Comparison of Some Mechanical and Corrosion Properties of Electroless and Electroplated Nickel-Phosphorus Alloys

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The mechanical and corrosion properties of electroless and electroplated nickel-phosphorus alloys of four different compositions are compared. All deposits had low ductility. Electroplated Ni-P had higher moduli of elasticity. The moduli and tensile strengths tended to be higher when the deposits contained both crystalline and amorphous constituents. Corrosion studies showed that the development of pits extending to the substrate can be prevented or inhibited when the top of a two-layer deposit has a lower phosphorus content and behaves sacrificially.

lectroless (autocatalytic) deposited nickelphosphorus coatings have some properties that are superior to those of electroplated nickel. Because of its phosphorus content, electroless nickel (EN) is harder and has better corrosion resistance. EN also exhibits good wear resistance, but is more expensive, due to the cost of the reducing agent, sodium hypophosphite. Electroplating Ni-P alloy is faster. The electroplating solution is more stable and has fewer replenishment problems. However, electroplated Ni-P does not coat complicated shapes with as uniform a thickness as electroless Ni-P.

There have been only a few studies of the properties of electroplated Ni-P alloys. Most were based on the bath that contained phosphorous and phosphoric acid, reported by Brenner, Couch and Williams.'Unannealed, essentially amorphous alloys had a Vickers hardness of about 600, which increased to over 800 by a 400° C heat treatment. Minier and Brenner showed that electroplated allovs containing 9 percent phosphorus compared favorably with EN coatings with a similar composition during outdoor exposure and salt spray corrosion tests. Recent reports³⁴ indicated that current pulsing increased the hardness of electroplated Ni-P. It was also found that the development of a banded structure, which previously had been attributed to variations in the phosphorus content,' depended on the plating conditions. Examination of corrosion pits showed that bands with the lower phosphorus content acted as sacrificial anodes, compared to bands with a higher phosphorus content. According to Gruss and Pearlstein, 'two layers of electroless nickel with different phosphorus contents were effective for protecting steel against corrosion.

No reports have appeared on the mechanical properties of electroplated NI-P alloys and only limited data are available for the mechanical properties of electroless Ni-P. According to bulge-test data, the tensile strength of EN from an alkaline chloride bath increased from about 400 to 800 MPa when the phosphorus content increased from 4.7 to 7.2 weight percent.⁷It was postulated independently' that the high strength alloy was attained where the structure changed from crystalline to amorphous. However, this structural change does not take place at a particular composition, but occurs over a range of phosphorus contents.

Yamasaki, Izumi and Hisakishi[°]reported a significant difference in the ductility and hardness of crystalline and amorphous structures. Fracture strain determined by fatigue tests increased and hardness decreased with the transition to the amorphous deposit associated with an increasing phosphorus content. In another report," a Young's modulus of about 120 GPa and a tensile strength of 450 MPa were reported for hollow tubes formed by plating electroless nickel containing about 5 percent phosphorus on copper tubes dissolved after plating.

One objective of our study was to compare the mechanical properties of electrodeposited and electroless Ni-P alloys of different compositions. A comparison of corrosion resistance and a study of two-layer deposits with different phosphorus contents were also conducted.

Experimental Procedure

Rolled, annealed and electropolished copper sheet was the substrate used for mechanical property measurements. The dimensions of individual copper panels were about 3x 4 cm. Tensile specimens were formed by plating bare areas defined by photolithography. Typically, six to eight specimens were plated simultaneously on a piece of copper subsequently dissolved in sulfuric-chromic acid solution. To avoid edge build-up on electroplated tensile specimens, the photoresist was also removed from the edges of the copper coupons to provide a "robber" frame surrounding the plated areas. About 25 µm of electroless nickel was deposited in each of three acid solutions containing nickel sulfate and sodium hypophosphite. One bath with a pH of 4.5 or 4.6 contained strong nickel chelates. A second proprietary solution contained lactic acid and was operated in the pH range of 4.5 to 5.0. The third was a strongly buffered solution with a pH ranging from 5.5 to 6.0.

Ni-P alloy was electroplated in a solution at 60° C containing 30 g/L of nickel sulfate hexahydrate, 10 g/L of sodium hypophosphite and 10 g/L of sodium acetate. The current density was 30 mA/cm². The pH was varied from 4 to 6 to obtain deposits with different phosphorus contents corresponding to those produced by electroless nickel deposition.

