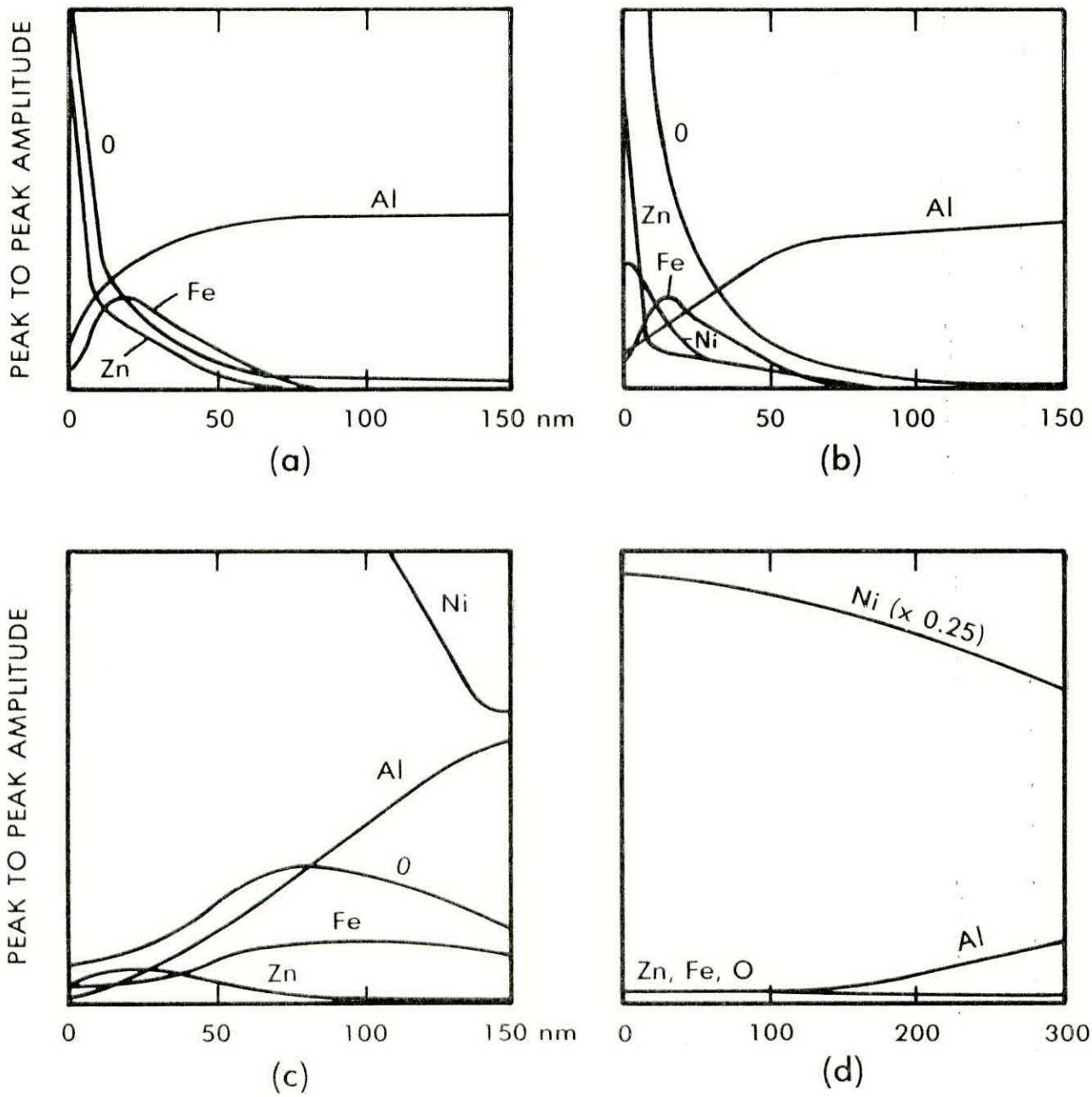


FIG. 2 TEM OF FRACTURE OF ALCOA 661
TREATED X7146 SHEET, 20,000X
(CARBON - PT REPLICA)



AUGER DEPTH PROFILES

(a) AFTER DOUBLE ZINC IMMERSION TREATMENT

(b) AFTER 15 SEC. IMMERSION IN Ni STRIKE BATH

(c) AFTER 5 SEC. APPLIED POTENTIAL IN Ni STRIKE BATH

(d) AFTER 2 MIN. APPLIED POTENTIAL IN Ni STRIKE BATH

FIG. 3

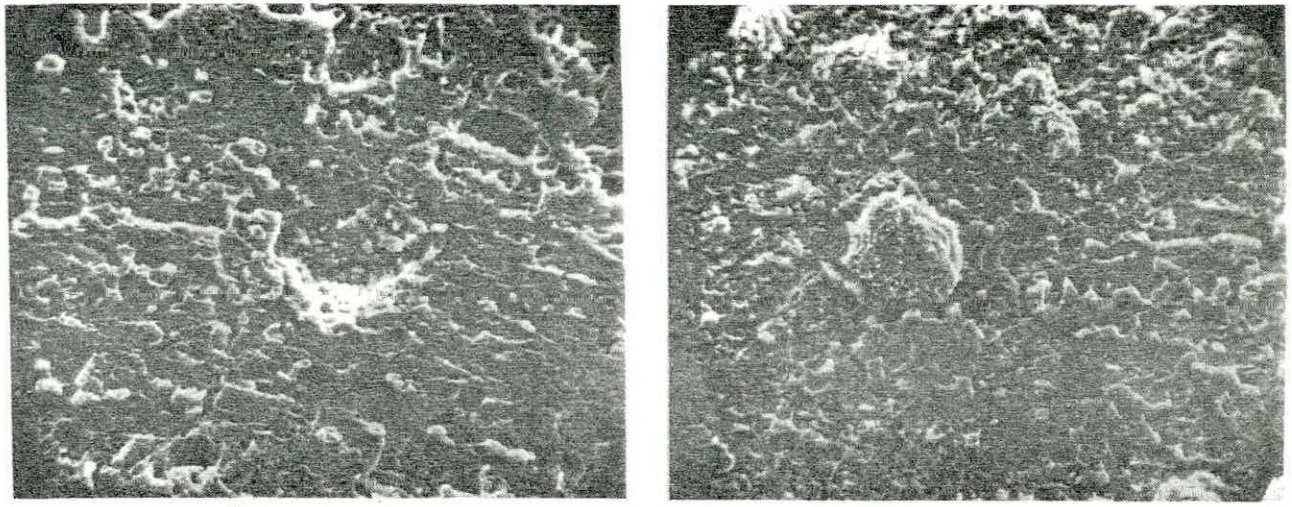


FIG. 4 SEM VIEWS DEMONSTRATE GOOD AHESION OF Ni PLATE/ALCOA 661 ON X7146 ALLOY. FAILURE IS BY FRACTURE OF ALUMINUM ALLOY SUBSTRATE.