Autocatalytic (Electroless) Plating on Aluminum

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Autocatalytic (electroless[a]) nickel plating on aluminum is practiced extensively, even though there are numerous problems in preparing aluminum alloys and selecting a compatible solution.

The use of aluminum is rapidly growing, because of its light weight, strength, ease of fabrication, and certain other desirable characteristics. The high affinity of aluminum for oxygen results in a natural, thin-oxide film that protects the aluminum from further corrosion in a mild environment. For many applications, however, the environment is too severe, and additional protection is required. Methods for increased protection have therefore been developed, including chromate conversion coatings, anodizing, paint systems, electroplating, and autocatalytic nickel-alloy plating. Each of these processes, or finishes, is suitable for different kinds of applications.

In particular, autocatalytic nickel-alloy coatings on aluminum exhibit good corrosion protection, increased resistance to abrasion and wear, high hardness, good solderability and electrical conductivity, and decorative appeal. It is because of one or more of these properties that autocatalytic nickel-plated aluminum has increased in use as a replacement for steel, stainless steel, cast iron, etc., in many applications (Table 1).

There are several problems in preparing aluminum surfaces for autocatalytic nickel plating. Although some methods are successful, others are not. The zincate immersion method is probably most widely used, but there still is a need for an improved method (or methods) of surface preparation.

Obstacles to Overcome

There are many obstacles in the way of successful nickel deposition on aluminum. Additional problems are encountered during deposition from an autocatalytic nickel solution. Some of these problems are discussed below.

Oxide Removal

The natural oxide film on aluminum must be removed before plating. For most processes, the aluminum must remain oxide-free to ensure adequate adhesion of the coating. The natural oxide is very thin—on the order of 5 nm (2 x 10^{-7} in.). It reforms very rapidly after removal, often faster than practical rinsing and transfer operations can take place. The oxide film is also amphoteric (soluble in both acid and alkali), making removal, control or replacement more complicated.

Anodizing procedures that remove the natural oxide and replace it with a controlled oxide film have been proposed as a means of overcoming the natural oxide obstacle.[1] The immersion zincate[2] process involves the simultaneous *removal* of the natural oxide and its *replacement* with a zinc deposit.

Chemical Displacement

Aluminum is an extremely active metal, chemically. It forms displacement reactions with different metal ions in solution. Displacement deposits usually tend to be non-adherent. Simply immersing aluminum into most plating solutions will result in a non-adherent immersion deposit before electroplating can start. Under specially controlled conditions, it is possible to achieve a good degree of adhesion with some displacement reaction ions. Immersion in special zincate and *stannate* solutions produces fairly adherent immersion deposits.

Galvanic Corrosion

Because aluminum is active (aluminum and its alloys are high in the electromotive series), it tends to protect most of the common metals (except zinc and cadmium) from corrosion. In a corrosive environment, galvanic action can occur between any exposed aluminum and the plated coating, resulting in a very rapid corrosion of the aluminum. Plated coatings on aluminum must be continuous (free of any pits or other discontinuities), and of sufficient thickness to assure good protection.

Thermal Expansion

Aluminum and its alloys are soft, somewhat malleable, and expand more after heating than autocatalytic nickel-alloy deposits. The difference in coefficient of thermal expansion gives rise to extreme stress at the deposit interface, which can result in adhesion failure (or apparent adhesion failure if the fracture occurs in the aluminum below the interface). Deforming plated aluminum parts produces extreme stress at the interface because the aluminum deforms much more easily than does the deposit. Cracking and apparent or actual adhesion failure can occur.

Alloying Constituents

As used in industry, aluminum consists of a large variety of alloys containing constituents used to give specific properties useful for an assortment of applications. Table 2 shows some common alloys and alloying constituents.

