Plating Challenging Substrates

By: Frank Altmayer, MSF, AESF Fellow, Technical Education Director, AESF Foundation/NASF

And: Relying heavily upon procedures developed/investigated by Dr. Jack Dini, Consultant, Dr. Chris Marzano (deceased) and numerous others.

Troublesome Substrates

- Aluminum
- Beryllium Copper
- Nickel Based Alloys
  - Inconel (Ni, Cr, Fe)
    - aka Chronin, Altemp, Haynes, Nickelvac and Nicrofer
  - Chromel (90% Ni, 10%Cr)
  - Alumel (95% Ni, 2% Mn, 2%Al, 1% silicon)
  - Invar (Fe, Ni)
  - Kovar (Fe, Ni, Co)
  - Stainless Steels (Fe, Cr, Ni)
  - Waspalloy (Ni, Cr, Co, Mo, Ti, Al)
- Molybdenum
- Niobium/Tungsten
- Non-traditional, Non-Conductors (photo)
- Titanium/Alloys
- Tungsten Carbide
- Zirconium Alloys

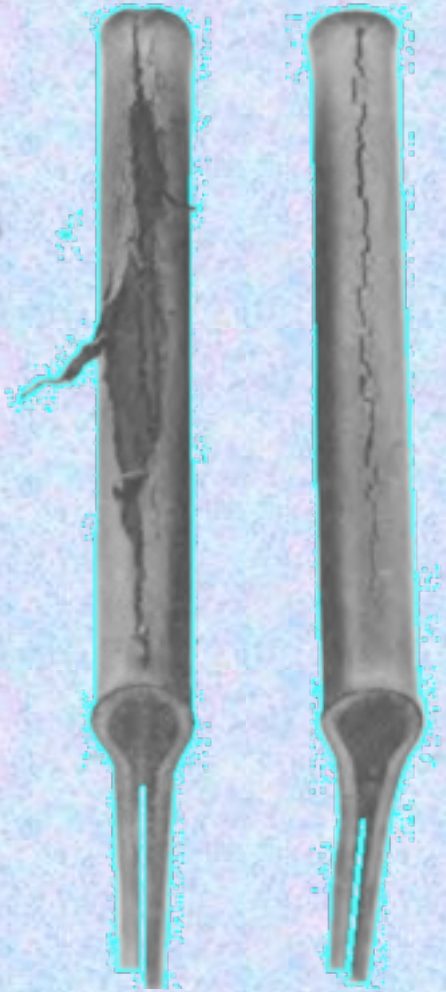
Note:
"Troublemakers"* produce a stable oxide film that is difficult to remove and can return prior to plating

*except non-conductors

Plating Adhesion

Primary Schemes for Improving Adhesion:

- Oxide film is removed for a sufficient time to permit an initial electrodeposit
- Oxide film is replaced by another film that does not interfere with adhesion
- Oxide film is incorporated into the deposit in a compatible manner
- Plated deposit is diffused into the substrate
- Surface of basis metal is etched to produce a larger surface area with mechanical bonding sites



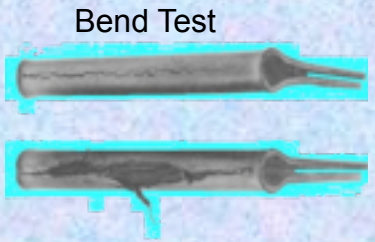
Plating Adhesion

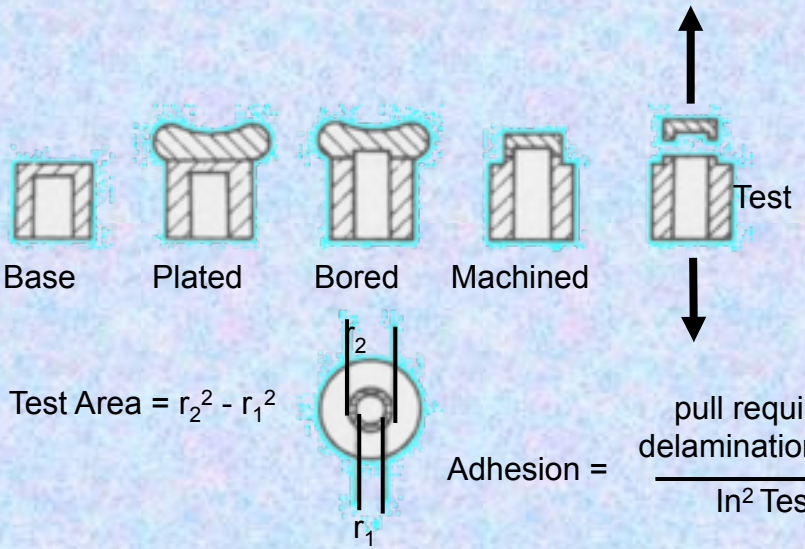
Adhesion Tests:
Qualitative (ASTM B571):

