Autocatalytic (Electroless) Nickel Systems

By Donald W. Baudrand, CEF
Updated by Dr. James H. Lindsay, AESF Fellow

The technology of autocatalytic (electroless*) nickel plating is advancing at a rapid pace. Today, there are many types of autocatalytic nickel-alloy processes, each with deposit characteristics that make it suitable for specific applications. Some of the prominent systems, their deposit properties and common applications are discussed in this article.

This article was written for the "AES Update" series that ran in this journal [*Plating*, 66, 18 (November 1979)] 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.

Nickel-Phosphorus Systems

Since the discovery by Brenner and Riddell[1] of an autocatalytic nickel-phosphorus plating system, researchers have developed a variety of chemical methods of altering deposit characteristics to meet specific applications. The solutions are more stable and much easier to use than ever before.

Acid Solutions

Generally, nickel-phosphorus alloys deposited from acid solutions have similar characteristics. Typically, the nickel content ranges from 88–93 percent and the phosphorus from 7–12 percent. It is difficult to obtain deposits that vary outside this range. The most common alloy is about 91 percent nickel and 9 percent phosphorus. Within the range of 7–12 percent phosphorus, there is little difference in most deposit characteristics. For example, the hardness of the as-plated deposit is around 450-513 DPH, [(HV, kgf/mm^2)(471-539 HK)] and after heat treatment (400°C [750°F]; 1 hr) it is 650-1000 DPH [686-933 HK]. However, other deposit characteristics such as porosity and resistance to chemical attack can be altered over a wide range by changing the complexing system (combination of organic complexing agents) and the type and amount of stabilizer.

For plating on aluminum, autocatalytic nickel solutions are available that have a high tolerance to zinc and other metallic contaminants likely to be introduced from the surface preparation line. Enhanced corrosion resistance is another important consideration for autocatalytic nickel plating on aluminum. The deposit still can have all the desirable physical characteristics such as high hardness, natural lubricity and wear resistance.

For plating on steel and stainless steel alloys, a different stabilizer and complexing system than that used for plating on aluminum can produce a high deposition rate, economical plating and good corrosion resistance.

Careful selection of combinations of complexing agents can result in a deposit with altered crystal structures. As a result, characteristics such as solderability, chemical resistance, surface microsmoothness and magnetic properties can be controlled. A common misconception regarding magnetic properties is that the higher the phosphorus content of the alloy, the lower the ferromagnetic retention. This is often true because the alteration of a complexing system that leads to low-magnetic, or so-called *non-magnetic* deposits also leads to high phosphorus content. However, it has been shown by Mallory[2] that low-phosphorus deposits can have low-ferromagnetic characteristics (non-magnetic). Low-magnetic electroless nickel deposits are used as a base coating for magnetic memory devices, usually made from aluminum. Bright and bright-leveled deposits also are plated from specially formulated baths. Properly done, there is no sacrifice in hardness or other desirable properties.

Alkaline Solutions

Plated deposits from alkaline solutions are typically low in phosphorus content, varying from a few tenths to 5 percent, but usually from 3–5 percent. These solutions are usually less stable than acid solutions. They plate somewhat slower, and are often more difficult to control. Low-phosphorus alloys find application primarily in the electronics industry when enhanced solderability is required. Some deposits can easily be brazed. Solutions that produce deposits low in phosphorus can be operated at low temperature, often room temperature, thus finding application for plating on plastics and on other materials which tend to distort or melt with heat.

Nickel-Boron Systems

Investigation of alternate reducing agents to sodium hypophosphite led to the use of borohydrides and amine boranes.[3] Some of the earlier patents issued cover sodium borohydride or dimethylamine borane as reductants.[4-7] Boron content of deposits from these solutions may vary from 0.1–10 percent, depending on the chemical makeup of the plating solution. The amount of boron codeposited can be controlled within narrow limits. When sodium borohydride is the reductant, a solution pH greater than 12 must be maintained to prevent rapid hydrolysis and decomposition of the solution. The complexing system used for

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**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 - JHL.]*

nickel, because of high pH, must be much tighter than that for acid or mildly alkaline solutions. Borohydride reductants result in a higher boron content in the deposit, usually from 3–6 percent boron. The higher boron content results in high as-plated hardness values. Values up to 800 DPH [826 HK] have been reported.[3] Typical values are 750 DPH [783 HK] for commercial solutions. After heat treating, the hardness increases to 1000-1200 DPH (Vickers) [>933 HK], about the same as nickel-phosphorus.

