

THE EFFECT OF METALLURGICAL STRUCTURE ON THE PROPERTIES OF ELECTROLESS NICKEL COATINGS

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INTRODUCTION

Different electroless nickel plating solutions are formulated for different objectives. Some are intended to provide high corrosion resistance or complete lack of magnetic response. Others are designed to have high hardness and improved wear resistance. Still others deposit coatings with a bright, aesthetically pleasing appearance, or even a dull, non reflective one.

While these are all valid goals for formulation, they result in coatings with widely varying compositions and with different metallurgical structures. Their phosphorus content may range from 1 to 13 percent, and they may contain crystalline or amorphous phases or a mixture of the two. These variations have a powerful effect upon the properties of the coating.

This paper describes the effect that composition and structure have on the properties of electroless nickel coatings. The internal stress, melting point, density, resistivity, magnetic response, strength and ductility, hardness and wear resistance, porosity, corrosion resistance and passivity of different coatings are described.

STRUCTURE

In the as-deposited condition, many electroless nickel coatings are amorphous by x-ray diffraction testing. The degree of a coating's amorphous nature, however, depends on its composition. Figure 1 is a phase diagram for electroless nickel-phosphorus alloys that shows the effect of composition on structure.¹

Electroless nickel coatings containing up to 4½ percent phosphorus consist of a microcrystalline, solid solution of phosphorus in nickel, called beta (β) phase.¹ The size of the crystals has been reported to be between 20 and 60 Å (compared with 100 to 500 Å for electrolytic nickel plating).²

When their phosphorus content exceeds 11 percent, electroless nickel coatings are totally amorphous, without any crystal structure. This glass like phase is called gamma (γ).¹ The lack of structure of high phosphorus deposits has been confirmed by electron diffraction at 150,000 magnifications.³ Both β and γ are metastable, non-equilibrium phases.

Between $4\frac{1}{2}$ and 11 percent phosphorus, electroless nickel coatings consist of a mixture of amorphous γ and crystalline β phases.¹ The changes in structure resulting from changing phosphorus content, and especially the transitions between phases, produce significant changes in the properties of these coatings.

When electroless nickel coatings are heated to high temperatures, nickel



Figure 1: Phase Diagram for Electroless Nickel Deposits

phosphide (Ni_3P) begins to precipitate and any amorphous material begins to crystallize. The formation of intermetallic phosphide particles in the deposit causes its hardness and wear resistance to increase, while its ductility and corrosion resistance declines.

The nature of the phosphide formation and the temperature at which it occurs also depends upon the phosphorus content of the coating. This is also illustrated by Figure 1. In low phosphorus β and high phosphorus γ phases, a single decomposition reaction occurs. The reaction is the conversion of the metastable phases to Ni₃P and α nickel. Alpha nickel is the equilibrium phase containing only 0.17 percent phosphorus dissolved in nickel. With low phosphorus deposits, this reaction occurs at about 400°C. With high phosphorus deposits, it occurs at temperatures between 330° and 360°C.

In the mixed β and γ phase region, a second decomposition reaction occurs at 250° to 290°C. This reaction is the conversion of beta phase to α nickel, which results in the precipitation of fine particles throughout the coating. Then, when the temperature is increased to 310° to 330°C, gamma converts to Ni₃P and α nickel. The second decomposition reaction, gives these alloys a second hardening reaction, and allows them to harden at lower temperatures.¹

PROPERTIES

The properties of electroless nickel coatings are summarized in Appendix 1 and described in the following paragraphs. Appendix 1 also compares the properties of electroless nickel coatings to those of electrolytic nickel and hard chromium deposits.^{1 4 5 6 7 8 9 10}

Internal Stress

The internal stress of an electroless nickel deposit is dependent upon the substrate being plated and the structure of the deposit. The internal stress in electroless nickel coatings consists of two components, a thermal stress due to the difference in thermal expansion between the coating and the substrate, and an intrinsic stress due to structural mismatch and non-homogeneity within the deposit. Both primarily depend on the coating's composition. Figure 2 shows the intrinsic stress of electroless nickel coatings as a function of their phosphorus content.¹

Low and high phosphorus coatings (which are both homogeneous phases) are compressively stressed. Typical stress values are 5 to 40 MPa (700 to 6000 psi).

