

## THE ENGINEERING PROPERTIES OF ELECTROLESS NICKEL COATINGS

Electroless nickel is a term used to describe plating of a nickel-phosphorus coating onto a suitable substrate by chemical reduction. Unlike electroplated coatings, electroless nickel is applied without an externally applied electric current. Instead, the coating is deposited onto a part's surface by reducing nickel ions to metallic nickel with sodium hypophosphite. This chemical process avoids many of the problems associated with most metallic coatings and provides deposits with many unique characteristics.

As applied, electroless nickel coatings are uniform, hard, relatively brittle, lustrous, easily solderable and highly corrosion resistant. They can be precipitation hardened to very high levels through the use of low temperature treatments, producing wear resistance equal to that of commercial hard chrome coatings. This combination makes the coating well suited for many severe applications and often allows it to be used in place of more expensive or less readily available alloys. The engineering properties of electroless nickel deposits, and how they relate to the use of the coating, are discussed in the following sections.

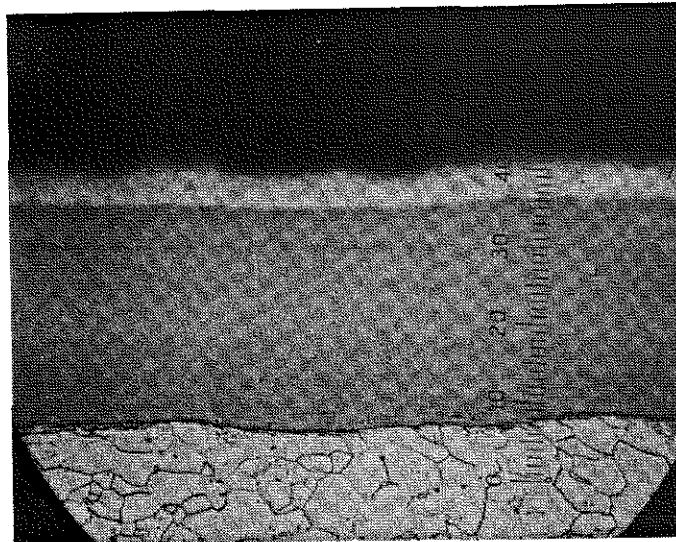
### STRUCTURE

Hypophosphite reduced electroless nickel is one of the very few metallic glasses used as an engineering material. Depending on the formulation of the plating solution, commercial coatings may contain 5 to 12 percent phosphorus dissolved in nickel, and as much as 0.25 percent other elements. The structure of these coatings depends upon their composition. Coatings containing up to 5 percent phosphorus consist of crystalline  $\beta$  nickel with phosphorus in solid solution. Those with phosphorus contents between 5 and 8½ percent, contain a mixture of  $\alpha$  and  $\beta$  phases and are partly crystalline. Coatings containing more than 8½ percent phosphorus consist only of  $\alpha$  phase nickel-phosphorus and are normally amorphous to x-rays. These high phosphorus deposits have no crystal structure or separate phases<sup>1,2,3</sup>. Electron diffraction studies of deposits have confirmed their lack of crystal structure at magnifications up to 150,000<sup>4</sup>.

The continuity of electroless nickel coatings also depends upon their composition. Coatings containing more than 10 percent phosphorus and less than 0.05 percent of impurities are typically continuous. A cross sectional view of one of these coatings is shown in Figure 1.

FIGURE 1

Cross sectional view of a 75  $\mu\text{m}$  thick Electroless Nickel deposit. 400X magnification. Etched in 2% nital.



Copper overplate

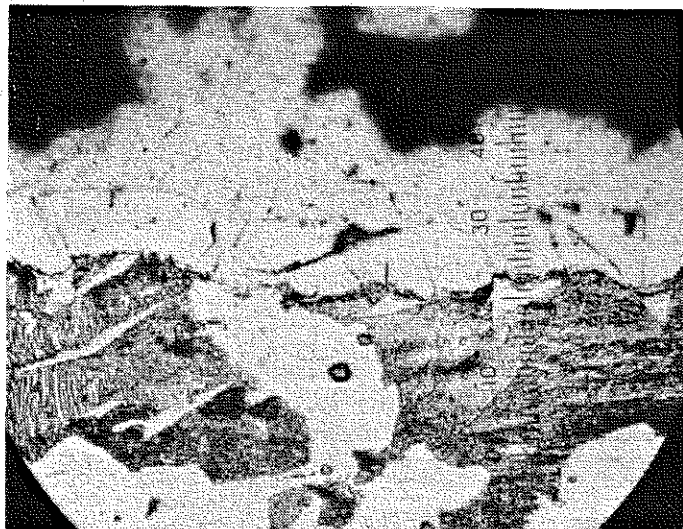
75  $\mu\text{m}$  thick coating

Steel substrate

Lower phosphorus coatings, and especially those applied from baths stabilized or brightened with heavy metals or sulfur compounds, are often porous. These deposits consist of columns separated by cracks and holes. The presence of such discontinuities has a severe effect on the deposit's properties, especially on its ductility and corrosion resistance. An example of this type of deposit is shown in Figure 2<sup>1,2,5,6</sup>.

FIGURE 2

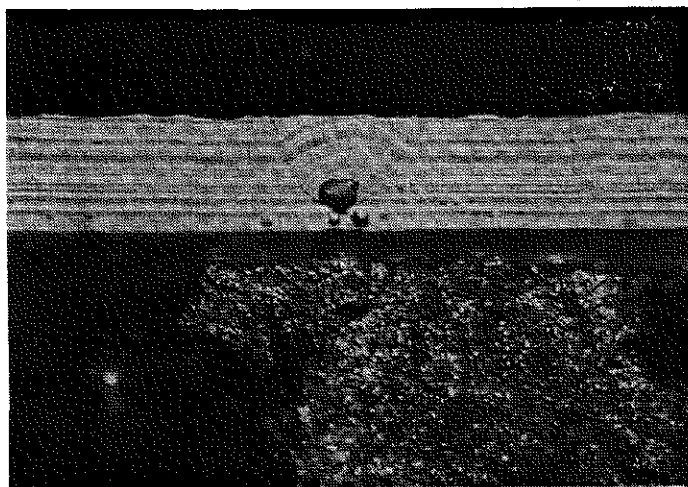
Cross sectional view of a 25  $\mu\text{m}$  thick electroless nickel containing approximately 8 percent phosphorus and 0.15 percent cadmium and lead. 400X magnification. Etched in 2% nital.



