Nickel Plating Overview

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

Nickel Plating Composition

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 autocatalytic or chemical plating. 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 phosphorus (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.

Composites are created by adding solids, which may enhance hardness, extend coating performance to higher temperatures, or achieve a 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.

NiP varies in the concentration of phosphorus, with commercial processes ranging typically 3-16% by weight. They are categorized by phosphorus weight fraction as low-phosphorus ($P < 5\%$), medium phosphorus ($6\% < P < 9\%$), and high-phosphorus nickel ($P > 10\%$). Lower phosphorus nickel coatings are typically harder than higher phosphorus coatings. Superior wear properties are also associated with lower phosphorus content. However, it is observed that NiP with medium-level phosphorus, like 8%, is less porous than corresponding 16% phosphorus levels. Higher phosphorus levels are more corrosion-resistant. 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.

Nickel Plating Formation Process

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 a 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.

Hydroxyacetic acid, hydroxypropionic acid, citric acid, or malic acid is often added to prevent the precipitation of insoluble nickel hydroxide:

Equation 1: $NiCl_2 + NaH_2PO_2 + H_2O \rightarrow Ni + NaH_2PO_3 + 2HCl$

Several other reactions occur in the solution. Significantly, hydrogen is generated in parallel to the nickel deposition by the hydrolysis of sodium hypophosphite, generating sodium dihydrogen phosphate:

Equation 2: $NaH_2PO_2 + H_2O \rightarrow NaH_2PO_3 + H_2$

Generally, the plating rate is primarily influenced by temperature, and the final phosphorus 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 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 surface roughness and microhardness.

Nickel Plating Advantageous Properties

Electroless nickel plating is widely considered superior to electrolytic plating across several performance parameters. Fundamentally, electroless nickel plating offers good corrosion and hardness properties with uniform coating thickness, even on complex form factors. However, the nature of the substrate, the pre-treatment of the substrate, and the process kinetics may also affect coating properties.

Electroless nickel can be applied to non-metallic substrates, making it a highly versatile technology. The electroless process does not require an applied voltage, eliminating 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 uniform coating 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 for high-precision part fabrication.

The corrosion of both electrolytic and electroless nickel has been studied extensively. Organic compounds added to the plating bath can influence the morphology and corrosion resistance of the plated nickel. For instance, studies comparing the use of 3-S isothiuronium propyl sulfonate (UPS) versus thiourea (TU) show different corrosion rates in various environments, demonstrating the importance of understanding application conditions.

Regarding corrosion resistance, it has been observed that electroless nickel deposit takes about four times as long to remove as an electrolytic deposit of the same thickness in a cyanide etching solution. This supports the notion that electroless nickel has superior corrosion resistance.

In terms of hardness, electroless nickel typically ranges from 300-600 kg/mm^2 before heat treatment, while electrolytic nickel is usually around 190 kg/mm^2. However, electrolytic nickel has lower internal stress and does not crack during high-temperature heat treatment, unlike electroless nickel, which may show extensive cracking.

Electroless nickel's phosphorus content makes it more electrically resistive than electrolytic nickel, which can achieve 100% pure nickel deposition.

Additionally, electrolytic nickel is generally lower in cost than electroless nickel.

Nickel Plating Adhesion to NdFeB Magnet Surfaces

Nickel plating is typically used as a barrier coating rather than a sacrificial/anodic coating. For nickel deposited by ion beam sputtering onto NdFeB magnets, adhesive strength has been measured at 27 MPa. Electroless NiP coatings showed lower adhesive strength, around 10 MPa, even when using a phosphate interlayer to optimize bond strength. Electroplated nickel shows adhesion strength up to around 22 MPa.

Adhesion strength is highly dependent on surface preparation and deposition process parameters. For electrodeposition, bath pH and temperature are known to influence adhesive strength. Cracks in the nickel plating are often the source of adhesion failures.

The electroless nickel deposition process generates hydrogen gas as a by-product, which may lead to hydrogen embrittlement in the NdFeB substrate, causing voiding beneath the nickel plating and potential catastrophic failure. Alternative deposition methods, such as jet electrodeposition, multilayered Cu/Ni/Cu electrodeposition, or ion beam deposition, can mitigate hydrogen embrittlement.

Studies suggest that ion beam-deposited nickel and multilayered Cu/Ni/Cu coatings offer better corrosion protection for NdFeB magnets than electroless nickel under chloride corrosion test conditions.

Conclusion

Nickel plating, particularly electroless nickel plating, offers numerous advantages, including excellent corrosion resistance, uniform thickness, and superior wear properties. However, careful consideration of application requirements, substrate preparation, and process parameters is essential to optimize performance and select the appropriate nickel plating method.

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