- Bend
- Burnish
- Chisel/Cut
- Draw/File/Grind
- Heat Quench

Quantitative

- Ollard/Modified Ollard
- Ring Shear
- Other “pull” tests





Adhesion Units:
Pounds/in^2 (psi), MN or mega Pascals/m^2

Keys to Preparing Aluminum

Using Correct Acid Dip

- Dissolves surface alloying elements, and residuals that may be left on the surface by cleaners (such as silicates).
- Nitric acid needs to be fortified with fluorides to more adequately remove these metals from the surface, and to remove residual silicates from the cleaner(s).

Typical Acid Formulations:

- a. Nitric acid, 50% vol., containing 6lb./100 gal. (7 g/L) of ammonium bifluoride. This acid is used at 20-30°C. > 30°C, may cause localized etching or pitting.

- b. Tri-acid, (50%vol. nitric, 25%vol. sulfuric, 60 g/L ammonium bifluoride or 2% volume hydrofluoric acid). This acid is also used at 20-30°C. > 30°C, may cause localized etching or pitting.

Acid for High Mg Alloys (example 5000 series):

- Sulfuric acid, 25%vol., at 80-85°C (2-5 minutes) followed by a brief dip in 50% nitric acid at 20-30°C.

Keys to Preparing Aluminum

Typical Dilute Zincate Formulation	(g/L)
NaOH	120
ZnO	20
$FeCl_3$	2
Rochelle Salts	50
$NaNO_3$	1

- 70-75°F (20-25°C)
- 30 seconds maximum immersion time

- Note: Alloying Elements such as Cu, Fe, Si can retard the formation of a contiguous zinc film.

Keys to Preparing Aluminum

Zincate

- **Time should be carefully controlled to within the suggested time frame of the supplier of the zincate formulation, especially, the second zincate film.**
- **Typically between 30 seconds and 2 minutes depending on formulation.**
- **When double zincating, the second dip is normally much shorter in time than the first (typically 10-15 seconds).**
- **The use of a timer is important for manually produced zincate films.**

Zincated Aluminum Castings
Non-uniform gray color indicates potential problem with zincate

Keys to Preparing Aluminum

Zincate:

- Temperature and quality of rinsing after zincating are also commonly ignored variables
- The maximum temperature is typically 27°C (80°F). Zincating at too high a temperature will compromise adhesion
- The first rinse after zincating needs to flow at a high rate to avoid additional zincate film(s)
- Uniform agitation in rinse is critical

Non-uniform air agitation yields non-uniform rinse quality

Keys to Preparing Aluminum

First Deposit over Zincate:

- Minimum Thickness of 0.0001”-0.0002”
- Options:
- Electroless Nickel
- Cyanide Copper Strike
  - pH is critical (>10.5 compromises adhesion)
- High pH Nickel Strike:

$NiSO_4$	12-14 oz/gal
$NaSO_4$	12-14 oz/gal
NH_4Cl	4-6 oz/gal
H_3BO_3	2-4 oz/gal
°F	110-120
pH	5.2-5.6

Porous Copper Strike Yields Adhesion Failure

Preparing Nickel/Nickel Alloys

Activation Options:

Cathodic Treatments:

- **Sulfuric acid,10-25% vol.**
  - **70-90°F**
  - **1-5 minutes**
  - **3-5 ASF**
  - **Lead Anodes**
- **Hydrochloric acid,10-25% vol.**
  - **70-90°F**
  - **1-5 minutes**
  - **10-20 ASF**
  - **Nickel Anodes**

Immersion Treatments

- Sulfuric acid 20-50% vol.
  - 150-175°F
  - 1 minute after gassing starts

Note:
Rinse time must be minimized or (if possible) rinsing should be eliminated (if possible) to prevent oxide re-formation

Preparing Nickel/Nickel Alloys

Anodic Etches

Option 1:

H_2SO_4	40% vol.
Temperature	70-90°F
ACD, ASF	100
Time, Minutes	3

Option 1:

H_3NSO_3 , g/L	100
Temperature	70-90°F
ACD, ASF	100
Time, Minutes	3

Adhesion Comparison Wood's vs. Anodic Etch* on Ni

Process	Adhesion, psi
Wood's Ni Strike, 54ASF, 5 minutes	103,000
Option 1 (no Ni strike)	110,000
Option 2 (no Ni strike)	110,000

*Conical head tensile test of nickel plating over nickel substrate
Data from Dr. Jack Dini, Lawrence Livermore Labs.