Medium phosphorus coatings consist of a mixture of crystalline β and amorphous γ phases, which causes structural mismatch and tensile stresses. Typical stress values are between 20 and 50 MPa (3000 to 7000 psi). This high level of stress in these



Figure 2: Effect of Phosphorus Content on the Internal Stress of Electroless Nickel

coatings tries to tear them apart and promotes cracking, brittleness, porosity and poor corrosion resistance.

Melting Point

Electroless nickel coatings are eutectic alloys with a wide melting range. Unlike a pure compound, it does not have a true melting point. This is shown by the upper portion of the phase diagram in Figure 1. The triangular shaped region marked α + molten is a mixture of melted nickel-phosphorus and unmelted α nickel.

The melting range for electroless nickel coatings varies with the phosphorus content of the deposit. All electroless nickel coatings begin to melt at approximately 880°C, which is the eutectic temperature for the α nickel/Ni₃P system. The temperature at which the coating is completely liquid, however,

increases with decreasing phosphorus content from 880°C at 11 percent -- the eutectic point -- to 1450°C for pure nickel. Thus, the melting range becomes wider as the phosphorus content is reduced.

All electroless nickel coatings contain large quantities of liquid material at temperatures above 880°C. For example, at 900°C, coatings containing 5, 8 and 11 percent phosphorous are 46, 74 and 100 percent melted.

Physical Properties

The physical properties of electroless nickel coatings also vary with the deposit's composition and structure. Figure 3 illustrates this dependent and shows how the density of electroless nickel coatings decline with their increasing phosphorus content. Density varies from 8.89 g/cm³ for pure nickel metal to 7.75 g/cm³ for high phosphorus deposits to 7.2 g/cm³ for Ni₃P.⁴ ¹¹ ¹² ¹³ ¹⁴ The correct value of density must be known for thickness to be accurately determined by many quality control tests.



Figure 3: Effect of Phosphorus Content on the Density of Electroless Nickel

Phosphorus content does not appear significantly to effect the thermal expansion of electroless nickel. The coefficient of thermal expansion of coatings containing 2 to 12 percent phosphorus is between 12 and 14 μ m/m/°C, which is approximately equal to that of steel or pure nickel.^{4 9 13}

The effect of composition on the electrical and thermal properties of electroless nickel coatings is even stronger. The effect of phosphorus content on electrical resistivity is shown in Figure 4. Resistivity ranges from about 25 μ S-cm for coatings containing only 2 percent phosphorus to about 110 μ S-cm for 11 percent phosphorus deposits.^{4 8 11}

The thermal conductivity of electroless nickel coatings containing 9 to 13



Figure 4: Effect of Phosphorus Content on the Resistivity of Electroless Nickel

percent phosphorus is 0.05 to 0.08 W/cm°K. The conductivity of coatings containing 2.6 percent phosphorus is between 0.5 and 0.7 W/cm°K, which is similar to that of electrodeposited nickel.^{4 8 11 15}

Before heat treatment, electroless nickel coatings containing more than about 11 percent phosphorus are essentially nonmagnetic. The magnetic susceptibility of one deposit was measured to be about 10⁻⁴ mks at ambient temperature.¹⁶ This is illustrated by Figure 5, which shows the magnetic moment of different coatings as a function of their phosphorus content.¹⁷ ¹⁸ Lower phosphorus coatings, however, have some magnetic susceptibility. The coercivity of 2 to 6 percent phosphorus coatings is about 20 to 130 oersteds, while that