Lower phosphorus and heavy metal stabilized deposits also frequently appear to have a laminar structure parallel to their substrate. One of this type of coating is shown in Figure 3. These laminations result from variations in the phosphorus content of the different layers of the coating, which in turn are due to changes in the pH or stabilizer content of the bath during plating. The more sophisticated complexing and stabilizing systems used to apply high phosphorus deposits, eliminate these variations and produce the more homogeneous structure shown in Figure 1<sup>2,4,5,7</sup>.

FIGURE 3

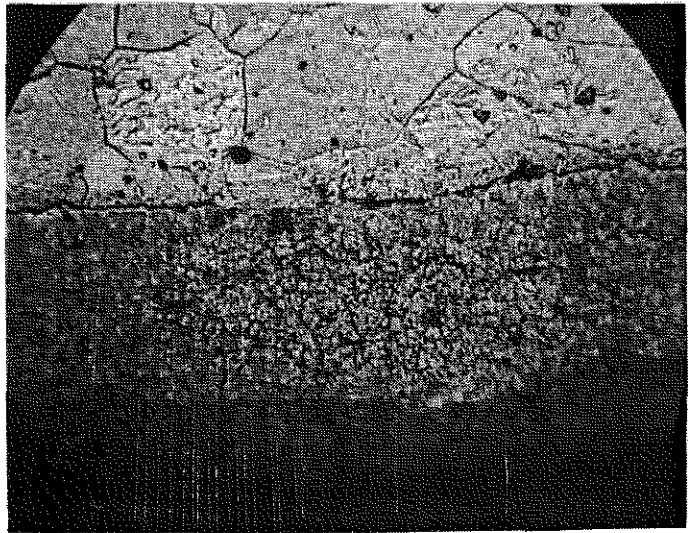
Cross sectional view of a laminar 15  $\mu\text{m}$  thick electroless nickel containing 7 to 9 percent phosphorus and small amounts of sulfur. The tulip shaped area is the result of a particle of sand or blasting media embedded in the deposit during plating. The coating was subsequently lapped, which removed the protrusion produced by the particle. 1000X magnification. Etched in 10% oxalic acid at 6 volts.



As electroless nickel deposits are heated to temperatures above  $220^{\circ}\text{C}$  to  $260^{\circ}\text{C}$  ( $420^{\circ}$  to  $500^{\circ}\text{F}$ ) structural changes begin to occur. First, coherent and then distinct particles of nickel phosphite ( $\text{Ni}_3\text{P}$ ) form within the alloy. Then at temperatures above  $320^{\circ}\text{C}$  ( $600^{\circ}\text{F}$ ) the deposit begins to crystallize and to lose its amorphous character. With continued heating the nickel phosphite particles conglomerate and a two phase alloy forms. With coatings containing more than 8 percent phosphorus a matrix of  $\text{Ni}_3\text{P}$  forms, while almost pure nickel is the predominate phase in lower phosphorus deposits. These changes cause a rapid increase in the hardness and wear resistance of the coating, but cause its corrosion resistance and ductility to be reduced. A cross sectional view of a fully hardened, coating is shown in Figure 4<sup>1,2,5,7,8</sup>. Heating also causes the deposit to shrink and can result in cracking through the coating to the substrate,<sup>9</sup>.

FIGURE 4

Cross sectional view of a 25  $\mu\text{m}$  thick, coating after heat treatment at 400 $^{\circ}\text{C}$  for 24 hours. 1000X magnification. Etched in 5%  $\text{CrO}_3$  at 6 volts.



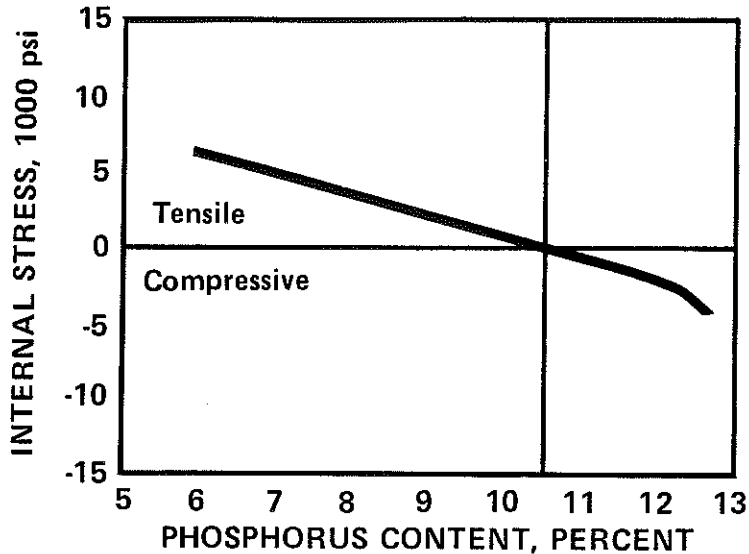
With prolonged heat treatment at high temperatures phosphorus from the region near the interface will diffuse into the substrate. This can be helpful in obtaining adhesion on passive metals like titanium or stainless steel. On mild steel, a nickel-iron intermetallic layer between the coating and the substrate can be produced by 4 hour heat treatments at temperatures above 650 $^{\circ}\text{C}$  (1200 $^{\circ}\text{F}$ ). This layer provides a very wear resistant surface, and in some environments will increase the corrosion resistance of the coating<sup>2,5,7,8</sup>.

#### INTERNAL STRESS

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 a structure stress due to structural mismatch within the deposit caused by non-homogeneity. Both are primarily a function of the coating's composition. As illustrated by Figure 5<sup>10</sup>, on steel the stress in coatings containing more than 10 percent phosphorus is neutral or compressive. With lower phosphorus deposits, however, tensile stresses of 15 to 45 MPa (2 to 6 ksi) occur. The high level of stress in these coatings promotes their cracking and porosity<sup>5</sup>.

FIGURE 5

Effect of phosphorus content on the internal stress of electroless nickel deposits on steel.



The structural changes during heat treatment at temperatures above 220°C (420°F), cause a volumetric shrinkage of up to 4 to 6 percent within electroless nickel deposits. This increases tensile stress or reduces compressive stress in the coatings<sup>2,8,9</sup>.

Deposit stress is also increased by the co-deposition of orthophosphites or contaminants, or by the presence of excess complexing agents in the plating solution<sup>9,11</sup>. Even small quantities of some metals can produce a severe increase in stress. For instance, the addition of only 5 mg/l of bismuth and antimony to most baths will cause the deposit stress to increase to as much as 350 MPa (50 ksi) tensile. High levels of internal stress also reduce the coating's ductility and increase its porosity<sup>2,9</sup>.

