

Nickel Plating

Overview

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Summary

Composition, Formation and Advantageous Properties of the Nickel plating process on NdFeB magnetic materials

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Generally speaking, nickel plating can be divided into two categories, electroless and electrolytic. Electroless nickel was first discovered in 1946 by Brenner and Riddell and is also called auto-catalytic or chemical plating.¹ Electrolytic plating is based on the traditional galvanic cell processes where Ni^{2+} ions in solution are reduced by an applied voltage, and where the supply of nickel ions is a nickel anode that continuously oxidizes and dissolves elemental nickel as a result of applied voltage.

Electroless nickel plating is further divided into three categories; alloy, metallic, and composite. Alloy plating generally refers to the deposition of an alloy of nickel, most commonly nickel phosphorous (NiP) or less commonly nickel boride (NiB), whereas metallic plating refers to the deposition of nickel alone. Composite nickel plating refers to the co-deposition of nickel with some suspended solid, e.g. polytetrafluoroethylene (aka Teflon), ZrO_2 , SiC, C, Al_2O_3 , TiO_2 , ZrB_2 , Si_3N_4 , CeO_2 and ceramics, or organic polymers.² Composites are created by adding solids which may enhance hardness, extend coating performance to higher temperatures, or achieve higher thermal shock cycle count before failure. The subject of composite nickel coatings is vast, but not so commercially significant so, we will focus only on the most common coatings, Ni metal and NiP alloy coatings.³

NiP varies in concentration of phosphorous, with commercial processes ranging typically 3-16% by weight. They are categorized by phosphorous weight fraction as low-phosphorous, $P < 5\%$, medium phosphorous, $6\% < P < 9\%$ and high phosphorous nickel, $P > 10\%$. Lower phosphorous nickel coatings are typically harder than higher phosphorous coatings. Superior wear properties are also associated with lower phosphorous content. However, it is observed that NiP with medium level phosphorous levels, like 8% are less porous than corresponding 16% phosphorous levels. Higher phosphorous levels are more corrosion resistant.⁴ In terms of purity, electrolytic nickel deposition can result in 100% pure nickel and electroless nickel deposition processes can result in purity greater than 99% nickel.

Electroless nickel is deposited onto a substrate when nickel ions in an aqueous solution react with a reducing substrate surface to make elemental nickel. The chemical processes are activated by heating the deposition bath to an appropriate temperature. Agitation is required to maintain uniform distribution of reagents in the plating solution.

At the chemical level, hydrogen, released from sodium hypophosphite (NaH_2PO_2) is oxidized and donates a negative charge to the substrate surface. Subsequently, Ni^{2+} ions are reduced at the negatively charged substrate surface and form an amorphous deposition of nickel on the substrate. Electroless nickel is deposited without the use of external electrical energy.

A variety of theories about the intermediate steps of the transformation exist, because the mechanism is not well understood, but, the overall reaction chemistry is illustrated in **Equation 1**.⁵ Hypophosphite, usually added as a sodium salt, (NaH_2PO_2) acts as the reducing agent to make the elemental nickel, Ni^0 , which readily bonds to many surfaces. Sodium hypophosphite is used in a typical bath process and is converted to sodium dihydrogen phosphate (NaH_2PO_3). A complexing agent is added to the bath and is required to keep the Ni^{2+} ions solubilized in the presence of the reducing agent. Typical complexing agents used include hydroxyacetic acid, hydroxypropionic acid, citric acid, or malic acid, and prevent the precipitation of insoluble nickel hydroxide.



There are several other reactions occurring in the solution, and significantly, hydrogen is generated in parallel to the nickel deposition by the hydrolysis of the sodium hypophosphite to generate the sodium dihydrogen phosphate, as shown in **Equation 2**.



Generally, the plating rate is primarily influenced by temperature and final phosphorous content is controlled by pH. Typical plating bath temperatures range from 30-90°C. Electroless nickel can be deposited from either acidic or basic media, making it a very versatile tool for a variety of substrates. Surfactants may also be incorporated into the plating bath formulation to influence the mechanical properties of the NiP coating, namely the surface roughness and microhardness.⁶

It is widely considered that electroless nickel plating is superior to electrolytic plating across several performance parameters.⁷ Fundamentally, the electroless nickel plating offers good corrosion⁸ and hardness properties with uniform coating thickness even on complex form factors.

This perspective is tempered by the observation that the nature of the substrate, the pre-treatment of the substrate, and the process kinetics may also affect coating properties.⁹ However, in general, the following considerations are typical regarding the superiority of electroless nickel over electrolytic nickel. Electroless nickel can be applied to non-metallic substrates, making it a highly versatile technology. The electroless process does not require an applied voltage, and eliminates all the accompanying equipment and process complexity. Additionally, since no electric current flow is involved, variations in resistance along a conductive path do not exist, resulting in the electroless coating depositing at a uniform thickness across complex contours of the substrate.

Electroless nickel is anti-galling relative to electrolytic nickel, and has superior corrosion and wear resistance. Furthermore, electroless coatings tend to have lower porosity than electrolytic coatings. Generally, electroless nickel is applied in the thickness range of 1 to 15 mils, and can be controlled to about ± 0.1 mil, which is very useful where high precision part fabrication is required.