The tensile specimens had a gage length of 2.5 mm and a width of 1 mm and were tested in the minitensile machine described by Kim and Weil." The strain rate was 4×10^{-1} /sec. A knoop indenter and a load of 100g were used to measure hardness on metallographically prepared cross sections.

Polished steel samples with dimensions of 10 x 15 cm were coated with about 25 μ m of electroplated or electroless Ni-P. Single layer alloy deposits of different phosphorus contents were supplemented with duplex deposits consisting of a low-phosphorus layer over a high-phosphorus coating, a low-phosphorus deposit over an intermediate P-concentration layer or an intermediate P deposit over a high-P coating. The bottom layer was about 15 μ m thick and the top about 10 μ m, based on predetermined plating rate data.

Single and double-layered electroplated and electroless nickel coated panels were subjected to 400 hr of neutral salt spray using the procedure described in ASTM Test Method B 117, after areas adjacent to the edges were coated with a stop-off lacquer and covered with acid-resistant tape.

After testing, 2.5 x 2.5 cm pieces were cut from the unexposed areas that had been protected by the stop-off lacquer. The samples were vapor-degreased in trichloroethane and rinsed in DI water. When surfaces were free of water breaks, corrosion potentials vs. a standard calomel electrode (SCE) and corrosion currents were measured by the procedure described by Ratzker, Lashmore and Pratt' in a solution of the same composition as that used in the salt spray test.

Deposit thickness was measured and surface morphology examined by scanning electron microscopy (SEM). The composition of all deposits was determined by energy dispersive X-ray analysis. Pitting density was determined and converted into ratings according to ASTM Standard Practice G46. According to this standard, ratings of 1,2,3 and 4 correspond to minima of $2.5x 10^3$, 1×10^4 , $5x 10^4$ and 1×10^5 pits/m², respectively. Two ratings were made for each sample. The first was assigned to pits that penetrated to the steel substrate, characterized by rust, and the second took into account all visible pits. After removing corrosion products with adhesive tape, panel surfaces were examined by SEM.

Results and Discussion

The mechanical properties of the Ni-P alloys are given in Table 1, which shows ranges of P contents that varied somewhat, probably because of the banded structure. No data could redetermined for electroplated alloy containing 1 to 3 percent P because internal stress caused bending when the substrate material was dissolved. The electroformed specimens fractured when an attempt was made to straighten them.

Deposits with 4 to 7 percent P had the highest values of Young's modulus. Although theoretical calculations have indicated that amorphous materials should have higher moduli than crystalline structures,¹²Table 1 data show that the highest moduli were produced with partially amorphous and partly crystalline structures. Ni-P alloys start to become amorphous at about 7 percent phosphorus.[®]However, it seems that properties depend not only on the amounts of the two structures, but also on their distribution. The moduli listed in Table 1 are smaller than previously reported values of 120¹⁰ and about 140 MPa.¹³ The 140 MPa value probably was a result of the unavoidable stretching of the specimen in the bulge tester before the load was applied. which would be expected to produce a smaller elastic strain and, therefore, a larger modulus. in uniaxial tensile tests where the load is applied vertically, the specimen also is generally stressed during mounting. Because our computer-controlled minitensile device permits horizontal mounting without stretching, the moduli in Table 1 are believed to be more accurate.

All stress-strain curves were linear to fracture. Therefore, deformation was essentially elastic to fracture. Because elongation is defined as the plastic strain at fracture, elongation, consequently, was less than 1 percent. Yield strength, defined as the stress producing a plastic strain equal to the so-called offset, could not be determined because such a strain was not attained.

The stress causing fracture, which is the tensile strength in this case, has a maximum value in the composition range where the structure changes from crystalline to amorphous. Tensile strength values in Table 1 generally agree with those reported by Graham, Lindsay and Read,' who also observed a small maximum in the composition range where a transition in structure occurs. Table 1 shows no significant