Preparing Nickel/Nickel Alloys

Nickel Strikes

Purpose/Goal:

To de-oxidize the surface using hydrogen gas generation and simultaneously deposit a thin layer of nickel

Woods Nickel Strikes:

Alternate-1

Solution (g/L):

Nickel Chloride	225
Hydrochloric acid	250 mL/L
Temperature	70-90°F

Nickel Anodes (no S)

- 5-120 sec anodic, 20-25 A/ft^2
- 5-10 minutes cathodic, 25-100+ A/ft^2

Alternate-2

Solution (g/L):

Nickel Chloride	225
Hydrochloric acid	120 mL/L
Temperature	70-90°F

Nickel Anodes (no S)

- 2-4 minutes cathodic, 50-200+ A/ft^2

Note: Studies have shown that higher CCD in Woods Ni = Higher adhesion

Preparing Nickel/Nickel Alloys

Current Density in Wood's Nickel vs. Adhesion on AM363 SS*

A/ft^2	Adhesion psi
5	6,900
10	7,000
15	7,800
25	46,100
50	48,900
100	70,700

*MA363 SS: 11.5% Cr, 4.5%Ni, 0.25%Ti, 0.04%C, 0.15% Mn, 0.05% Si
Process used was Alternate 2 on previous slide

Preparing Nickel/Nickel Alloys

Sulfate Based Nickel Strikes

Option-1:

Nickel may be plated over an activated nickel alloy surface with a Watts solution, if the pH of the Watts nickel solution is at about 2

Option-2:

Nickel Sulfate	225 g/L
Sulfuric Acid	2.5% vol.
Temperature	35-40°C
Time	5-10 minutes
Current Density	15-20 A/dm^2

Preparing Nickel/Nickel Alloys

Sulfamic Acid Based Nickel Strikes

Option-1:

Nickel Sulfamate	**40 oz/gal**
Sulfamic Acid	**20 oz/gal**
Temperature	**70-120°F**
Current Density	**50 ASF**
Time	**5-10 min**
Ni Anodes (S is OK)	

Option-2

Nickel Sulfamate	**40 oz/gal**
pH (adj with Sulfamic Acid)	**1.5**
Boric acid	**4 oz/gal**
Temperature	**70-120°F**
Current Density	**20-100ASF**
Time	**5-10 min**
Ni Anodes (S is OK)	

Note: solution will not attack bare aluminum surfaces

Stainless Steel

Rigorous Process for SS:

- Anodic cleaning in hot alkaline solution at 30 A/ft^2, 3minutes
- Immersion in 20% vol. HCl at room temperature for 1 minute
- Anodic etch (optional) in 40% vol. sulfuric acid at 100 A/ft^2 for 3 minutes
- Wood's strike at 25-50A/ft^2 for 5 minutes
- Sulfamate nickel plate

Impact of Anodic Etch on Ring Shear Adhesion on 17-4PH SS Substrate:

Without Anodic Etch
28,200psi

With Anodic Etch
68,300psi

Kovar/Invar

Kovar* (53% Fe, 29% Ni, 17% Co)

- Developed to make vacuum seal to glass

Invar** (64%Fe, 36%Ni)

- Has a very low coefficient of expansion

Preparation Options:

- Cathodic Clean
  - 30-120 seconds
  - 140-180°F
  - Anodes: Stainless Steel
  - Current Density: 50 ASF
- Sulfuric Pickle or
- Hydrochloric pickle or
- Sulfuric or Hydrochloric pickle plus Wood's Strike

Unconventional Non-Conductors

General Scheme:

Bronze plated baby shoe

- Porous parts must be covered in hard resin/ many coats of lacquer
- Surface to be plated is roughened by tumbling in sand
- Plastics are further roughened by chemical etching
- Roughened surface can be treated in palladium chloride solution-then EN plated

Spider/Web

*Excluding plastics that are commonly plated (eg ABS etc.)

