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FRANK J. SEILER RESEARCH LABORATORY

FJSRL TECHNICAL REPORT-76-0018
NOVEMBER 1976

THE ELECTROLYTIC REMOVAL OF ALUMINUM FROM A TWO-PHASE ALUMINUM-TRIALUMINUM NICKELIDE MATRIX

PROJECT 2303

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The selective electrolytic removal of aluminum from a two-phase matrix of aluminum containing an aligned microstructure of a eutectic alloy, Al_3Ni, has been demonstrated feasible in aluminum chloride containing molten salts. Both the 1:1 molar ratio aluminum chloride-sodium chloride melt at 175°C and the 2:1 aluminum chloride-1-ethylpyridinium bromide melt at 23°C were found suitable for this separation. The anodic decomposition potential of Al_3Ni in these melts was

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estimated using linear sweep voltammetry. An apparatus of novel design was used to provide a continuously flowing electrolyte stream past the matrix sample effecting an efficient removal of aluminum.

SRL-TR-76-0018

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TECHNICAL REPORT SRL-TR-76-0018

NOVEMBER 1976

DIRECTOR OF CHEMICAL SCIENCES
FRANK J. SEILER RESEARCH LABORATORY
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FOREWORD

This report was prepared by the Directorate of Chemical Science, Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado. The work was initiated under Project No. 2303, "Chemical Synthesis and Characterization," Task No. 2303-F2, "Physical Chemistry and Electrochemistry," Work Unit No. 2303-F2-08, "Aluminum Matrix Separation."

The report covers work conducted from July 1975 to September 1976.

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This technical report has been reviewed and approved.

BEN A. LOVING, Lt Col, USAF
Director, Chemical Sciences

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INTRODUCTION

The growth of an aligned microstructure of a controlled eutectic alloy trialuminum nickelide (Al_3Ni) has been investigated by several workers as a means of providing tensile strength enhancement in aluminum (1). A practical method of producing Al_3Ni whiskers in an aluminum matrix utilizes a unidirectional solidification technique (1-3). Small diameter fibers composed of Al_3Ni are also expected to find useful application in industrial and military microelectronics if they can be removed undamaged from the aluminum matrix in which they are imbedded. Investigators of the Rome Air Development Center (RADC), Hanscom AFB, MA, have succeeded in growing Al_3Ni fiber bundles longitudinally in a rod shaped aluminum matrix with a process which shows promise for industrial pilot plant scale-up (4). Thus, the development of a practical means of removing and separating aluminum from a two phase Al-Al_3Ni matrix without damage to the Al_3Ni fibers promises to solve a fundamental problem in their mass production.

Previous attempts using aqueous electrolytes or acid etches for removing or dissolving aluminum from an Al-Al_3Ni matrix have almost always been accompanied by gas evolution resulting in "birdsnesting" of the fiber bundles as they are exposed (4). Another problem reported to be encountered with aqueous acid etches is low selectivity of attack; i.e., the Al_3Ni fibers are dissolved as well as the bulk aluminum (4). An electrolyte that would sustain aluminum electrolysis without gas evolution while permitting selective attack on the bulk aluminum phase would be a potential way to circumvent these problems.

Aluminum has been anodized in aprotic media (5,6), but generally the rate of removal of aluminum is limited by the low electrical conductivity of these media. Application of molten salt media, particularly those containing aluminum chloride, to the anodization of aluminum has been demonstrated in both alkali chloride - aluminum chloride (7,8) and organic salt - aluminum chloride (9,10) mixtures. Separation procedures using these types of materials provide a number of advantages over the use of other electrolytes. Foremost, the method is electrolytic in nature, and therefore provides a great deal of control in the attack. Secondly, the process results in formation of an additional amount of one of the components of the electrolyte, a chloroaluminate ion:

$$4Cl^- + Al \longrightarrow AlCl_4^- + 3e^- \qquad [1]$$

This process is not accompanied by gas evolution provided the electrode is not made so anodic as to decompose the melt. Finally, because the electrolyte used is a molten salt, the conductivity is high, allowing a rapid removal of material.

King, Brown, and Frayer (7) showed that the anodic dissolution of aluminum proceeds at 100% efficiency at 175°C in a 2:3 molar ratio $NaCl-AlCl_3$ melt over the current range 63-500 mA/cm^2. Recently, Gale and Osteryoung (8) found similar results in a 1:1 $NaCl-AlCl_3$ melt over the current range 0.03-6.30 mA/cm^2 at 175°C. Anodization of aluminum in an organic containing room temperature molten salt such as 2:1 $AlCl_3$-1-ethylpyridinium bromide was also reported to occur with 100% current efficiency (10).

This investigation was undertaken to examine the practicability of using these types of electrolytes to remove the bulk aluminum from a two phase $Al-Al_3Ni$ matrix.

EXPERIMENTAL

All experiments were conducted in a glove box (Vacuum/Atmosphere Co., Model HE 43-6 DRI-LAB). The moisture content was maintained below 10 ppm; the oxygen concentration was determined to be between 10 and 25 ppm as measured with a calibrated light bulb (11).