The corrosion of both electrolytic nickel¹⁰ and electroless nickel has been studied extensively, and has been found to be influenced, in part, by the addition of organic compounds to the plating bath that affect the morphology of the finished plated nickel. The work by Liu et. al.¹¹ illustrates that relative corrosion rates depend on the conditions being studied. For example, when comparing the difference in corrosion behavior of electroless nickel deposited with an organic additive, 3-S isothiuronium propyl sulfonate, (UPS) to corrosion behavior of nickel plating deposited from the same plating process but with a different organic additive, thiourea, instead, (TU) it was shown that, in a sodium chloride corrosion test environment, there was no difference in corrosion rate.

By contrast, in a nitric acid corrosion test, the TU increased the corrosion rate, but, the UPS decreased the corrosion rate. This example demonstrates the value of understanding the application conditions thoroughly, so that the correct process parameters may be selected to optimize the product performance and to understand that categorical laboratory tests e.g. "corrosion test" may not be universal.

Regarding corrosion performance between electrolytic nickel and electroless nickel, it takes about four times as much time to remove electroless nickel deposit as it does an electrolytic deposit of the same thickness in a cyanide etching solution, an observation consistent with the notion that electroless nickel has superior corrosion resistance.¹² In terms of hardness, typical electroless nickel has hardness of 300-600 kg/mm² prior to any heat treatment, but, electrolytic nickel is normally in the range of 190 kg/mm².

It should always be considered that it may be useful to consider the application load on the coating to decide whether electrolytic nickel or electroless would be a better choice for a given design. For example, it has been shown that electrolytic nickel has lower internal stress than electroless nickel.¹³ This manifests itself in the observation that electrolytic nickel does not crack with heat treatment, but, electroless nickel shows extensive cracking with high-temperature heating, e.g. 680°C. A general increase in cracking of electroless nickel plating with annealing temperature has been observed.¹⁴ However, in general, electroless nickel has higher ductility at moderate temperatures. Furthermore, electrolytic nickel deposits faster than electroless nickel, which may be important for cost considerations in an industrial application.

Because electroless nickel often contains phosphorous, it is more electrically resistive than electrolytic nickel, which can be deposited as 100% pure nickel. Electrolytic nickel is generally also lower cost than electroless nickel.

In a study of electrolessly nickel plated steel rebar, virtually no difference in corrosion rate was observed whether chloride ion was present or absent in the cement. Ordinarily, we would expect metal subjected to a chloride environment to corrode faster, suggesting that the electroless nickel is an excellent performer against the normally corrosive chloride ion.¹⁵

In the case of electroless NiP, it has been shown that corrosion resistance has been related to phosphorous level, as well as morphology of the deposited NiP layer. ^{16, 17, 18, 19} In acidic environments, high phosphorous nickel generally resists chemical attack better than low phosphorous, but, the reverse is often true in alkaline environments.

Because electroless nickel plating does not rely on electric current distribution through a part, it can be applied to non-conductive materials, including ceramics, glass, and plastics. ²⁰ Because it is diffusion-driven in a water bath, the process is not "line-of-sight" limited, and allows the uniform coating of complex shapes, including internal surfaces of parts.



NiP alloy has extensive application for several reasons, but, for aerospace applications, in particular, it has a melting point range, dependent on phosphorous level, from 880°C to 1455°C ²², as well as excellent tribological ²³ and wear properties ²⁴.

The high melting point property allows for both elevated temperature application, as well as high temperature post processing of the coating.

Nickel plating is generally considered for application as a barrier coating, not as a sacrificial/anodic coating. Anodic coatings are those that dissolve slowly to protect the substrate, such as zinc. Nickel does not dissolve in its application as a protective coating.

For nickel deposited by ion beam sputtering onto NdFeB magnets, adhesive strength was measured as 27 MPa²⁵, but, electroless NiP coatings showed lower adhesive strength in the range of 10 MPa including use of a phosphate interlayer to optimize bond strength.²⁶ Electroplated plated nickel has adhesion strength varying up to around 22MPa. In most cases, adhesion strength depends on surface preparation and deposition process parameters. In the case of electrodeposition, bath pH and temperature are known to influence adhesive strength. Also, cracks in the nickel plating tend to be the source of adhesion failures.

Because the electroless nickel deposition process always generates hydrogen gas (H₂) as a by-product, hydrogen embrittlement of the NdFeB is sometimes observed.²⁷ Even during electrolytic deposition, hydrogen reactions with the Nd grain boundary have been observed. If the underlying NdFeB substrate undergoes hydrogen embrittlement, then, voiding beneath the nickel plating can occur, and cause catastrophic failure of the entire structure. Alternative methods of deposition of nickel on NdFeB that are hydrogen gas-free include jet electrodeposition²⁸, electrodeposition of multi-layered Cu/Ni/Cu^{29, 30} and ion beam deposited nickel.

At least one study claims better corrosion protection of NdFeB magnets with ion beam deposited nickel than electroless nickel³¹. In the study by Shen, et. al. the Cu/Ni/Cu multilayered coating performed better than electroless nickel under chloride corrosion test conditions.

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