Unconventional Non-Conductors

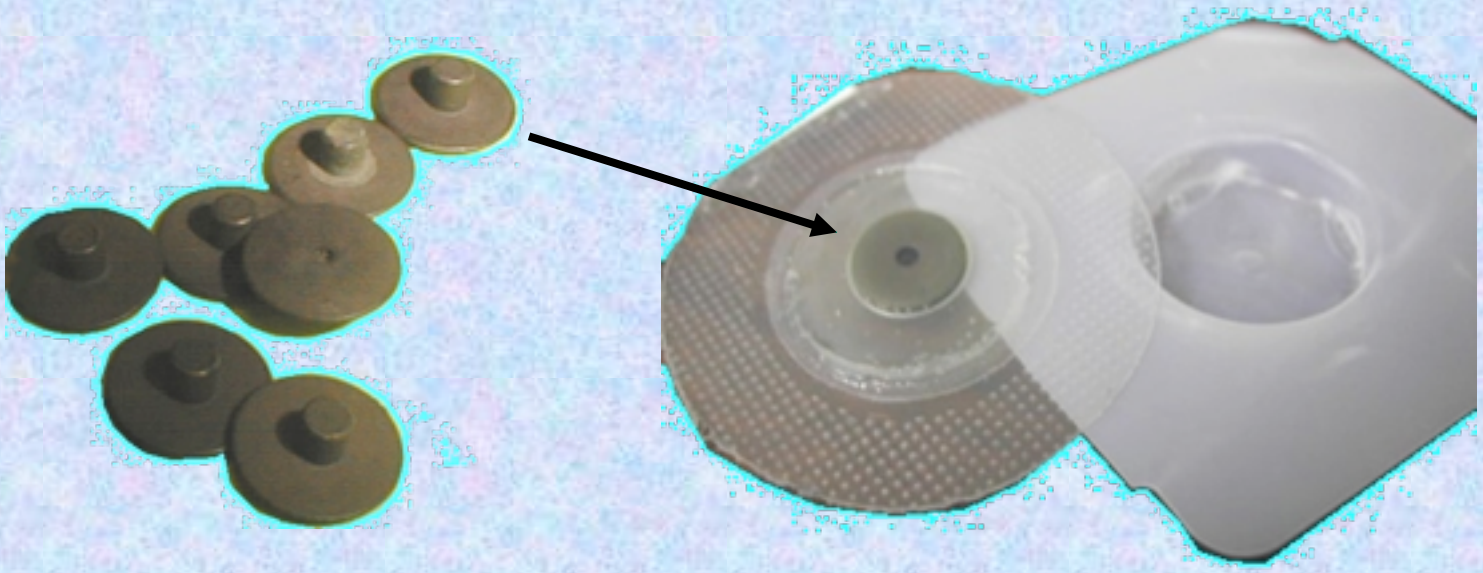
Chess Pieces ("non-plateable" plastic)

- Etched in 50% sulfuric acid plus 2-5% peroxide for 10-12 hours
- 1 minute soak in stannous chloride suspension
- Prepare silvering solutions as follows:
  - A. Dissolve 10 g silver nitrate in ~ 50 mL DI water. Add enough NH_4OH to just re-dissolve the formed precipitate and dilute to 100 mL final volume.
  - B. Prepare 75g/L KOH solution and 75 g/L Dextrose solution.
  - C. Mix equal volumes of each solution in B to create reducing solution
- One immersion coating is produced by diluting the silver nitrate solution 10: 1 , and adding approximately 10 mL reducing solution per liter of silver nitrate solution
- Silver deposits on container and parts within the container
- Repeat 6-8 more times to build up silver thickness
- Electroplate over the silver deposit

Conventional Non-Conductors With a Twist

Quiz Question:

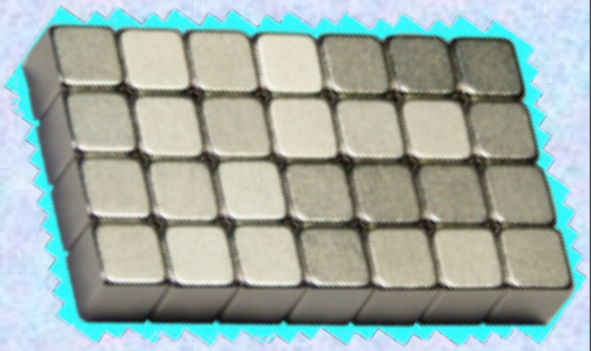
- How do you barrel silver plate the parts shown, when they float in water?