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[a] *ASTM has recommended that the term "autocatalytic" be used in place of the term "electroless," as being more definitive. [Of course, since this article was written in 1979, that recommendation has not taken root—Ed.]*

Table 1—Applications for Autocatalytic Nickel on Aluminum

- Heat sinks (solderability & corrosion protection)
- Candle molds (good release properties)
- Electroforming mandrels (scratch resistance)
- Small engine blocks (lubricity)
- Aircraft pistons
- Aluminum gas-gauge housings
- Food equipment (aluminum baking pans)
- Connectors (including glass-sealed)
- Marine hardware
- Mixer beater blades
- Precision fit of mating parts
- Servo valves
- Piston heads
- Alternator heat sinks
- Pistons for anti-skid devices (wear resistance)
- Pistons for disc brakes (wear resistance, lubricity)
- Air-conditioning tubing (hardness)
- Electronic packages (modular)
- Mass course adjustor
- Signal selector (high frequency)
- Wave guides
- Carburetor components
- Hydraulic cylinders
- Lock nuts
- Shafts
- Slide tube assembly
- Slide valve plates
- Threaded fittings

Table 2—Composition of Some Commonly Plated Aluminum Alloys

Aluminum	Composition, per cent					
Alloy	Cu	Mn	Mg	Cr	Si	Zn
1100						
3003		1.2				
2024	4.5	0.6	1.5			
5052			2.5	0.25		
6061	0.25		1.0	0.25	0.6	
7075	1.6		2.5	0.3		5.6
319	3.5				6.0	
355	1.3		0.5		5.0	
350	3.5				8.0	

The alloying materials are not always soluble in the aluminum, nor are they always uniformly dispersed throughout the body of the aluminum.[2] Particles of metals or other alloying materials at the surface can result in a corrosion cell that accelerates the corrosion rate of the surrounding aluminum. Sometimes, these alloying constituents are difficult to remove from the surface during preparation for plating. For example, silicon-containing alloys are best prepared by using solutions containing fluorides, whereas copper-containing alloys can be treated in nitric acid.

Surface Preparation

Although many methods have been proposed and used commercially for preparing aluminum alloys for autocatalytic nickel deposition, there is no single, simple method suitable for preparing *all* aluminum alloys.

Zincate Method

The zincate process[3] typically includes the following steps:

1. *Solvent clean.* This step is only necessary to remove heavy oil and grease. It should be omitted if colloidal metal particles or other small-particle solids are to be removed, because those particles or colloids may adhere more tightly to the aluminum surface after solvent cleaning, thereby interfering with subsequent steps.
2. *Etch-clean* in a very mild acid cleaner. Several proprietary, phosphoric-acid-based cleaners are capable of maintaining the surface finish of polished or machined surfaces and the close tolerance of machined parts.
3. *Rinse.*
4. *Deoxidize* in a non-chromated solution (*e.g.*, nitric acid) that will not remove metal.
5. *Rinse.*
6. *Alkaline zincate*. A typical formulation includes:
    500 g/L (67 oz/gal) sodium hydroxide (NaOH)
    100 g/L (13 oz/gal) zinc oxide (ZnO)
    1 g/L (0.1 oz/gal) ferrous chloride ($FeCl_2$)
    10 g/L (1.3 oz/gal) Rochelle salts
   For 2024 alloy, immerse for 120 sec at 20°C (70°F).
   For 6061 alloy, immerse for 30 sec at 15°C (60°F).
   For 7075 alloy, immerse for 60 sec at 20°C (70°F).
7. *Rinse* thoroughly.
8. *Strip zincate* at 50%-by-volume nitric acid.
9. *Rinse.*
10. *Immerse in zincate solution* for 30 sec at 20°C (70°F).
11. *Rinse* thoroughly.
12. *Rinse* thoroughly.
13. *Immerse in a mild acid,* such as 0.25% sulfuric acid (H_2SO_4) or 7.5 g/L (1 oz/gal) sulfamic acid, for 10–15 sec at room temperature. This removes the tightly adherent, strongly alkaline film from the zinc surface without stripping the immersion zinc. A strongly alkaline surface can harm an autocatalytic nickel solution and interfere with deposit adhesion.
14. *Rinse*.
15. *Nickel plate*.

Good adhesion is obtained with the zincate process on a multitude of aluminum alloys. Coupled with a properly selected autocatalytic nickel solution, this process provides excellent corrosion resistance. The disadvantages of the process are: (1) there are many steps, (2) the steps are critical with little tolerance for variations of time, temperature solution composition, and other factors, and (3) for scribed panels, creep corrosion attributed to the zinc film has been reported.[4]

Other Methods

Chloride-free Nickel Strike

Following a zincate process such as that above, a special nickel strike for about 2 min at 2 A/dm^2 (20 A/ft^2) has been suggested.[5] The solution consists of 375 g/L (50 oz/gal) of nickel sulfate, 45 g/L (6 oz/gal) of boric acid, with a pH of 3.6 to 4.5 and an antipitting agent, operated at 35 to 40°C (95 to 104°F). Note that chloride ion is absent in this formulation. The nickel-coated aluminum alloy is transferred without rinsing to a semi-bright nickel solution for buildup of nickel plate, or to an autocatalytic nickel solution for buildup of nickel alloy.