Figure 5: Effect of Phosphorus Content on the Magnetic Moment of Electroless Nickel

of deposits containing 7 to 9 percent phosphorus is typically 1 to 2 oersteds.⁷

Mechanical Properties

Electroless nickel coatings, like other glasses, have high strength and limited ductility. Except lower phosphorus deposits, the ultimate tensile strength of most coatings exceeds 700 MPa (100,000 psi). This is equal to that of many hardened steels and allows the coating to withstand considerable abuse. The strength of a deposit varies with its phosphorus content as shown in Figure 6. The strength of low phosphorus coatings is only about one third that of nickel metal.¹⁹²⁰

The ductility of electroless nickel coatings is limited when compared with most electroplated deposits or with conventional materials of construction. That of γ phase coatings is generally between 1 and 2 percent, while β phase deposits containing less than 2 percent phosphorus have been reported to have a ductility as high as 2.8 percent. The elongation of medium and most low phosphorus coatings is typically less than 1 percent. This is illustrated by Figure 7, which shows the ductility of different deposits.^{1 4 8 21 22}



Figure 6: Effect of Phosphorus Content on the Strength of Electroless Nickel



Figure 7: Effect of Phosphorus Content on the Ductility of Electroless Nickel

Hardness

Hardness and resulting wear resistance of electroless nickel coatings are very important properties for many applications. Before heat treatment, the microhardness of medium and high phosphorus coatings is between 500 and 600 HV₁₀₀. Low phosphorus coatings have hardnesses as high as 650 to 700 HV₁₀₀. This is very approximately equal to 50 and 56 HRC respectively and equivalent to many hardened alloy steels. Structure has a pronounced effect on the



Figure 8: Effect of Phosphorus Content on the Hardness of Electroless Nickel

deposit's hardness as illustrated by Figure 8.¹ The crystalline low phosphorus alloys have the highest hardness, while amorphous high phosphorus coatings have the lowest. Certain additives can increase the hardness of some low phosphorus coatings to even higher values. In one study, the hardness of coatings containing 2.6 to 3.0 percent phosphorus was found to be between 860 and 880 HV₁₀₀.⁸

Heat treatment will cause electroless nickel coatings to precipitation harden and can produce hardness values as high as 1100 HV_{100} . Hardenability, however also depends on phosphorus content and structure.

Hardening begins to occur after the Ni_3P decomposition temperature is exceeded. Low and high phosphorus alloys can experience only one decomposition reaction to α phase and Ni_3P . Since this reaction does not



Figure 9: Effect of Phosphorus Content on the Hardenability of Electroless Nickel

occur until the temperature is raised to above 330°C, significant hardening cannot start until this point is reached. Mixed β and γ alloys, however, experience a second decomposition reaction at temperatures between 250° and 290°C. Thus, these coatings begin to harden earlier and at lower temperatures than either pure beta or gamma alloys. The difference in hardenability of different alloys is illustrated by Figure 9.⁶

Because of their glass like state, the Young's modulus of most electroless nickel coatings is only about one third to one half that of crystalline nickel metal. Between 2 and 10 percent phosphorus content, the biaxial modulus of elasticity is

about 100 to 130 GPa and is not significantly affected by phosphorus content. The modulus of elasticity of coatings containing more than 10 percent phosphorus, however, is higher, and typically between 170 and 200 GPa.^{4 5 21}

Wear Resistance

Because of their high hardness and natural lubricity, electroless nickel coatings have excellent resistance to both adhesive and abrasive wear. Wear resistance can be further improved by heat treatment.