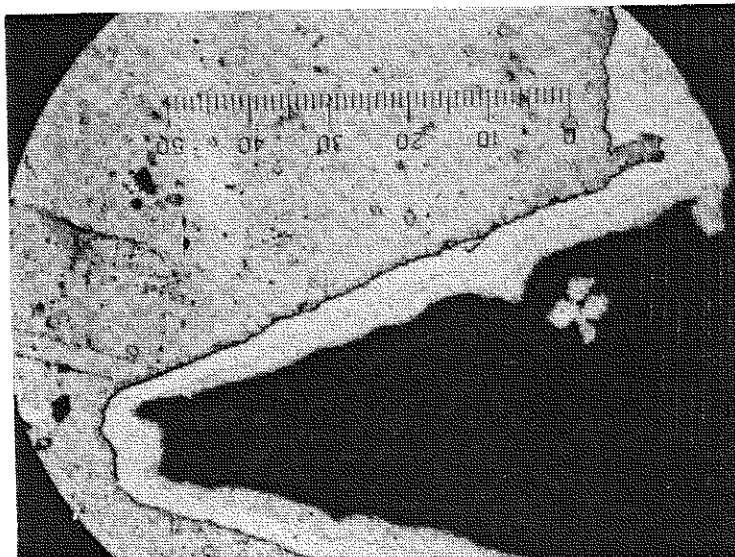
#### UNIFORMITY

One especially beneficial property of electroless nickel is its uniform coating thickness. With electroplated coatings, thickness can vary significantly depending upon the part's configuration and its proximity to the anodes. Not only can these variations effect the ultimate performance of the coating, but they can also cause additional finishing to be required after plating.

With electroless nickel the plating rate and coating thickness are the same on any section of the part exposed to fresh plating solution. Grooves, slots, blind holes, and even the inside of tubing will have the same amount of coating as the outside of a part. This is illustrated by Figure 6 which shows the uniform thickness on the internal threads of a small spray nozzle.

FIGURE 6

An example of the uniformity of electroless nickel coatings. Unlike the copper overplate, the 25  $\mu\text{m}$  thick electroless nickel coating reproduces the profile of the internal threads of the part. The substrate is leaded steel. 100X magnification. Etched in 1% picral.



Because of its uniformity, often the overall finishing cost of a part will be less with electroless nickel than with electroplated coatings, even though the material cost of the process is higher. For example, the substitution of electroless nickel for hard chromium on many of the cylinders and rolls used in the printing and textile industries has not only reduced the cost of plating by 40 percent, but also has allowed 55 percent of the grinding time to be saved<sup>12</sup>.

With electroless nickel, coating thickness can be controlled to suit the application. Coatings as thin as  $2\frac{1}{2}$   $\mu\text{m}$  (0.1 mil) are commonly applied for electronic components, while those as thick as 75 to 125  $\mu\text{m}$  (3 to 5 mils) are typical for corrosive environments. Coatings thicker than 250  $\mu\text{m}$  (10 mils) are used for salvage or repair of worn or mismachined parts<sup>5</sup>.

#### ADHESION

The adhesion of electroless nickel coatings to most metals is excellent. The initial replacement reaction, which occurs with catalytic metals, together with the associated ability of the baths to remove submicroscopic soils, allows the deposit to establish metallic as well as mechanical bonds with the substrate. The bond strength of coatings to properly cleaned steel has been found to be 400 MPa (60 ksi) or more<sup>1,3</sup>. The adhesion to aluminum and aluminum alloys is less, but usually exceeds 300 MPa (40 ksi)<sup>2,5,7</sup>.

With non-catalytic or passive metals, such as stainless steel, an initial replacement reaction does not occur and adhesion is reduced. With proper pretreatment and activation, however, the bond strength of the coating normally is at least 140 MPa (20 ksi)<sup>2,5,7</sup>. The adhesion to copper alloys is usually between 300 and 350 MPa (40 and 50 ksi)<sup>2</sup>.

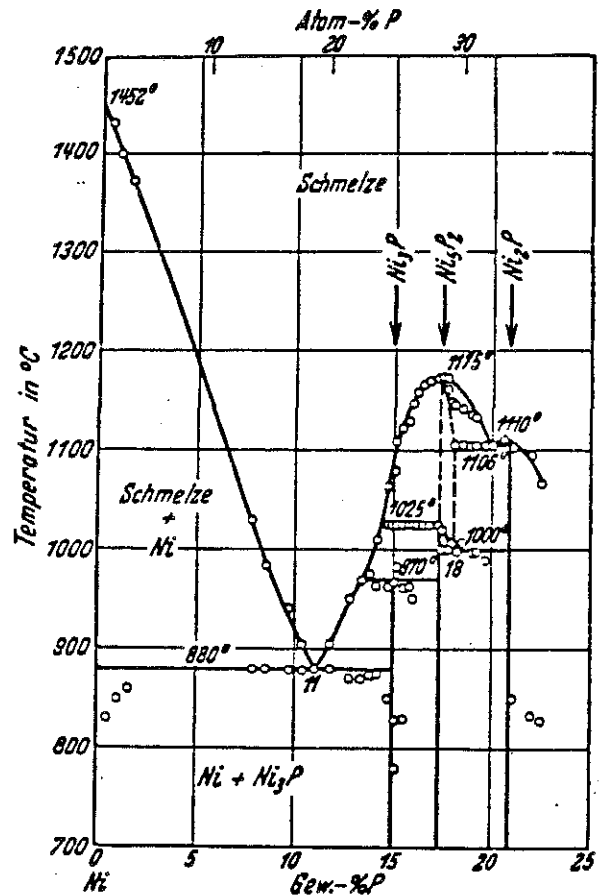
With metals such as aluminum it is common practice to bake parts after plating for 1 to 4 hours at  $130^{\circ} + 200^{\circ}\text{C}$  ( $270^{\circ}$  to  $400^{\circ}\text{F}$ ) to increase the adhesion of the coating. These treatments relieve hydrogen from the part and the deposit and provide a very minor amount of codiffusion between the coating and substrate. They are most useful where pretreatment has been less than adequate and adhesion is marginal. With properly applied coatings, baking will have only a minimal effect upon bond strength<sup>2,5,8</sup>.

#### MELTING POINT

Electroless nickel is an eutectic alloy with a wide melting range. Unlike a pure compound, it does not have a true melting point. This is illustrated by the phase diagram for nickel-phosphorus alloys shown in Figure 7<sup>14</sup>.

**FIGURE 7**

Phase diagram for nickel-phosphorus alloys.