1-ethyl pyridinium bromide (EPB) was prepared by refluxing ethyl bromide (Baker A.R. Grade) with 10% excess pyridine (Baker A.R. Grade) in acetone (Eastman) as the solvent for 5-6 hours. The resulting white hygroscopic crystals were suction dried, washed with anhydrous diethyl ether (Baker A.R. Grade) and vacuum dried at 34°C overnight. After drying, the salt was transferred to a stoppered storage bottle in the glove box. The melting point of the dried EPB was 121°C and compared favorably with the literature (12).

A 2:1 molar ratio room temperature melt of $AlCl_3$-EPB was prepared by adding aluminum chloride (Fluka, A.G., iron free) to the EPB. Considerable evolution of heat accompanies the addition and precautions should be taken to keep the temperatures of the mixture below 50°C; otherwise, some EPB may decompose during the addition resulting in a mixture which is difficult to purify. All glassware containing this melt was painted black since experience in this laboratory and that of other workers (13) indicates that the material is photosensitive. A melt of 1:1 molar ratio $AlCl_3$-NaCl was prepared by fusing the correct amounts of aluminum chloride and sodium chloride (Baker, A.R. Grade) at 175°C in the glove box.

Both of the melts were purified utilizing a constant current electrolysis procedure (14). After approximately 10 days of electrolysis both melts were clear and water-like. They exhibited no peaks with cyclic voltammetry at a glassy carbon electrode (Figure 1).

Constant current and controlled potential electrolysis were accomplished with a potentiostat/galvanostat (Princeton Applied Research Corp, Model 173). A voltage programmer (Princeton Applied Research Corp, Model 175) was coupled to the potentiostat/galvanostat for linear sweep voltammetry.

Samples of the Al-Al_3Ni matrix were obtained from RADC as 1.25 inch by 0.125 inch diameter rods. In addition, a pure sample of Al_3Ni alloy was furnished which had been produced by fusing stoichiometric quantities of aluminum and nickel. Electrodes were fashioned from the samples by wrapping aluminum wire around the ends of the specimens that were not immersed in the melt to provide electrical contact. The immersed area of the particular Al-Al_3Ni specimen under investigation was measured geometrically. The Al_3Ni electrode was quite porous, and only an approximate geometrical area, 1 cm^2, could be measured.

In a typical electrolysis experiment the Al-Al_3Ni matrix rod or a piece of Al_3Ni was used as a working electrode in a three electrode cell (Figure 2). The cell was constructed of Pyrex. Cell temperature for experiments with the 1:1 $AlCl_3$-NaCl melt was maintained to ±0.5°C by means of a platinum resistance controlled furnace. The counter electrode was a cup shaped piece of aluminum foil (Research Organic/Inorganic Co., m5n purity), while the reference electrode was a spiral aluminum wire (Alfa-Ventron, m5n purity) isolated from the melt by a 10 nm fine porosity Pyrex frit. All potentials described during this investigation were measured against this electrode, i.e., the Al(III)/Al couple.

For experiments requiring a flowing electrolyte stream, a centrifugally induced conventive stirrer (Figure 3) was constructed. When this device was turned with an electrode rotator (Pine Instrument Co., ASR-2) at speeds above 50 RPM, a flowing electrolyte stream was present at the electrode suspended in the center of the stirrer.

RESULTS AND DISCUSSION

In order to determine the approximate potential range in which aluminum could be removed by electrolysis without appreciable damage to the trialuminum nickelide filaments, current-potential curves for the anodization of aluminum and trialuminum nickelide were constructed using linear sweep voltammetry. The working electrode was either pure aluminum wire or Al_3Ni, respectively. The potential of the working electrode was varied linearly from a potential of 0.0V vs. Al(III)/Al to the anodic limit of the melt under consideration. In the 1:1 $AlCl_3$-NaCl melt at 175°C the practical limit is about 2.2V anodic of the aluminum reference electrode and represents the oxidation of chloride to chlorine (14). The useful limit of the 2:1 $AlCl_3$-EPB melt is about 1.75V (Figure 1) and probably represents the oxidation of bromide to bromine. The potential at which attack on the Al_3Ni occurs in 2:1 $AlCl_3$-EPB is about 1.0V (Figure 4) at the 20 mV/sec sweep rate used for these studies.

The voltammogram for aluminum anodization in the 2:1 $AlCl_3$-EPB melt (Figure 4) exhibits an interesting feature. The shape of the current-voltage curve suggests formation of a passivating layer of aluminum chloride. Similar behavior has been obtained in other aluminum chloride rich melts (7,15). This feature was not observed for the 1:1 $AlCl_3$-NaCl melt (Figure 5) during the time span of the voltammogram. Two factors may have contributed to the absence of passivation in the latter case. First, the melt is able to solvate approximately an additional mole of aluminum chloride per mole of electrolyte before forming a solid aluminum chloride layer. Second, thermal convection currents in the heated melt prevented formation of a sodium ion depleted diffusion layer. Therefore, passivation behavior can be alleviated somewhat by using some type of forced convection. A special stirrer (Figure 3) was constructed in order to provide uniform forced convection. An experiment with this device is described below. Such a stirrer should provide other advantages as well; for example, a more complete stripping of aluminum from the interior of the exposed filament bundle as a result of the flowing electrolyte stream.