*ABS Eyelets used in manufacture of ECG electrodes

Neodymium Magnets

$Nd_2Fe_{14}B$



- Discovered in 1982 (GM and Sumitomo)
- May be melt-spun (GM) or sintered (Sumitomo)
- Nickel plated for corrosion protection

European Patent: 0325-088*

- Prepare a combination of Oakite 195 and 90 as the primary cleaning solution: 200 g/gal Oakite 195 + 140 g/gal Oakite 90
- Cathodic for 5 seconds
- Anodic for 5-10 seconds
- Cold water rinse
- Immerse for 5 seconds in 70 g/L sulfuric acid
- Cold water rinse
- Sulfamate nickel strike

*patent is primarily for phosphating Nd magnets

Magnesium Alloys

- Quickly reacts with oxygen to produce oxide film
- Highly reactive metal
  - Fires
  - Dissolves in alcohol
  - Cleaners must be below pH 11
- Used in cell phones, laptops, cameras, solar collectors and other electronic components

Magnesium has 66% the weight of Al, common alloying elements are Al, Zn, Mn, Th

Black chromium plated magnesium casting used in manufacture of solar collector

Magnesium

Preparation Process:

- Clean cathodically in an alkaline (<pH11) cleaner
  - Anodic cleaning is not suitable
- Pickle (30-120 seconds):

Option 1:

Chromic acid (CrO_3) ..... 180 g/L
Ferric nitrate [$Fe(NO_3)_3$-$9H_2O$] ..... 40 g/L
Potassium fluoride (KF) ..... 3.5-7 ”
Note: Use low KF for wrought products and high KF for castings

Option 2:

Undiluted 85% phosphoric acid

Option 3 (For sheet, extrusions, and forgings):

Glacial acetic acid (CH,COOH) ..... 280 ml/L
Sodium nitrate (NaNO,) ..... 80 g/L

Option 4 (no dimensional change) :

Chromic Acid at 180 g/L, 2-10 minutes
70-200°F depending on desired processing time

Note:

- Chromic acid containing pickles need to be followed by hydrosulfite dip to eliminate Cr^{+6}

Magnesium

Preparation Process*:

Activation:

Prior to zincate, Mg must be activated:

Phosphoric acid (85% H3P04) ..... 200 ml/L
Ammonium bi-fluoride (NH_4HF_2) ..... 100 g/L
2-5 minutes at 70°F

Where the surface is free of a chromates:

Tetrasodium pyrophosphate ($Na_4P_2O_7$) ..... 40 g/L
Borax ($Na_2B_4O_7 \cdot 10H_2O$) ..... 70 g/L
Sodium fluoride (NaF) ..... 20 g/L
2-5 minutes at 170°F

*by H. K. DeLong
Dow Metal Products Co., Midland, Mich.

Zincates for Magnesium Alloys

Option 1 (Dr. Dini):

- 5.5 oz/gal $Zn_2P_2O_7 \cdot 7H_2O$
  - May be hard to find
- 26 oz/gal $Na_4P_2O_7 \cdot 10H_2O$
- 2 oz/gal $KF \cdot 2H_2O$
- pH 10
- Temp 160°F
- 1.5-2.0 minutes

Notes:

- Double zincate required for M1660, M13120, M13310, M13312 Alloys
- Solubility of LiF is limited to the required concentration
- Fluoride controls the deposition rate. The quality of the deposit is heavily dependent on its concentration

Option 2 (ASTM B480*):

- 4 oz/gal $ZnSO_4$
- 16 oz/gal $Na_4P_2O_7$
- 0.75 oz/gal Na_2CO_3
- 0.75 oz/gal NaF
- or 0.3 oz/gal LiF
- Immersion Time (minutes)
  - Al containing alloys 5-12
  - Non-Al Alloys, 4-9
  - Pure Mg, 4-9
- pH 10.2-10.4
- Temp 160°F

*Originally proposed by H. K. DeLong, Dow Metal Products Co

Plating Mg without Zincate*

- Clean, Electroclean, pickle as described previously (use chromic acid or 90% vol phosphoric solution)
- Etch 20-60 seconds:
  - For Al containing alloys use 11% vol nitric acid containing 16 oz/gal chromic acid
  - For others use 9% vol. nitric containing 8 oz/gal chromic acid
- Acid dip, (5-20% vol HF) 10 minutes, room temp
  - 8-12 oz/gal NH_4HF_2 may be substituted for HF
- EN plate in special formulation bath

Note: Only Ni from a fluoride based formulation has been found to produce successful adhesion

*Originally proposed by H. K. DeLong, Dow Metal Products Co

Plating Mg without Zincate*

Initial Deposit Options

Electroless Nickel

- Nickel Carbonate……..1.25 oz/gal
- Hydrofluoric acid……0.6% vol.
- Citric acid ……..5.2 g/L
- NH_4HF_2……1.25 oz/gal
- NaH_2PO_2…….2.5 oz/gal
- NH_4OH…….. to pH 5.5-6.3
- Temperature…… 170-180°F
- Applies very thin deposit - follow with regular EN plate