The melting range for electroless nickel coatings varies depending upon the phosphorus content of the deposit. All electroless nickel coatings begin to melt at approximately 880°C (1620°F), which is the eutectic temperature for nickel phosphide (Ni<sub>3</sub>P). The temperature at which the coating is completely liquid, however, increases with decreasing phosphorus content from about 880°C (1620°F) at 11 percent -- the eutectic point -- to approximately 1450°C (2640°F) for pure nickel. Thus, the melting range becomes wider as the phosphorus content is reduced.

Practically this means that all commercial coatings contain large quantities of liquid material at temperatures above 880°C (1620°F). For example, at 900°C (1650°F) coatings containing 5, 8 and 10½ percent phosphorous are 46, 74 and 100 percent melted.

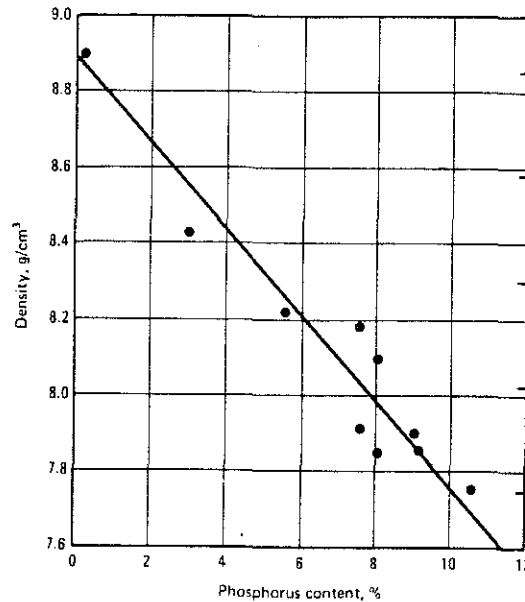
PHYSICAL PROPERTIES

The density of electroless nickel coatings is inversely proportional to their phosphorus content. As shown in Figure 8, density varies from about 8.5 gm/cm<sup>3</sup> for very low phosphorus deposits, to 7.75 gm/cm<sup>3</sup> containing about 10½ percent phosphorus<sup>2,7,15,16,17</sup>.



FIGURE 8

Effect of deposit phosphorus content on the density of electroless nickel.



The thermal and electrical properties of these coatings also vary with composition. For high phosphorus coatings electrical resistivity and thermal conductivity are generally about  $90 \mu\Omega\text{-cm}$  and  $0.08 \text{ W/cm-}^\circ\text{K}$  ( $4.6 \text{ Btu/ft-hr-}^\circ\text{F}$ ) respectively<sup>18,19</sup>. Accordingly, these coatings are significantly less conductive than conventional conductors such as copper.

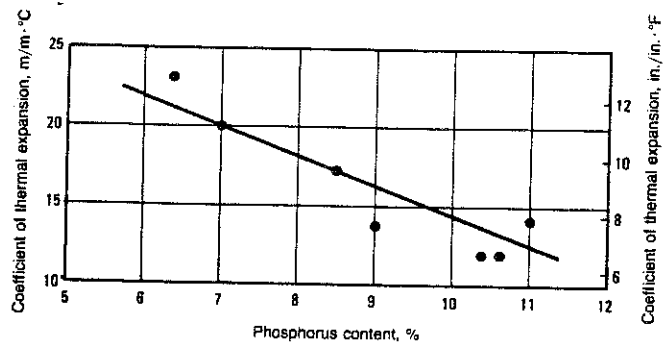
Because of the relatively thin layers used, however, for most applications the resistance of electroless nickel is not significant. coatings are being successfully used for such applications as exchanger tubing and electrical switches and contacts.

Heat treatments precipitate phosphorus from the alloy and can increase the conductivity of electroless nickel by 3 to 4 times<sup>2,7</sup>. The formulation of the plating solution can also affect conductivity. Tests with baths complexed with sodium acetate and with succinic acid showed electrical resistivities of  $61$  and  $804 \mu\Omega\text{-cm}$  respectively<sup>2</sup>.

Phosphorus content also has a strong effect on the thermal expansion of electroless nickel. This is shown in Figure 9, which is based on deposit stress measurements on different substrates<sup>10</sup>. The coefficient of thermal expansion of coatings is approximately equal to that of steel.

FIGURE 9

Effect of deposit phosphorus content on the coefficient of thermal expansion on electroless nickel.



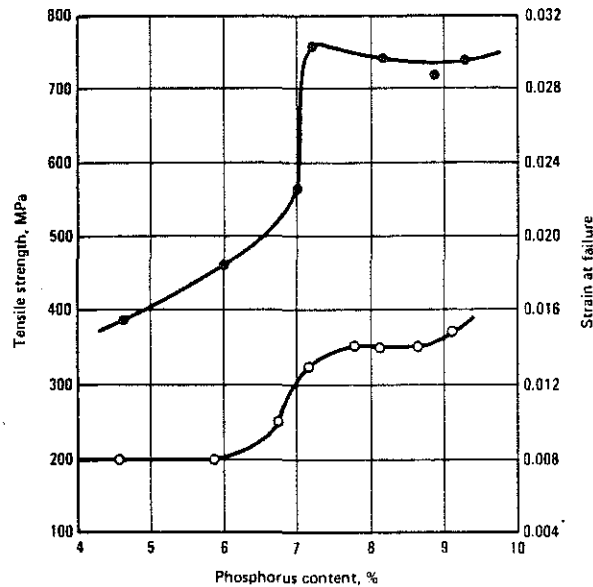
As deposited, coatings containing more than 10 percent phosphorus are completely non-magnetic. The magnetic susceptibility of deposits is on the order of  $10^{-4}$  mks at ambient temperature. Lower phosphorus coatings, however, have some magnetic susceptibility. The coercivity of 3 to 6 percent phosphorus coatings is about 20 to 80 oersteds, while that of deposits containing 7 to 9 percent phosphorus is typically 1 to 2 oersteds. Heat treatment at temperatures above  $260^{\circ}\text{C}$  ( $500^{\circ}\text{F}$ ) improve the magnetic response of all electroless nickels and can provide coercivities of about 100 to 300 oersteds <sup>20,21</sup>.

#### MECHANICAL PROPERTIES

The mechanical properties of electroless nickel deposits are similar to those of other glasses. They have high strength, limited ductility and a high modulus of elasticity. The ultimate tensile strength of most coatings exceeds 700 MPa (100 ksi). This is equal to that of many hardened steels and allows the coating to withstand a considerable amount of abuse without damage. The effect of phosphorus content upon the strength and strain at fracture of electroless nickel deposits is shown in Figure 10<sup>22</sup>.