The phosphorus content and structure of electroless nickel coatings also strongly affects wear resistance. This effect is illustrated by Figure 10. Under abrasive wear conditions, the Taber wear of medium and high phosphorus coatings is typically between 15 and 19 mg/1000 cycles. With coatings containing 2 to 4 percent phosphorus, however, the TWI is reduced to 10 to 12 mg/1000 cycles.¹ However, Taber wear values as low as 4 or 5 mg/1000 cycles have been observed for some additive hardened, low phosphorus deposits.⁸



Figure 10: Effect of Phosphorus Content on the Abrasive and Adhesive Wear of Electroless Nickel Coatings

With adhesive wear, an opposite trend has been observed. After heat treatment at 400°C for 1 hour, Falex wear dropped from 5.1 mg for a coating containing 4.4 percent phosphorus to 0.5 to 0.6 mg for coatings containing 9.1 and 11.2 percent phosphorus.⁶ This trend is also shown in Figure 10.

Porosity

The structure of electroless nickel coatings also affects their porosity. The salt spray resistance of coatings undergoes a transition at a phosphorus content of about 10½ percent as shown by Figure 11.⁴ This step type improvement in protection is probably the result of the completely amorphous nature of γ phase alloys. The performance of low phosphorus β alloys has been reported to be similar to that of medium phosphorus deposits.²¹



Figure 11: Effect of Phosphorus Content on the Salt Spray Resistance of Electroless Nickel

Corrosion Resistance

The effect of phosphorus content and structure on the corrosion resistance of electroless nickel coatings is shown in Figure 12. In 10 percent (by weight) HCI, electroless nickel coatings are in their most passive and fully corrosion resistant state when they are composed only of amorphous gamma phase. With this phase, the corrosion rate is only about 50 μ m/y (2 mil/y). When only crystalline beta phase is present, its level of corrosion in hydrochloric acid is similar to that of unalloyed nickel, about 2000 μ m/y (80



Figure 12: Effect of Phosphorus Content on the Corrosion of Electroless Nickel in 10% Hydrochloric Acid

mil/y).²² Increasing the phosphorus content of the beta phase helps to improve its corrosion resistance, but not to the same level as gamma phase.¹

Once the phosphorus concentration is increased to more than about 4½ percent, and gamma begins to form, corrosion is again increased. The mixture of the two phases, with two different compositions, produces active/passive cells within the alloy, causing it to suffer severe chemical attack.¹

Passivity

The passivity of electroless nickel in concentrated nitric acid is also greatly improved when a coating's phosphorus content is increased to more than $10\frac{1}{2}$ percent. Little protection is obtained from mixed β and γ alloys. Very low phosphorus β alloys are different from other coatings. They do not blacken and instead develop a milky white color after one minute. This is illustrated by Figure 13, which shows the time required to blacken a deposit in the nitric acid test.¹



Figure 13: Effect of Phosphorus Content on Nitric Acid Resistance of Electroless Nickel

CONCLUSION

In the as-deposited condition, electroless nickel coatings can contain crystalline and amorphous phases. The relative amounts of these phases depend on the formulation of the bath and on the composition of the resulting deposit. The coating's composition and metallurgical structure also determine its properties. Completely amorphous, gamma phase deposits typically provide coatings with the lowest porosity and best corrosion resistance, the lowest magnetic moment and the highest hardness and wear resistance after heat treatment. Completely crystalline, beta phase deposits provide coatings with the lowest electrical and thermal conductivity and the highest as-deposited hardness and wear resistance. Coatings containing a mixture of phases also provide useful hardness, wear resistance and corrosion resistance. Accordingly, the properties required for each application should be carefully reviewed to ensure that the best coating is selected.