Ni Electroplating Solution

- HF..... 43 ml/L
- Nickel carbonate ..... 120 g/L
- Citric acid ..... 30 g/L
- Sodium lauryl sulfate.... 1.0g/L
- Temperature..... 120-140°F
- Current density..... 30-100 ASF
- Cathode rod agit. 12-16 ft/min
- pH..... 3.0

Titanium & Titanium Alloys

- Alloys use in aerospace include Ti6Al4V, Ti2Cu, IMI 685 and Ti6Al12Sn4Zr2Mo
- Alloys typically contain
  - Al (typically 3%)
  - V (typically 2.5%)
- High strength to weight ratio even @ elevated temperature
- Oxide formation upon air exposure

Titanium & Titanium Alloys

Plating Titanium (Example Ti6Al-4V)

Option-1:

- Aluminum Oxide blast (150 grit) and/or Soak Clean
- HCl Pickle
  - 25-50% vol
  - 70-90°F
  - 3-5 minutes
- EN Plate
- Diffuse (Ar atmosphere)
  - 1350-1450°F
  - 30 minutes

Note: Thermal diffusion treatments may produce brittle intermetallics

Option-2 (Pratt & Whitney):

- Aluminum Oxide blast (150 grit) and/or Soak Clean
- HCl Pickle
  - 25-50% vol
  - 70-90°F
  - 3-5 minutes
- Bright Dip
  - 12% HF, 1% HNO_3
- Anodic Etch
  - 83% Acetic Acid + 13% HF
  - 6 minutes
  - 40°C
  - 15 A/ft^2
- Ni Plate
  - 25 µm
- Diffuse (Ar atmosphere)
  - 1350-1450°F
  - 2 hours

Plating Ti Alloys W/O Thermal Treatment

Option-3:

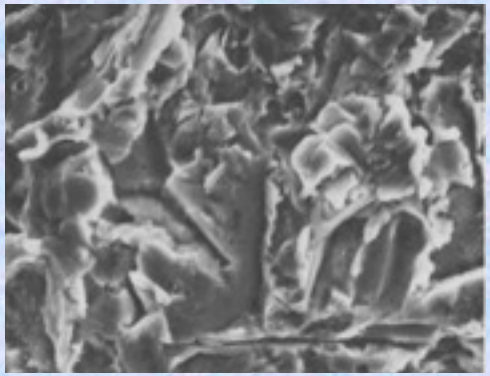
- Aluminum Oxide blast (150 grit) and/or Soak Clean
- Pickle
  - 15% HCl + 3-5%HF
  - 70-80°F
  - 3-5 minutes
- Zinc Strike
  - 20% HF + 80% ethylene glycol (no water)
  - 70-75°F
  - 5-10 minutes
  - 10 A/ft^2
  - Graphite Anodes

Option-4:

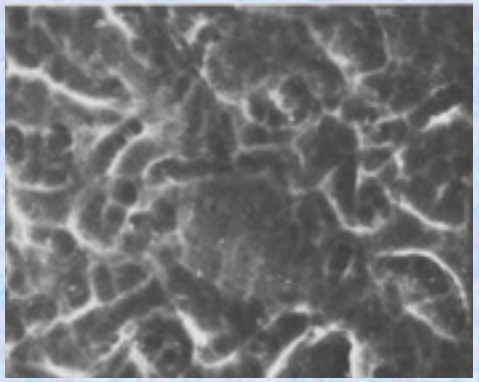
- Aluminum Oxide blast (150 grit) and/or Soak Clean
- Pickle
  - 15% HCl + 3-5%HF
  - 70-80°F
  - 3-5 minutes
- Platinum Strike
  - 10-20 g/L $PtCl_2$ + 150-200 g/L HCl
  - 110-160°F
  - 5-10 minutes
  - 10-20 A/ft^2
- Graphite Anodes

Plating Ti Alloys W/O Thermal Treatment or "Weird" Strikes

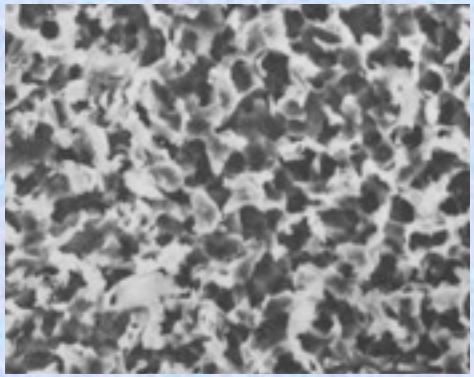
- Vapor Degrease/Blast
- Etch:
  - Nitric Acid: 400g/L
  - HF: 5g/L
  - Time: 15 minutes
  - Temperature: 25°C
- Activate:
  - H_2SiF_6: 0.6 mol/L
  - HF: 0.3 mol/L
  - CrO_3: 1.8 mol/L
  - Time: 15-50 minutes
  - Temperature: 35° to 100° C
- Sulfamate Ni, Acid Cu or EN Plate