FIGURE 10

Effect of phosphorus content on strength and strain at fracture of electroless nickel deposits.



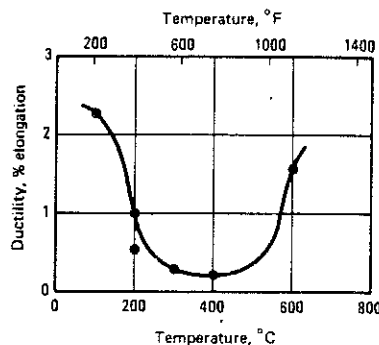
The ductility of electroless nickel coatings also varies with composition. The ductility of coatings is about 1 to 1½ percent (as elongation). While this is less than that of most engineering materials, it is adequate for most coating applications. Thin films of the deposit can be bent completely around themselves without fracture, and the coating has been used successfully for springs and bellows. Electroless nickel, however, should not be applied to articles which subsequently will be bent or drawn. Severe deformation will crack the deposit, reducing corrosion and abrasion resistance. With lower phosphorus deposits, or with deposits containing metallic or sulfur impurities, ductility is greatly reduced and may approach zero<sup>5,8</sup>. The effect of phosphorus content upon the strain at fracture of electroless nickel coatings is also shown in Figure 10<sup>22</sup>.

Hardening type heat treatments reduce both the strength and the ductility of electroless nickel deposits. Exposure to temperatures above 220°C (420°F) cause a 80 to 90 percent reduction in strength and can destroy ductility, especially in lower phosphorus coatings. This is illustrated by Figure 11, which shows the effect of different one hour heat treatments on the elongation at fracture of brass panels coated with a 6 percent phosphorus electroless nickel<sup>20</sup>. Because

of their high phosphorus content and high purity, the effect of heat treatment on the ductility of deposits is not as pronounced. The ductility of coatings is not significantly reduced until it is heated to above 260°C (500°F)<sup>5</sup>.

FIGURE 11

Effect of heat treatment on the ductility of a 6 percent phosphorus electroless nickel.



The modulus of elasticity of non-heat treated electroless nickel coatings containing 10 to 11 percent phosphorus is about 200 GPa (28x10<sup>6</sup>psi) and is very similar to that of steel<sup>2,22</sup>.

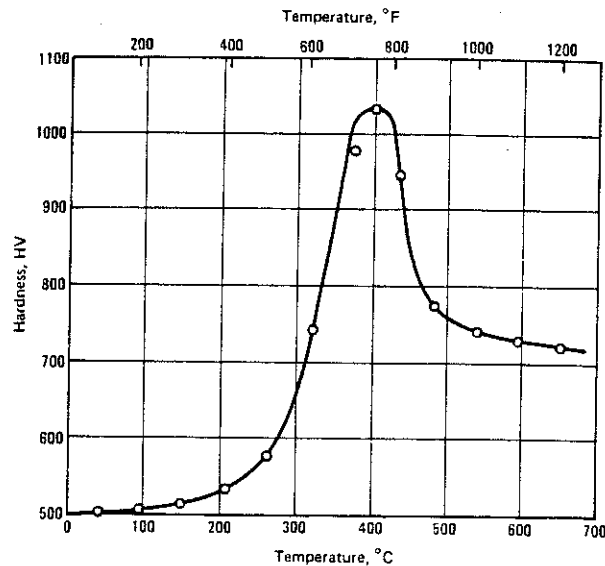
The modulus of deposits containing 7 to 8 percent phosphorus is only about 120 GPa (18x10<sup>6</sup>psi) and is more similar to that of copper alloys. Heat treating electroless nickel coatings at temperatures above 200°C (400°F) causes their modulus of elasticity to increase significantly<sup>2,23</sup>.

#### HARDNESS AND WEAR RESISTANCE

Two of the most important properties for many applications are hardness and wear resistance. As deposited, the micro-hardness of electroless nickel coatings is about 500 to 600 VHN<sub>100</sub>. This is approximately equal to 48 to 52 HRC and equivalent to many hardened alloy steels. Heat treatment causes these alloys to age harden and can produce hardness values as high as 1100 VHN<sub>100</sub>. This is equal to most commercial hard chromium coatings. Figure 12 shows the effect of different 1 hour heat treatments on the hardness of electroless nickel deposits<sup>2,5</sup>.

FIGURE 12

Effect of heat treatment at different temperatures on the hardness of Electroless Nickel.

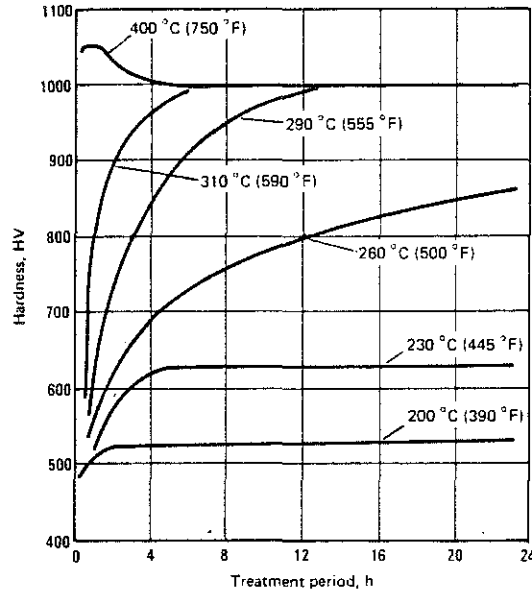


For some applications, high temperature treatments cannot be tolerated because of part warpage or because of their effect on the substrate. For these, it is sometimes possible to use longer times and lower temperatures to obtain the desired hardness. This is illustrated by Figure 13, which shows the effect of different treatment periods on the hardness of coatings<sup>5</sup>.

Treatments at 340°C (650°F) for 4 to 6 hours and at 290°C (550°F) for 10 to 12 hours are commonly used for electroless nickel deposits. These can produce hardness values of 950 to 1000 VHN<sub>100</sub>. Treatments at 260°C (500°F) are also occasionally used, although the resulting hardness is lower. At temperatures of 230°C (450°F) and below, only a minimal increase in hardness is obtained. Accordingly such treatments are only rarely used, except for hydrogen relief or adhesion improvement<sup>5</sup>.