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Appendix 1

Property	Ni-3P	Ni-8P	Ni-11P	Nickel	Chromium
Composition	3-4%P, balance Ni	6-9%P, balance Ni	11-12%P, balance Ni	100% Ni	100% Cr
Structure	Micro crystalline	Mixed crystalline and amorphous	Amorphous	Crystalline	Crystalline
Internal stress	-10 MPa	+40 MPa	-20 MPa	+140 MPa	+200 MPa
Final Melting Point	1275°C	1000°C	880°C	1450°C	1890°C
Density	8.6 g/cm ³	8.1 g/cm ³	7.8 g/cm ³	8.9 g/cm ³	7.1 g/cm ³
Coefficient of Thermal Expansion	12.4 µm/m°C	13 µm/m°C	12 µm/m°C	14 µm/m°C	8.4 µm/m°C
Electrical Resistivity	30 µS-cm	75 µS-cm	100 µS-cm	8 µS-cm	40 µS-cm
Thermal Conductivity	0.6 W/cm°K	0.05 W/cm°K	0.08 W/cm°K	0.95 W/cm°K	0.67 W/cm°K
Specific Heat	0.25 cal/g°K	ND	0.11 cal/g°K	0.11 cal/g°K	0.11 cal/g°K
Magnetic Coercivity	130 Oe	1.4 Oe	0	70 Oe	ND
Tensile Strength	300 MPa	900 MPa	800 MPa	400 MPa	120 MPa
Ductility	0.7 %	0.7 %	1.5 %	28 %	0.1 %
Modulus of Elasticity	130 GPa	110 GPa	170 GPa	180 GPa	120 GPa
Hardness, as deposited	700 HV ₁₀₀	600 HV ₁₀₀	530 HV ₁₀₀	170 HV ₁₀₀	1000 HV ₁₀₀
Hardness, heat treated	960 HV ₁₀₀	1000 HV ₁₀₀	1050 HV ₁₀₀	NA	NA
Coefficient of Friction	ND	0.38	0.45	ND	0.43
Taber Wear Index, as deposited	11 mg/ 1000 cycles	16 mg/ 1000 cycles	19 mg/ 1000 cycles	25 mg/ 1000 cycles	2 mg/ 1000 cycles
Taber Wear Index, heat treated	9 mg/ 1000 cycles	12 mg/ 1000 cycles	12 mg/ 1000 cycles	NA	NA
Corrosion Protection, salt fog resistance	24 hours	96 hours	1000 hours	24 hours	<24 hours

Typical Properties of Electroless Nickel, Nickel and Chromium Coatings

ND = Not Determined NA = Not Applicable

Ronald N. Duncan

BIOGRAPHICAL SKETCH

In Memory of Ron Duncan

Ron Duncan served as Vice President of Palm International, Inc., where he led the company's technical and educational initiatives. Prior to joining Palm, he was Director of Research at Elnic, Inc., focusing on electroless nickel formulation and materials research.

Before entering the metal finishing industry, Ron spent 12 years in the oil sector with Exxon and Caltex Petroleum Corporations, tackling materials and corrosion challenges. His work took him across the globe—including the United States, Middle East, Europe, South America, and Africa—where he developed a reputation for his deep expertise and practical problem-solving.

Ron held a BE in Mechanical and Metallurgical Engineering from Vanderbilt University. He was a Registered Professional Engineer and a certified Corrosion Specialist through NACE. A leader in technical standards, he chaired NACE task groups T-1G-19 and T-6A-53, contributing to authoritative reports on electroless nickel and other metallic coatings. He also served on the AESF's Electroless Committee.

Throughout his distinguished career, Ron authored more than fifty technical papers on corrosion, coatings, and electroless nickel. His work appeared in Materials Performance, Plating and Surface Finishing, Metals Progress, Products Finishing, and Finishers Management, as well as in numerous industry conferences. He was the principal author of the electroless nickel chapter in Volume 5 of the Metals Handbook and was honored with the AESF Gold Medal in 1996 for the best paper published in Plating and Surface Finishing.

Ron also directed the Electroless Nickel School, a comprehensive four-day seminar presented by Palm, which educated professionals in all aspects of electroless nickel technology.

Ron Duncan passed away on December 15, 2006. He is deeply missed by his family, colleagues, and the broader surface finishing community. His legacy of innovation, mentorship, and integrity continues to inspire all who had the privilege of working with him.