The relative amounts of material that can be removed anodically from an aluminum specimen in the two melts examined in this study can be judged by comparison of the linear sweep voltammograms at a given potential (Figures 4 and 5). At 0.8V vs. Al(III)/Al the current at an aluminum wire electrode in the 1:1 $AlCl_3$-NaCl melt was about 20 times that of a similar electrode in the 2:1 $AlCl_3$-EPB melt. Since the quantity of material that can be removed anodically is governed by Faraday's law, the weight in grams of aluminum, W, that can be removed by electrolysis in t seconds at a current of i amperes is:

$$W = 9.33 \times 10^{-5}\ it \qquad [2]$$

For a typical specimen of 1.28 g containing 20 wt-% Al_3Ni as the rod phase, an electrolysis time of 15 hours in the 1:1 $AlCl_3$-NaCl melt and 336 hours in the 2:1 $AlCl_3$-EPB melt would be required to remove all bulk aluminum. These times were calculated for an unstirred solution assuming that the limiting current at the electrode is that reflected at 0.8V vs. Al(III)/Al from the linear sweep voltammograms. The values calculated represent an upper bound in time since stirring increases the current density. For example, Holleck and Giner (14) observed that the anodic current increased linearly with the square root of the rotation rate at a rotating aluminum electrode. Their study was an example of ideal forced convection and such efficiency was not realized with the apparatus used in the present work.

Preliminary electrolysis experiments were accomplished in the 2:1 $AlCl_3$-EPB melt by anodizing the Al-Al_3Ni matrix working electrode while stirring with a propeller. Portions of the rod which were not desired to be anodized were coated with heat shrinkable Teflon* tubing. A microphotograph of an unpolished Al-Al_3Ni matrix specimen prior to electrolysis (Figure 6) shows no evidence of exposed Al_3Ni whiskers. The same specimen was subjected to anodization by constant current at 0.16 A/cm^2 in a stirred solution of 2:1 $AlCl_3$-EPB, removed and washed successively with dimethylsulfoxide, distilled water, and acetone. Microphotographs (Figure 7) revealed that bulk aluminum had been removed from the surface of the specimen and exposed Al_3Ni whiskers were present. Visual inspection revealed no discernible damage to the fibers. During electrolysis the potential of the Al-Al_3Ni electrode rose to 0.1V vs. Al(III)/Al. An experiment at 0.54 A/cm^2 with 0.22V polarization produced the same result (Figure 8). At this current density the cell potential exceeded 3V vs. A(III)/Al when stirring had been discontinued.

Al-Al_3Ni electrolysis was accomplished in the 1:1 $AlCl_3$-NaCl melt in a manner similar to the procedure used for the 2:1 $AlCl_3$-EPB melt. Electrolysis at a current density of 0.180 A/cm^2 in an unstirred solution resulted in a polarization of 0.3V vs. the Al(III)/Al couple. Microphotographs revealed essentially the same result as that obtained previously, except that electrolysis was much faster and no stirring was required to offset passivation.

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*Registered Trademark

The centrifugally induced stirrer (Figure 3) containing an Al-Al_3Ni rod was rotated at about 160 RPM during passage of a 0.10 A/cm^2 current. An apparent resistance polarization of 0.5V was noted indicating that the device had caused moderate shielding of the Al-Al_3Ni electrode within. Microphotographs (Figure 9) of a portion of the matrix sample after electrolysis showed that even removal of bulk aluminum from the specimen had taken place. At the outset of this experiment removal of the entire bulk aluminum phase was intended using this device. However, this could not be realized because the specimen rod was permeated with numerous voids (Figure 10) throughout the length of the specimen. These voids would not allow a fiber bundle to be formed for as the fibers were exposed they became detached from the rod and were deposited in the bottom of the cell.

CONCLUSION

The electrolytic removal of aluminum from a two phase matrix of aluminum containing trialuminum nickelide whiskers has been demonstrated in two different molten salt electrolytes. Both electrolytes were shown to possess certain advantages and disadvantages. The 2:1 aluminum chloride-1-ethyl-pyridinium bromide melt was easiest to use since it could be prepared and maintained at room temperature. However, this melt suffered from severe passivation during anodization, i.e., the high aluminum chloride content did not allow efficient solvation of additional aluminum chloride produced during anodization. In contrast, the inorganic melt, 1:1 aluminum chloride-sodium chloride, demonstrated no passivation in the current ranges examined in this study. This was attributed to the ability of 1 mole of 1:1 $AlCl_3$-NaCl to solvate almost an additional mole of aluminum chloride. Unfortunately, this electrolyte was more difficult to use because it must be maintained at temperatures above its freezing point of 160°C.

A forced convection stirring device constructed for this investigation has been shown to be practical for complete removal of aluminum from a two phase specimen. However, this could not be demonstrated unambiguously because of imperfections present in the samples tested.