FIGURE 13

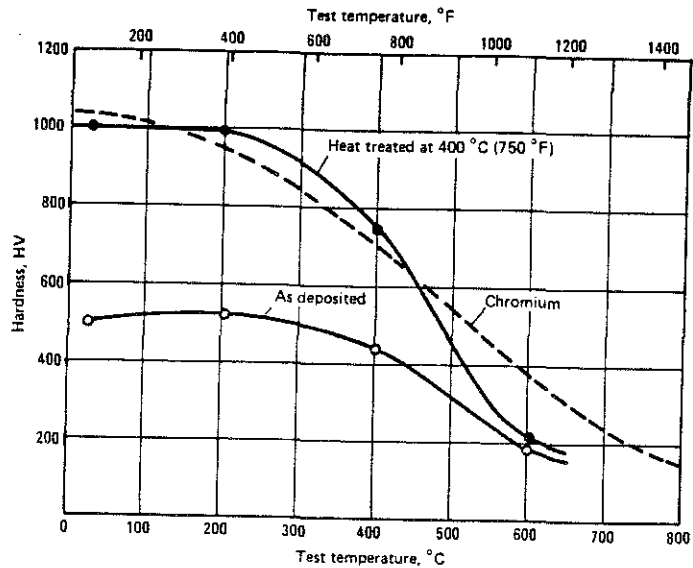
Effect of different heat treatment periods on the hardness of Electroless Nickel.



Electroless nickel coatings also have excellent hot hardness. Up to about 400°C (750°F) the hardness of heat treated electroless nickel is equal to or better than that of hard chromium coatings. As-deposited coatings also retain their hardness to this temperature, although at a lower level. The effect of elevated temperature on a 10 percent phosphorus coating is shown in Figure 14<sup>24, 25</sup>.

FIGURE 14

Effect of temperature on the elevated temperature hardness of a 10 percent phosphorus electroless nickel.



Because of their high hardness, electroless nickel coatings have excellent resistance to wear and abrasion, both in the as-deposited and hardened conditions. Laboratory tests have shown fully hardened coatings to have wear resistance equal to hard chromium under both dry and lubricated conditions. This is illustrated by Table 1, which shows the results of typical Taber Abraser Wear tests of electroless nickel coatings, and compares them to electroplated nickel and chromium<sup>26,27,28</sup>. The excellent resistance of electroless nickel often allows it to replace high alloy materials and hard chromium.

TABLE 1  
COMPARISON OF THE TABER ABRASER RESISTANCE  
OF DIFFERENT ENGINEERING COATINGS

<u>COATING</u>	<u>HEAT TREATMENT</u>	<u>TWI, mg/1000 Cycles<sup>(1)</sup></u>
Watts Nickel	None	25
Electroless Ni-9%P	None	17
Electroless Ni-9%P	300°C/1 hr	10
Electroless Ni-9%P	500°C/1 hr	6
Electroless Ni-9%P	650°C/1 hr	4
Electroless Ni-5%B	None	9
Electroless Ni-5%B	400°C/1 hr	3
Hard Chromium	None	3

(1) Taber Wear Index, CS-10 abraser wheels, 1000 gram load, determined as average weight loss per 1000 cycles for total test of 6000 cycles.

Tests with electroless nickel coated vee-blocks in a Falex Wear Tester have confirmed a similar relation between heat treatment and wear, and shown the coating to be more resistant than hard chrome under lubricated wear conditions. This is illustrated by Table 2 for an electroless nickel containing approximately 9 percent phosphorus.

TABLE 2

COMPARISON OF THE FALEX WEAR RESISTANCE  
OF CHROMIUM AND ELECTROLESS NICKEL COATINGS

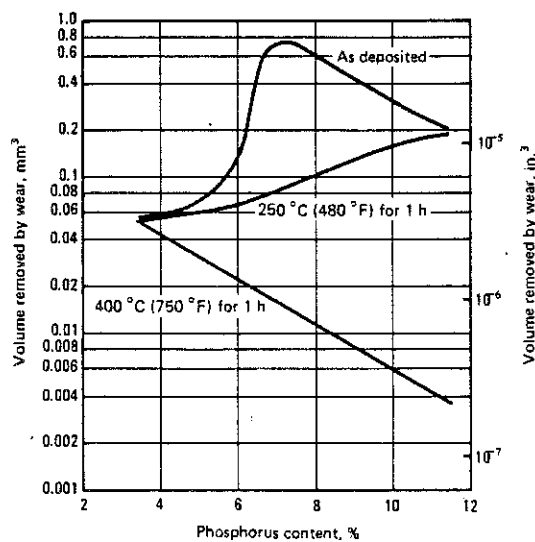
<u>COATING</u>	<u>PLATED V-BLOCKS</u>			<u>UNPLATED STEEL PINS</u>
	<u>Heat Treatment</u>	<u>Hardness, VHN</u>	<u>Wear mg (1)</u>	<u>Wear, mg (1)</u>
Chromium	None	1100	0.5	1.9
Electroless Nickel	None	590	6.6	0.2
Electroless Nickel	290°C/2 hrs	880	1.2	0.1
Electroless Nickel	290°C/16 hrs	1050	0.4	0.1
Electroless Nickel	400°C/1 hr	1100	0.5	0.2
Electroless Nickel	540°C/1 hr	750	1.4	0.1

(1) Falex Wear Test under 180 kg (400 lb) for 40 minutes with white oil lubricant. Unplated pins were SAE 9310 steel at 60 HRC hardness.

The effect of phosphorus content upon the wear experienced by electroless nickel coatings under lubricated conditions is summarized in Figure 15. These rotating ball tests showed that after heat treatment, high phosphorus deposits like 1 provide the best resistance to adhesive wear<sup>29,30</sup>.

FIGURE 15

Effect of phosphorus content on the wear of electroless nickel coatings in rotating ball tests.





## FRICTIONAL PROPERTIES

The frictional characteristics of electroless nickel coatings are excellent. Their phosphorus content provides a natural lubricity, which helps to minimize heat buildup and reduces scoring and galling and which can be very useful for applications such as plastic molding.

The coefficient of friction for electroless nickel versus steel is about 0.13 for lubricated conditions and 0.4 for unlubricated conditions. This is approximately 20 percent lower than chromium, one-half of that of steel, and much lower than aluminum or stainless steel. The frictional properties of these coatings vary little with either phosphorus content or with heat treatment<sup>2,26,30</sup>.

## SOLDERABILITY AND WELDABILITY

Electroless nickel coatings can be easily soldered and are commonly used in electronic applications to facilitate soldering of light metals, like aluminum. For most components, mildly activated rosin (RMA) flux is specified together with conventional tin-lead solder. Preheating the component to 100° to 110°C (210° to 230°F) will improve the ease and speed of joining. With moderately oxidized surfaces, such as those resulting from steam aging, activated rosin (RA) flux is usually required to obtain wetting of the coating<sup>2,31</sup>.