Amine boranes can be used from acid pH 4.0 to alkaline pH 10.5. It is possible to produce essentially pure nickel deposits (99.9%) by carefully selecting the complexing agents and operating conditions. High electrical conductivity, good solderability, good diode bonding (ultrasonic method) and excellent wetting of brazing alloys are characteristic of deposits in the 1 percent or less range of boron content. It is possible to increase the boron content of a deposit from amine borane-reduced systems up to 3–5 percent by adding certain exaltants,[8] depending on operating conditions. The advantage of this technique is that the solution is easier to operate and control. It is more stable than the high-pH borohydride solutions, and will produce high as-plated hardness. The hard deposits can eliminate the need for heat treatment. This becomes a great advantage when the basis metal is aluminum or another metal whose properties might change due to heat treatment.

Polyalloys

It is possible to include a number of different alloy constituents into autocatalytic nickel plating solutions, thereby producing a wide variety of alloy deposits with a multiplicity of deposit characteristics. Many of these alloys show superior corrosion resistance, superior hardness, high-temperature resistance and interesting and unusual electrical characteristics, including non-magnetic as well as magnetic behavior. There are many commercial polyalloy solutions available.[7,8]

Prior to 1963, alloys deposited by autocatalytic means were limited to nickel-phosphorus and Group VIII metals (Fe, Co, Ni). In 1963, Pearlstein, Weightman and Wick[8] reported autocatalytic nickel-tungsten-phosphorus alloys. Others[9] reported nickel-rhenium-phosphorus and nickel-copper-phosphorus.[10] Mallory[7] introduced ternary and quaternary alloys of nickel with boron, phosphorus, molybdenum, tungsten, tin, copper, iron and cobalt in many combinations.

Nickel-molybdenum-boron and nickel-tungsten-boron exhibit properties which make them suitable for diode bonding (ultrasonic method). Both alloy deposits are solderable, and the Ni-W-B system shows unique ductility as well as superior corrosion resistance. Nickel-tin-boron and nickel-tin-tungsten-boron alloys show outstanding chemical resistance while having favorable soldering characteristics. One of the nickel-molybdenum-boron solutions will plate directly on copper without any previous activation steps or contacts with dissimilar metals. In other words, copper appears to be catalytic to this solution. It finds application for plating isolated circuit patterns rendering protection, good electrical conductivity and a solderable surface.

Another alloy plating solution produces a non-magnetic coating whose magnetic properties do not change after heat treating or aging, thus providing a superior base coating for magnetic memory devices.

Table 1—Autocatalytic Nickel Systems Most Suitable for Obtaining Specific Deposit Characteristics

Characteristics Desired	*Autocatalytic Systems Most Suitable*
Wear resistance	1. Nickel-phosphorus, acid solution.
Corrosion resistance	1. Nickel-phosphorus, acid solution formulated for maximum corrosion resistance on the basis metal selected.
	2. A polyalloy of nickel-tin-phosphorus, nickel-tin-boron, nickel-tungsten-phosphorus, nickel-tungsten-boron, nickel-tungsten-tin-phosphorus, nickel-tungsten-tin-boron or nickel-copper-phosphorus*
Hardness	1. Nickel-phosphorus, acid solution, heat-treated.
	2. If heat treatment is not practical, use nickel-boron of 3% or more boron.
Lubricity	1. Nickel-phosphorus, acid solution, highest phosphorus content.
Chemical resistance	1. Nickel-phosphorus, acid solution.
	2. Polyalloy system.
Solderability	1. Nickel-boron, low boron content, less than 1%.
	2. Polyalloys, exhibit excellent shelf-life solderability.
Diode-bonding	1. Polyalloys.
	2. Nickel boron, less than 1% boron.
Nonmagnetic	1. Polyalloys.
Magnetic (for memory)	1. Nickel-cobalt-phosphorus.
	2. Nickel-cobalt-boron.
	3. Cobalt-phosphorus.
	4. Nickel-cobalt-iron-phosphorus.
Electrical conductivity	1. Nickel-boron with boron less than 0.3% (Resistivity is about 5.8-6.0 $\mu\Omega/cm/cm^2$.).
Electrical resistance	1. Some polyalloys.
	2. Nickel-phosphorus, high-phosphorus content.
Rhodium replacement	1. Nickel boron, 1-3% boron.
Gold replacement	1. Nickel boron, low boron for soldering, 0.1-0.3% B; higher boron for contacts, 0.5-1.0% B.
	2. Polyalloys of phosphorus or boron if below 0.5% P or B.

*Selection depends on severity of requirements and on economics. Boron-reduced systems are about five times more costly [in 1979] in terms of $/mil/$ft^2$. However, thinner deposits may be used

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