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Figure 1. Cyclic voltammograms of the 2:1 $AlCl_3$-EPB melt, A, and the 1:1 NaCl-$AlCl_3$ melt, B, at a glassy carbon electrode (A = 0.215 cm^2), sweep rate = 100 mV/sec.

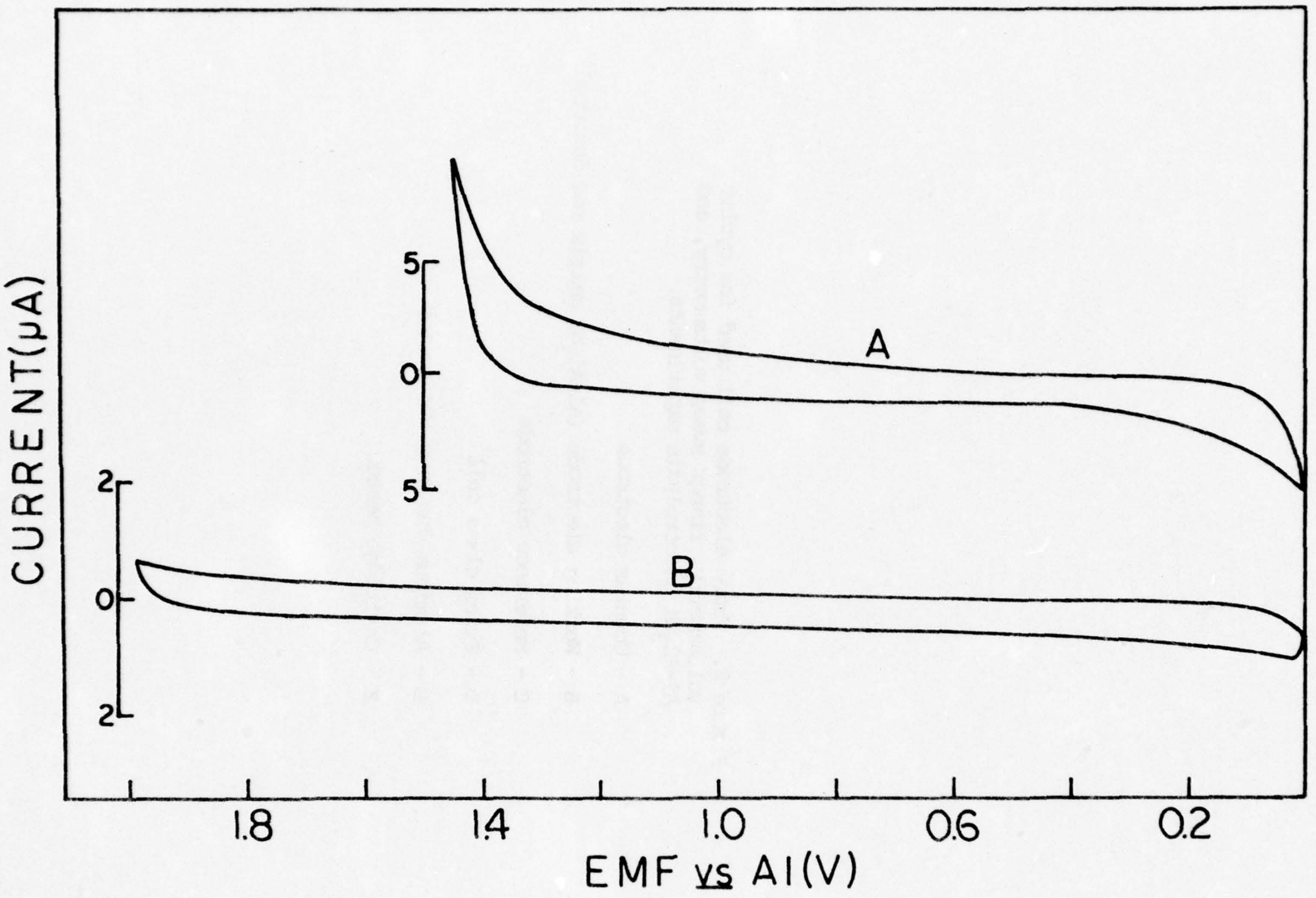

CURRENT(μA)
5
0
5
2
0
2
A
B
1.8
1.4
1.0
0.6
0.2
EMF vs Al(V)

Figure 2. Three electrode cell used for cyclic voltammetry, linear sweep voltammetry, and Al-Al$_3$Ni electrolysis experiments.