Welding of electroless nickel coated components is more difficult due to the low welding point of the alloy and because phosphorus can diffuse into an embrittle steel. Some success has been reported using special high purity stainless steel electrodes and inert gas shielding. With piping high nickel backup rings are also sometimes used<sup>2</sup>.

## CORROSION RESISTANCE

Electroless nickel is a barrier coating, it protects its substrate by sealing it off from the environment, rather than by sacrificial action. Because of its amorphous nature and passivity, however, the corrosion resistance of the coating is excellent and in many environments superior to that of pure nickel or chromium alloys. Amorphous alloys generally have better resistance to attack than equivalent polycrystalline materials, because of their freedom from grain or phase boundaries, and because of the glassy films which form on and passivate their surfaces.

Effect of Environment. When properly applied, Electroless Nickel is almost totally resistant to alkalis, to salt solutions and brines, to chemical and petroleum environments, and to all types of hydrocarbons and solvents.

deposits also have good resistance to ammonia solutions, to organic acids, and to reducing inorganic acids. They are only significantly attacked by strongly oxidizing media<sup>32</sup>. Some examples of the corrosion experienced in different environments is shown in Table 3<sup>2,9,32</sup>.

Effect of Composition. The corrosion resistance of an electroless nickel coating is a function of its composition. Most deposits are naturally passive and very resistant to attack in most environments. Their degree of passivity (and corrosion resistance), however, is greatly affected by their phosphorus content. Alloys containing more than 10 percent phosphorus are generally more resistant to attack than those with lower phosphorus contents<sup>9,15</sup>. This is illustrated by Figure 16, which compares the corrosion experienced by electroless nickel coatings containing 5 to 10½ percent phosphorus in aerated, 6 percent citric acid at 50°C (120°F)<sup>33</sup>.

FIGURE 16

Effect of phosphorus content on the corrosion of electroless nickel coatings.

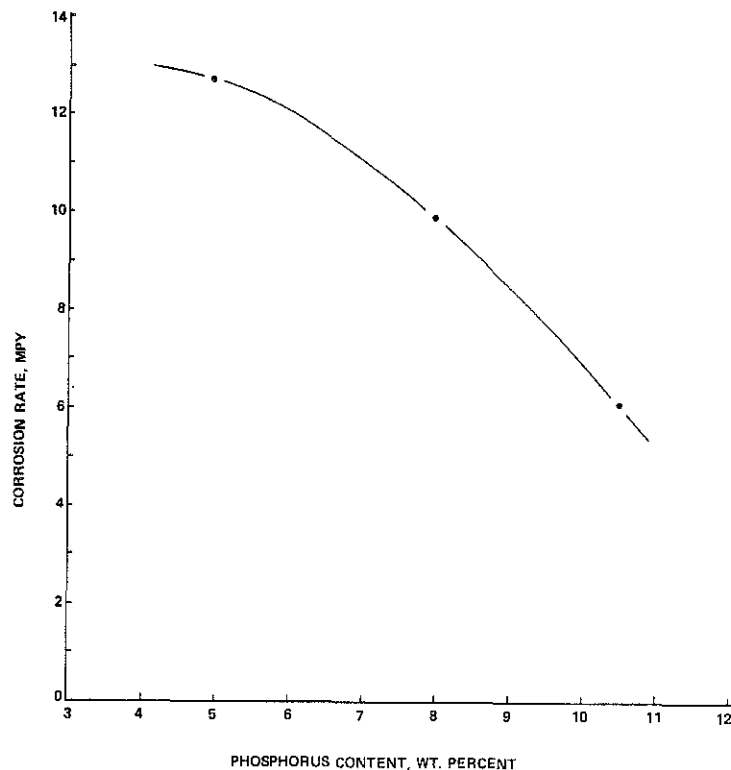


TABLE 3  
CORROSION OF ELECTROLESS NICKEL IN  
VARIOUS ENVIRONMENTS

ENVIRONMENT	TEMPERATURE °C	CORROSION RATE	
		µm/Y	mpy
Acetic Acid, Glacial	20	0.8	0.03
Acetone	20	0.08	0.003
Aluminum Sulfate, 27%	20	5	0.2
Ammonia, 25%	20	16	0.6
Ammonium Nitrate, 20%	20	15	0.6
Ammonium Sulfate, Saturated	20	3	0.1
Benzene	20	Nil	Nil
Brine, 3½% Salt, CO <sub>2</sub> Saturated	95	5	0.2
Brine, 3½% Salt, H <sub>2</sub> S Saturated	95	Nil	Nil
Calcium Chloride, 42%	20	0.2	0.01
Carbon Tetrachloride	20	Nil	Nil
Citric Acid, Saturated	20	7	0.3
Cupric Chloride, 5%	20	25	1.0
Ethylene Glycol	20	0.6	0.02
Ferric Chloride, 1%	20	200	8.0
Formic Acid, 88%	20	13	0.5
Hydrochloric Acid, 5%	20	24	0.9
Hydrofluoric Acid, 2%	20	27	1.1
Lactic Acid, 85%	20	1	0.04
Lead Acetate, 36%	20	0.2	0.01
Nitric Acid, 1%	20	25	1.0
Oxalic Acid, 10%	20	3	0.1
Phenol, 90%	20	0.2	0.01
Phosphoric Acid, 85%	20	3	0.1
Potassium Hydroxide, 50%	20	Nil	Nil
Sodium Carbonate, Saturated	20	1	0.04
Sodium Hydroxide, 45%	20	Nil	Nil
Sodium Hydroxide, 50%	95	0.2	0.01
Sodium Sulfate, 10%	20	0.8	0.03
Sulfuric Acid, 65%	20	9	0.4
Water, Acid Mine, 3.3 pH	20	7	0.3
Water, Distilled, N <sub>2</sub> deaerated	100	Nil	Nil
Water, Distilled, O <sub>2</sub> Saturated	95	Nil	Nil
Water, Sea (3½% Salt)	95	Nil	Nil

In these tests, corrosion of the deposit was only about one half of that of the lower phosphorus coatings.

Often, the tramp constituents present in an electroless nickel are even more important to its corrosion resistance than its phosphorus content. Most coatings are applied from baths inhibited with lead, tin, cadmium or sulfur. Codeposition of these elements in more than trace amounts causes a severe reduction in the coating's passivity and corrosion resistance. This is illustrated by Table 4, which shows the results of corrosion tests with 6 different electroless nickel deposits in CO<sub>2</sub> saturated, 3½ percent salt brine at 95°C (200°F)<sup>9</sup>.