Ti6Al4V, after blast, 1000X



Ti6Al4V, after pickle, 1000X



Ti6Al4V, after activation, 1000X

US Pat. 4,414,039 Martin Thoma mtu Motoren- und Turbinen-Union Miinchen GmbH Miinchen, West Germany

Plating Ti Alloys W/O Thermal Treatment or "Weird" Strikes

Notes:

- The adhesion values for nickel plating on titanium are on the order of 14,000psi
- Heat treatment up to 400°C does not bring about any improvement in the adhesion
- Heat treatment at 480°C for 2 hours increases the adhesion to 40,000 psi with Ti6Al4V and to 20,000 psi with Ti2Cu
- No hydrogen absorption occurs from plating with Ni, EN, acid Cu
- Avoid chromium strike (excessive hydrogen absorption)

US Pat. 4,414,039 Martin Thoma mtu Motoren- und Turbinen-Union Miinchen GmbH Miinchen, West Germany

Beryllium Copper

Berylco 10* and Berylco 25**

Alternate 1:

1. Degrease
2. Caustic-soak
3. Pumice-scrub
4. Anodic-treat in Oakite 90 for 2 minutes at 268 A/m^2 (27ASF)
5. 1 minute in 18% (by wt) HCl
6. Nickel sulfamate or electroless nickel-plate to thickness

Alternate 2:

- Degrease
- Caustic-soak
- Pumice-scrub
- Anodic-treat in alkaline cleaner for 2 minutes at 268 A/m^2
- Fluoboric acid (48%) at 12% vol. 1 minute at 60°C; H_2SO_4 (66° Baume) 25% vol. 1 minute at 56°C
- Bright-dip 515 ml H_3PO_4 24 ml acetic, 5.25 ml HCl, 17.5 ml H_2O for 20 s at 66°C
- Fluoboric acid for 30 s at 60°C
- Sulfamate or electroless nickel-plate to thickness

Notes:

- Adhesion levels: 100 to 400 MN/m^2 (~ 14,500-58,000psi)
- Thermal diffusion treatments do not appear to improve adhesion on Be-Cu
- Tools made of Be-Cu do not produce sparks

Beryllium Copper

Alternate 3:

1. Pre-clean etc.
2. Chemical Dip (Chose one)
   - 65%vol H_2SO_4, 35% vol HNO_3 + .05 fl oz/gal HCl, or
   - 20-30% vol H_2SO_4 @ 160-180°F, or
   - 12 oz/gal NaCN + 12 oz/gal NaOH @ 160-180°F
   - Proprietary Sulfuric-Peroxide Dip
3. Acid Dip
   - 50% HCl
4. Activate
   - 0.5-2 oz/gal Ammonium Persulfate
   - 15-45 seconds
5. Cyanide Copper Strike

Beryllium

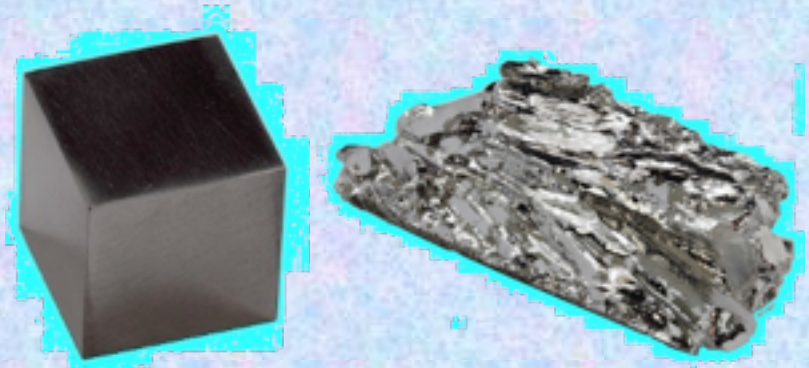
Preparing Be for Plating:

- Cleaning
- Acid etch: 20 parts HNO_3, 1 part HF, 20 parts water at 23°C for 5 min
- Zincate in 30 g/L ZnO, 15 g/L KF and 25 ml/L H_2SO_4 at 27°C for 10 seconds (pH 3.2)
  - Control of Zincate pH is critical to adhesion
- Cyanide copper strike 2-3 min at 16 A/ft^2
- Sulfamate nickel plate

Molybdenum

Features:

- Very high melting point (~5,000°F)
- Forms hard, stable carbides in ferrous alloys
- Instantly produces oxide film (MoO_2 and MoO_3) when exposed to air
- High corrosion resistance
- Ability to withstand high temperature without softening
  - Used in military armor, aircraft parts, electrical contacts, industrial motors and filaments



*Avoid alkaline solutions (produce oxide films)

Prep Cycle:

1. Solvent Clean*
2. Anodic Etch in 65% vol Sulfuric acid
   - 70-90°F
   - 100-300 A/ft^2
   - 30 seconds
3. Acid dip, 10% sulfuric
   - 70-90°F
   - 30 seconds
4. Chromium Strike
   - Conventional plating solution
   - 120°F
   - 150 A/ft^2
   - 1-3 minutes
5. Woods Nickel strike
   - 25-50 A/ft^2
   - 2-5 minutes

Tungsten/(W) Alloys

Preparation of W/Alloys*:

1. Clean
2. Etch in 3 parts HF, 1 part HNO_3, 4 parts H_2O for 5 minutes at RT
3. Options:
   - (alternate patented etching process used successfully on WC) Anodic etch, 1.5 ASI, 68-140°F, 10-30 minutes 100-250g/L $Na_2P_2O_7$
   - Etch anodically in 300g/L KOH @50C, 100ASF, 5 minutes plus chromium strike
   - Better matches coefficient of expansion
4. Sulfamate Ni Plate

W: Highest melting point of all elements

*Procedure from Dr. Chris Marzano (deceased), IIT Metallurgy Dept.
Adhesion level is only marginal ~3,000psi (ring shear)

Zirconium Alloys

Example: Zircaloy-2 (1.5 Sn, 0.13 Fe, 0.10 Cr, 0.05 Ni)

Process Sequence 1:

- Vapor Degrease
- Cathodic alkaline clean
- Pickle Option 1:

NH_4HF_2	15g/L
H_2SO_4	0.5mL/L
Time:	1 minute
Temperature	22°C

- Pickle Option 2:

NH_4HF_2	45g/L
Time:	3 min.
Temperature	22°C

- Sulfamate Ni plate

Note:

Adhesion is very low (~3,000psi) unless the deposit is diffusion treated @ 700°C in a constrained condition using TMZ (Tungsten-Molybdenum-Zirconium) containment (25 micron clearance). The adhesion increases X10

Source: Dr. Jack Dini

Zirconium Alloys

Pickling solution for Zirconium, Zircaloys and Hafnium:

HNO_3 25 to 50%

HF 2 to 5%

Pickling solution for Zirconium-Niobium alloys

H_2SO_4 28 to 32%

HNO_3 28-32%

HF 5-10%

Notes:

- Both metals are very sensitive to traces of hydrogen, which lowers their fracture toughness
- Pickle temperatures should not exceed 65°C (150°F), to prevent excessive pickup of hydrogen
- To help prevent formation of insoluble fluoride surface stain, a stop bath consisting of 70% HNO_3, and 30% H_2O can be used
- HF attacks Zr/Hf, and HNO_3 oxidizes the hydrogen formed by the reaction and prevents its absorption by the metal.
- HNO_3 /HF should not be less than 10 to 1 in normality

Source: R. Terrence Webster, Metallurgical Consultant, Surface Engineering Handbook

Zirconium Alloys

Plating Process Sequence 1:

- Degrease,
- Etch Option 1:
  - Ammonium bifluoride 45 g/L
  - Sulfuric acid + 0.5 mL/L
  - Time 1 min
  - Temperature 22°C (72°F)
- Etch Option 2:
  - Ammonium bifluoride 45 g/L
  - Time 3 min
  - Temperature 22°C (72°F)
- Sulfamate nickel plate, pH 3.8-4.0, CCD 20 ASF, 50°C or Acid copper plate @ 200ASF.
- Diffusion Treat Ni plated part @ 1300 °F in vacuum for 1 hr or Cu plated part @350F for 3 hr with the plated article placed in a molybdenum alloy, TZM ring, or constrained case
  - Coefficient of thermal expansion for molybdenum is lower than that of zirconium and nickel, it provides a stress on the plating as the assembly is heated

Zirconium Alloys

Plating Sequence 2:

- Degrease
- "Load" activating solution by immersion of pickled zirconium for 10 min@ 22°C in:
  - Ammonium bifluoride 10 to 20 g/L plus
  - Sulfuric Acid 0.75 to 2.0 g/L
- Etch in Activating Solution for 1 minute @ 22°C
- Remove any loosely adhering film or smut
  - Use ultrasonics or
  - Use 2-10% vol HBF_4
- Same Thermal Treatment as procedure 1 is required

The End, Thank You!