A - Counter electrode

B - Working electrode (Al-Al$_3$Ni matrix rod depicted)

C - Reference electrode

D - Pyrex glass cell

E - Aluminum cup with Teflon top

F - Cartridge heater

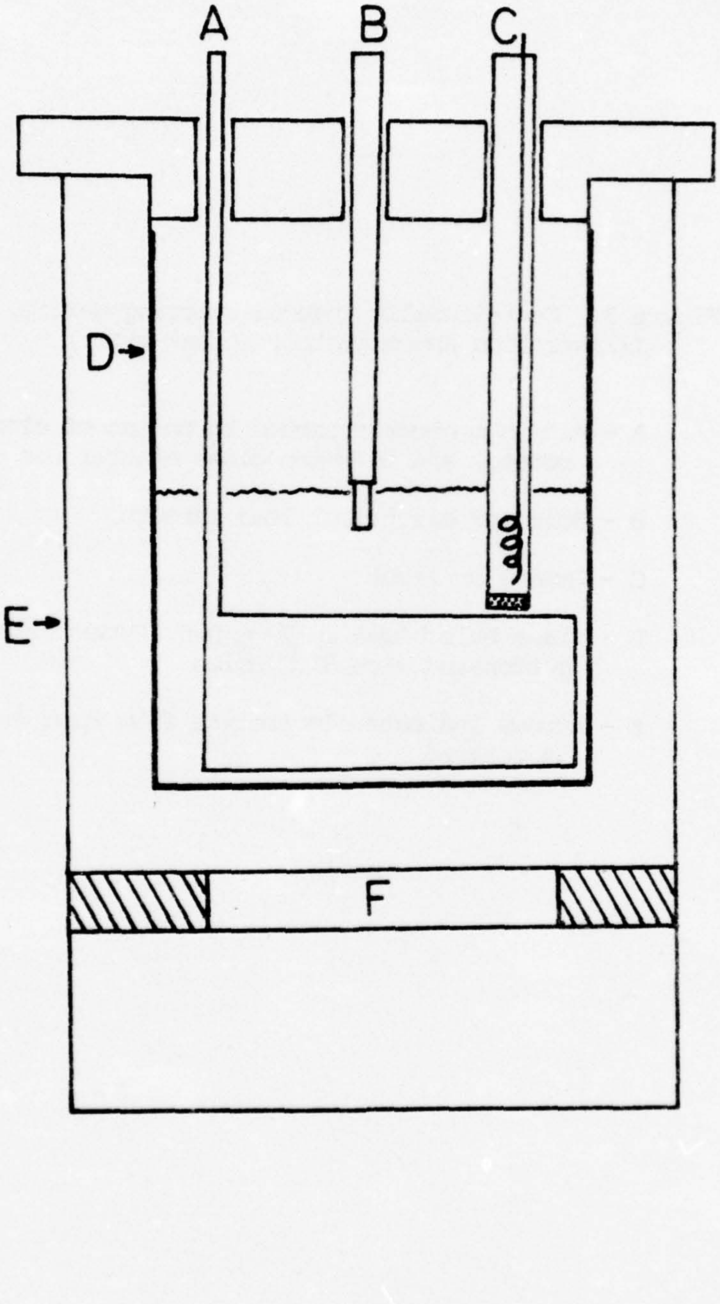

A
B
C
D
E
F

Figure 3. Centrifugally induced stirring device.
(Illustration approximately actual size.)

A - Aluminum chuck attached to collet of electrode rotator and to which glass stirrer was cemented

B - Hole for electrical lead through

C - Immersion level

D - Glass bulb blown in 7 mm O.D. Pyrex tubing and perforated with 3 mm holes

E - Arrows indicate electrolyte flow when device is rotated

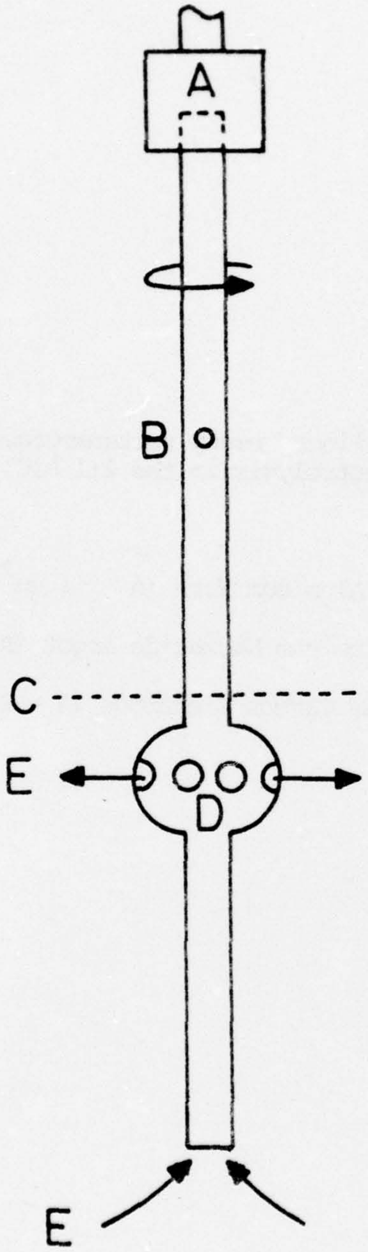

A
B
C
E
D
E

Figure 4. Anodic linear sweep voltammograms for Al and Al_3Ni electrolysis in the 2:1 $AlCl_3$-EPB melt at 23°C

——— Pure Aluminum Wire (A = $\sim$1 cm^2)

------ Trialuminum Nickelide Ingot (A = $\sim$1 cm^2)