TABLE 4

EFFECT OF COMPOSITION ON CORROSION RESISTANCE  
OF ELECTROLESS NICKEL IN CO<sub>2</sub> SATURATED,  
3½ PERCENT SALT BRINE AT 95°C

<u>DEPOSIT</u>	<u>PHOSPHORUS</u>	<u>OTHER</u>	<u>CORROSION RATE</u>	
	<u>CONTENT, %</u>	<u>ELEMENTS, %</u>	<u>µm/y</u>	<u>mpy</u>
ELNIC	10.2	trace	5	0.2
B	11.8	0.04 Sn	7	0.3
C	8.3	0.05 Cd	24	0.9
D	10.3	0.12 Pb	15	0.6
E	8.0	0.13 S	15	0.6
F	10.4	0.05 Pb and 0.08 Cd	11	0.4

Similar tests in 10 percent HCl at ambient temperature showed losses ranging from 15 µm/y (0.6 mpy) for Deposit B to 660 µm/y (26 mpy) for Deposit D.

The primary difference between these deposits was not their phosphorus content, but their baths' inhibitor. Deposits B, D, and F all contained more than 10 percent phosphorus.

Deposits B to F, were applied from baths inhibited with metals or sulfur and contained significant amounts of these elements<sup>9</sup>.

Effect of Heat Treatment. One of the most important variables effecting the corrosion of electroless nickel is its heat treatment. As electroless nickel deposits are heated to temperatures above 220° to 260°C (420° to 500°F) nickel phosphide particles begin to form, reducing the phosphorus content of the remaining material. This reduces the coating's corrosion resistance. The particles also create small active/passive corrosion cells, further contributing to the deposit's destruction. The effect of these changes is illustrated by Table 5, which shows the results of tests with deposits, heat treated to represent different commercial treatments and then exposed to 10 percent HCl at ambient tempertaure. A secondary effect of heat treating is that the deposit shrinks as it hardens, which can crack the coating and expose the substrate to attack. A cross-sectional view of the cracks through an electroless nickel coating after heat treatment at 400°C (750°F) is shown in Figure 7<sup>9</sup>.

FIGURE 17

Cross sectional view of a 75 mm thick electroless nickel deposit after heat treatment at 400°C for 1 hour. Cracks formed due to shrinkage of the deposit. 100X magnification. Etched in 2% nital.

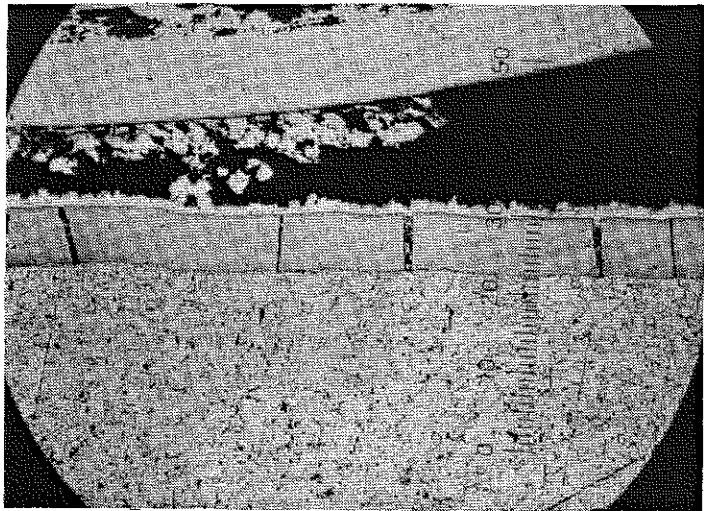


TABLE 5

THE EFFECT OF HEAT TREATMENT  
ON THE CORROSION OF ELECTROLESS NICKEL  
IN 10% HCl

HEAT TREATMENT	DEPOSIT HARDNESS, VHN <sub>100</sub>	CORROSION RATE	
		$\mu\text{m}/\text{y}$	mpy
None	480	15	0.6
190°C (375°F) for 1½ hours	500	20	0.8
290°C (550°F) for 6 hours	900	1900	75
290°C (550°F) for 10 hours	970	1400	55
340°C (650°F) for 4 hours	970	900	35
400°C (750°F) for 1 hour	1050	1200	47

Baking at 190°C (375°F), like that used for hydrogen embrittlement relief, caused no significant increase in corrosion. Hardening, however, caused the coating's corrosion rate to increase from 15  $\mu\text{m}/\text{y}$  (0.6 mpy) to more than 900  $\mu\text{m}/\text{y}$  (35 mpy). Tests in other environments showed a similar reduction in resistance after hardening. Where corrosion resistance is required, hardened coatings should not be used<sup>9</sup>.

SUMMARY OF THE PROPERTIES OF ELECTROLESS NICKEL

COMPOSITION	Alloy of 10 to 11 percent phosphorus dissolved in nickel, containing less than 0.05 percent other impurities
STRUCTURE	Completely amorphous, without any crystal or phase structure, lamination or internal segregation  During heat treatment, particles of Ni <sub>3</sub> P precipitate and the coating crystallizes
INTERNAL STRESS	20 to 30 MPa (2.5 to 4 ksi) compressive
DENSITY	7.75 g/cm <sup>3</sup>
MELTING POINT	890°C (1630°F)
ELECTRICAL RESISTIVITY	90 μΩ-cm, as deposited
THERMAL CONDUCTIVITY	0.08 W/cm-°K (4.6 Btu/ft-hr-°F), as deposited
MAGNETIC SUSCEPTIBILITY	Approximately 10 <sup>-4</sup> mks
TENSILE STRENGTH	>700 MPa (>100 ksi), as deposited
DUCTILITY	1 to 1½ percent elongation, as deposited
MODULAS OF ELASTICITY	200 GPa (28 x 10 <sup>6</sup> psi)
COEFFICIENT OF THERMAL EXPANSION	12 μm/m/°C (6.7 μin/in/°F)
ADHESION STRENGTH	300 to 400 MPa (40 to 60 ksi)
HARDNESS, AS DEPOSITED	480 to 500 VHN <sub>100</sub>
HARDNESS, HEAT TREATED (400°C/1 hr)	1000 to 1100 VHN <sub>100</sub>
COEFFICIENT OF FRICTION VS. STEEL	0.13 (lubricated) to 0.4 (non-lubricated)
TABER WEAR RESISTANCE, AS DEPOSITED	18 to 20 mg/1000 cycles
TABER WEAR RESISTANCE HEAT TREATED (400°C/1 hr)	10 to 12 mg/1000 cycles
CORROSION RESISTANCE	A barrier coating with excellent resistance to attack by all but the most severely oxidizing environments

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