Buffered Nickel Strike

An acetate-buffered nickel glycolate-strike plating solution for use after zincate has been proposed.[6] A method that *eliminates* the zincate process[7] consists of the following steps:

1. *Degrease*.
2. *Etch* (the most important step) in a solution of 350 to 360 g/L (47 to 48 oz/gal) nickel chloride ($NiCl_2.6H_2O$) and 500 mL/L (16N) concentrated nitric acid. Another etch suitable for a wider variety of alloys consists of 640 g/L (85 oz/gal) nickel chloride ($NiCl_2.6H_2O$) and 100 mL/L of 85% lactic acid.

3. *Nitric acid dip* (2 to 5 mL of 48% hydrofluoric acid (HF) per liter of 8N HNO_3). Immerse for 2 to 3 min. For 380 casting alloy, increase HF to 80 to 100 mL/L.
4. *Activate* by immersion in a solution containing 25 g/L (3.3 oz/gal) sodium hypophosphite and 25 mL/L of concentrated ammonium hydroxide, followed by an activation strike in a solution containing 25 g/L (3.3 oz/gal) of sodium hypophosphite, 25 g/L (3.3 oz/gal) of nickel sulfate hexahydrate and 50 g/L (6.6 oz/gal) of ammonium citrate. Operate at 85 to 90°C (185 to 194°F) and use ammonium hydroxide to adjust pH from 9.0 to 9.5.
5. Without rinsing, *plate* aluminum in a conventional autocatalytic nickel-alloy solution.

Anodic Coating

Anodizing as a pretreatment for electroplating on aluminum has been proposed and may find application for autocatalytic deposits.[8-11] A method that utilizes AC current with brass plating solution to replace zincate immersion has also been reported.[12] Preparation (after cleaning) in an ammonium-bifluoride-dimethylamine borane dip, followed by a dimethylamine borane-reduced nickel solution, has been advocated.[13] Another proposition is a hydrofluoric acid/metal salt that is catalytic to deposition in a bath containing amine borane.[14]

Mixed Acid/Metal Salt

One more method of preparing aluminum for plating[15] consists of: (1) degreasing, (2) rinsing, (3) pretreatment in a solution of mixed acids and a metal salt (nickel, chromium, cobalt, manganese, magnesium or zinc) at room temperature for 20 sec to 1 min, depending on the alloy, (4) rinsing, and (5) electroplating, preferably nickel or autocatalytic nickel plate.

Nickel Solution

The influence of bath composition for plating on aluminum is profound. The selection of complexing agents is especially important. The nickel ions must be completely complexed (except for plating on steel) to avoid poorly adherent displacement films of nickel. Secondary complexors are useful in the baths designed for plating on aluminum and should be capable of complexing aluminum. Under certain circumstances, aluminum hydroxide could form. This precipitate can lead to instability by neutralizing the bath stabilizers, and by forming nuclei for "plating out," causing roughness or spontaneous decomposition of the bath.

The selection of stabilizers is another key factor. Usually, two or more different types are used, and in quantities somewhat larger than for plating on ferrous alloys.

The bath must also have a *tolerance* for zinc contamination if the zincate pretreatment is performed. This tolerance is supplied by certain patented additives.[16] Furthermore, it has been found that a low concentration of chloride, or no chloride at all, promotes good adhesion. Numerous other factors affect adhesion, as previously mentioned.

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Editor's Note*: The preceding article is based on an article contributed by Donald W. Baudrand, CEF, for the "AES Update" series that ran in this journal in the late 1970s and early 1980s. Since this article was written there has been considerable history added to electroless nickel technology. Nevertheless, the reader may benefit both from the information that remains relevant and the historical perspective of the technology in 1979. The attempt to imprint "autocatalytic" instead of "electroless" into common usage is but one interesting sidelight. The Update series was begun and coordinated by the late Dr. Donald Swalheim, and brought practical information to the metal finisher. In some cases here, words were altered [in brackets] for context.*

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[b] *Updated from original text reference B253-68.*