······ Glassy Carbon Electrode (A = 0.215 cm^2)

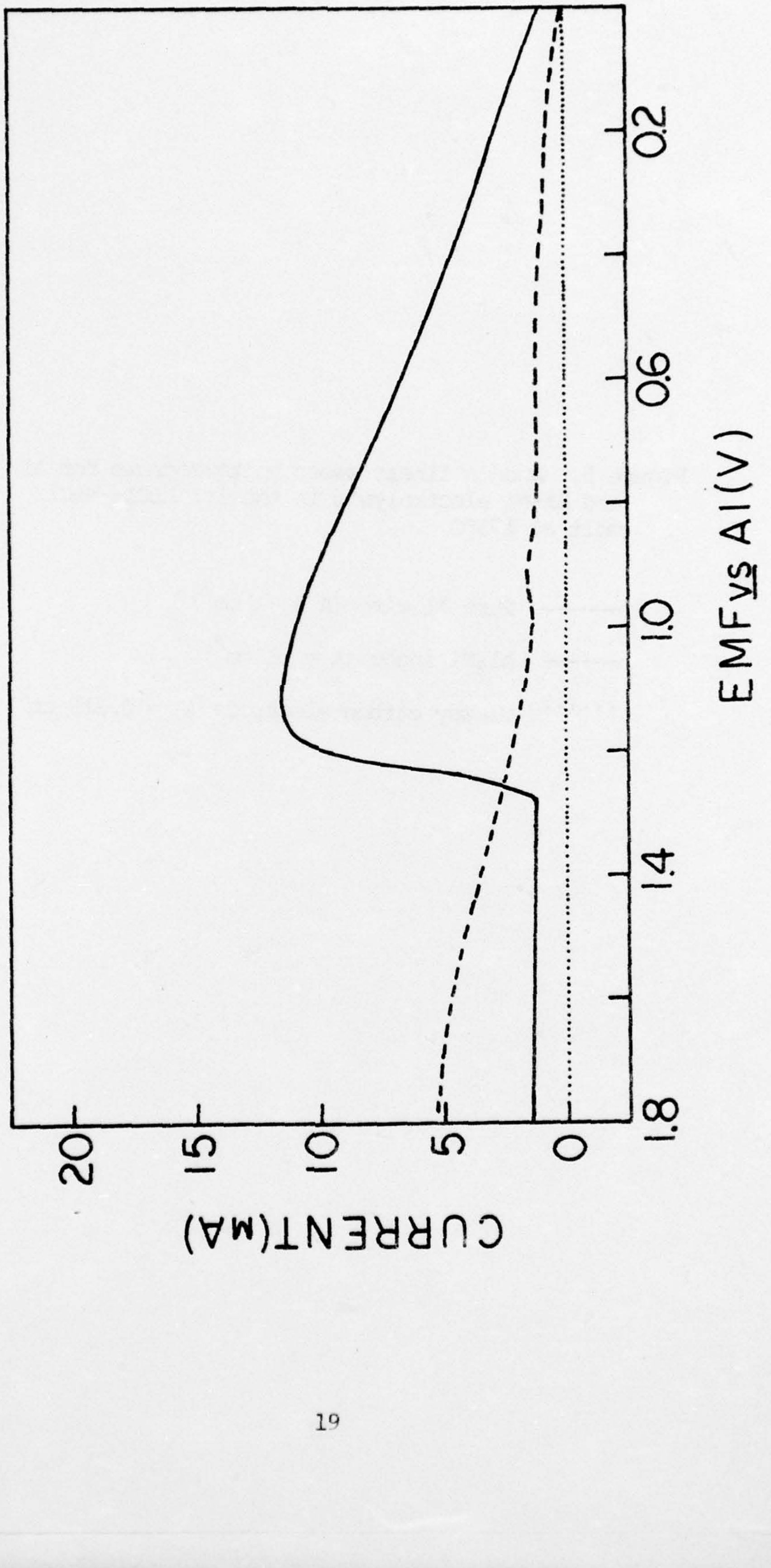

CURRENT(mA)
20
15
10
5
0
1.8
1.4
1.0
0.6
0.2
EMF vs Al(V)

Figure 5. Anodic linear sweep voltammograms for Al and Al_3Ni electrolysis in the 1:1 $AlCl_3$-NaCl melt at 175°C

——— Pure Al wire (A = $\sim$1 cm^2)

------ Al_3Ni ingot (A = $\sim$1 cm^2)

······ Glassy carbon electrode (A = 0.215 cm^2)

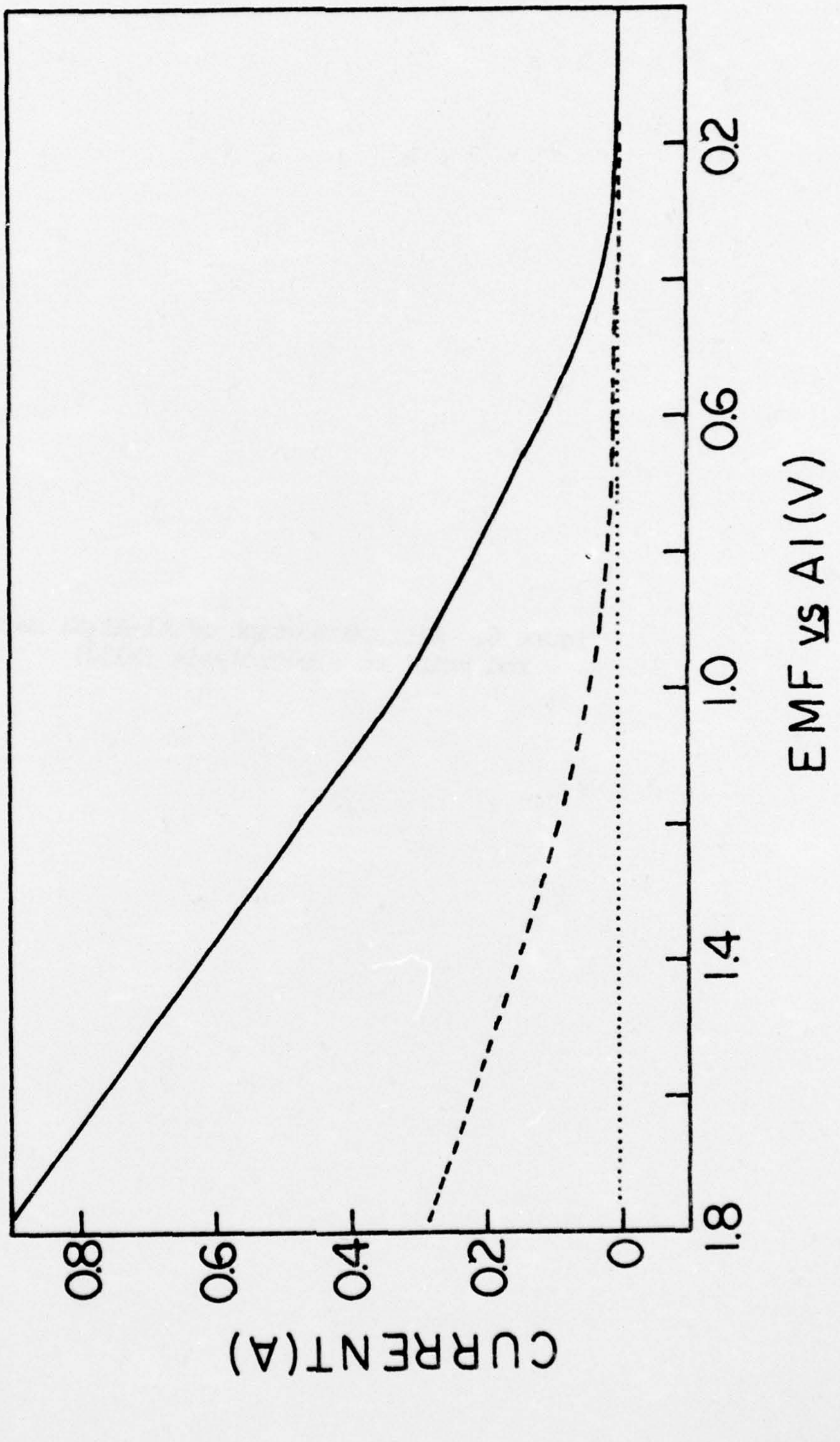
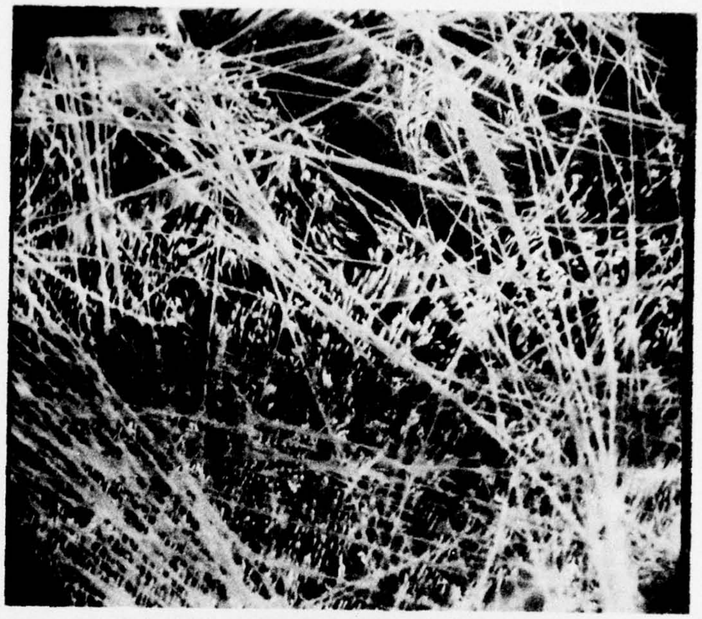

CURRENT(A)
0.8
0.6
0.4
0.2
0
1.8
1.4
1.0
0.6
0.2
EMF vs Al(V)

Figure 6. Microphotograph of Al-Al_3Ni matrix rod prior to electrolysis (X350)

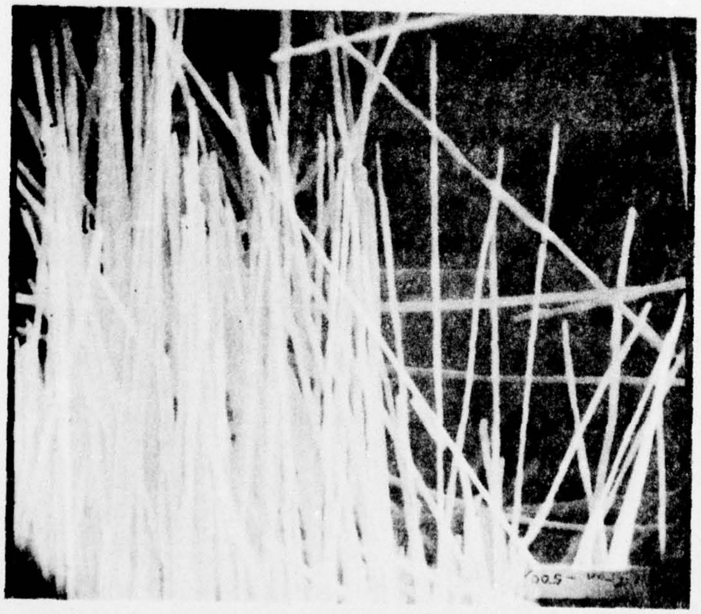
Figure 7. Microphotographs of Al-Al_3Ni matrix rod surface after anodization at 0.16 A/cm^2 in a stirred solution of 2:1 $AlCl_3$-EPB at 23°C

A X740

B X1860



A



B

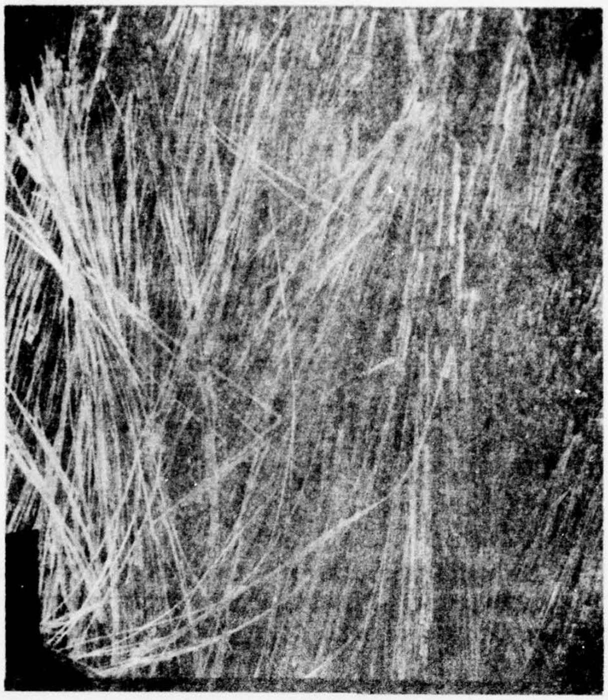
Figure 8. Microphotograph of Al-Al_3Ni matrix rod surface after anodization at 0.54 A/cm^2 in a stirred solution of 2:1 $AlCl_3$-EPB at 23°C

X2760

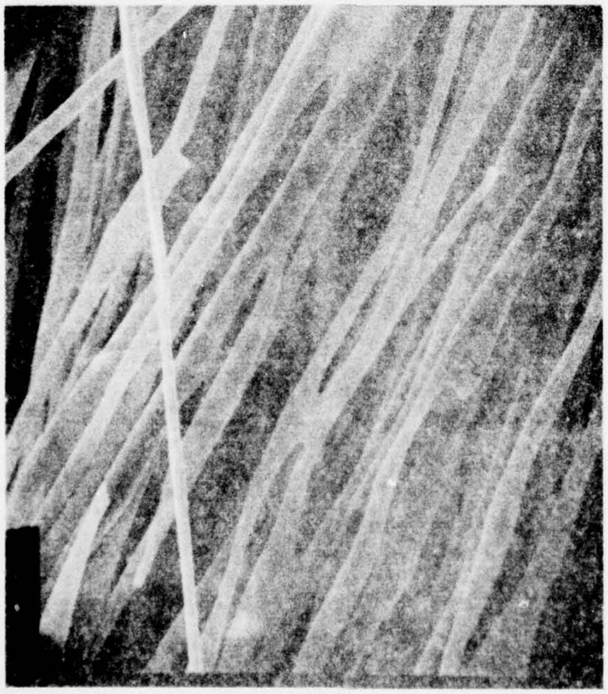
Figure 9. Microphotograph of Al-Al_3Ni matrix rod surface after anodization at 0.10 A/cm^2 with centrifugally induced stirring in 1:1 NaCl-$AlCl_3$ at 175°C

A X170

B X1360



A



B

Figure 10. Microphotograph of Al-Al_3Ni rod surface after anodization illustrating void introduced into rod during growth of two phase matrix

X41