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a na stan a s	Me	chanical Prope and Electropia	rties of Elect ted NI-P Allo	roless ys		
	Property	1-3% P	4-7% P	7-9% P	10-12% P	
	Young's Modulus, GPa* Electroless Electroplated	50-52 —	62-66 90-95	50-60 70-80	50-70 67-72	
	Tensile Strength, MPa** Electroless Electroplated	150-200 	420-700 760-780	800-1100 1000-1150	650-900 610-720	
	Hardness, KHN Electroless Electroplated		600 665	485 475	455 560	
	*1 GPa = 1.43 x 10' psl **MPa = about 1000 psl					

	followers and for which the			Corr	Corrosion		Corrosion	
	State of the second second			Pote	ntial,	Current	Densit	
	Phosphorus	Rat	ing*	-mV vs. SCE		μ Α/cm		
	Lovel	EN	EP	EN	EP	EN	F P	
	Low	4/4	2/2	0.44	0.55	1.55	0.6	
	Medium	1/1	2/2	0.57	0.50	0.19	1.2	
	High	1/2	2/2	0.50	0.73	0.62	0.0	
	Med + Low	1/2	1/1	0.58	0.41	0.28	0.3	
	High + Low	2/2	0/1	0.46	0.27	1.42	0.1	
iner in space of the second	High + Med	n/i	2/2	0.42	0.54	0.66	0.4	

difference in the tensile strength of electroless and electroplated Ni alloy with 10 to 12 percent P. The relatively low strength of EN with 1 to 3 percent P may be due to the high internal tensile stress characteristic of EN with a low P content. Tensile stress decreases and shifts to a compressive stress with an increasing P content.]'

Electroplated alloys with 5 to 7 percent P were stronger than EN with the same P content. The difference is attributed to variations in the distribution of the crystalline and amorphous constituents, which seems to be more important than their relative amounts. Unfortunately, it is not possible to determine the amounts and distribution of the crystalline and amorphous phases by X-ray diffraction. The number of metal-metalloid bonds also can affect the strength. ¹²Tensile strength values within each range in Table 1 vary because materials such as the Ni-P deposits that do not deform plastically are very notch sensitive. According to fracture mechanics, the tensile strength is then inversely proportional to the square root of the flaw size. The most likely flaws are pits. There undoubtedly were variations in the sizes of the pits in different samples within any particular composition range. Variations over the gage length of the tensile specimens in their thickness, measured with the scanning electron microscope, were insignificant and, therefore, not responsible for variations in tensile strength.

Corrosion Properties

The appearance of test panels after salt spray exposure, rinsing and drying is depicted in Figure 1. Table 2 lists the ratings assigned in accordance with ASTM Recommended Practice G46. Of the EN-plated panels, only that with a low (1 to 3 percent) P content in the coating exhibited extensive pitting that extended to the steel substrate. A panel with a medium-P coating over a high-P layer showed no pits. The others had a few such pits.



Fig. I-Panels after salt spray testing.



Fig. 2—Scanning electron micrograph of salt-spray-tested low-P electroless nickel after removal of corrosion products.



Fig. 3-The same sample as in Fig. 2, before removal of corrosion products.

Electroplated panels with deposits that had an intermediate- or high-P content showed more pits that reached the steel than the corresponding EN-plated samples, probably because the electrodeposits contained more pits before salt spray testing. Many corrosion pits were observed on panels that were electroplated with a low-P layer over a deposit with a high-P content, but the corrosion products were green and not red, which indicated that corrosion pitting did not extend to the steel substrate. Pit penetration through the nickel was inhibited by the greater nobility of the high-P layer and the sacrificial character of the layer with the lower P content.

A larger magnitude of negative potential and a lower corrosion current density are indicative of resistance to general corrosion rather than pitting corrosion. Thus, the potentials and current densities in Table 2 do not necessarily correspond to the salt spray pitting data. Although the corrosion rate at a pit is locally rapid, the weight loss averaged over the whole area is relatively small. Thus the corrosion current density also would be small.

Figure 2 shows the surface structure of a low phosphorus EN deposit after corrosion products had been removed. Many small pits are uniformly distributed over the surface. Rounded nodules and ridges, sometimes called "orange peel," also are evident in the background, but there is no indication of general corrosion—just pitting. Thus, weight loss indicative of general corrosion was negligibly small. Some specimens showed a weight gain because corrosion products remained in some pits.

Figure 3 is a highly magnified view of the same surface before corrosion products had been removed. The products cover most of the surface and mask the orange peel morphology. These corrosion products originated at pits in the steel and spread over the surface of the deposit.

Figure 4 is a highly magnified surface view of a high phosphorus EN deposit after corrosion products had been removed. Fine surface pitting and the characteristic orange peel background are evident. Energy dispersive X-ray analysis of the corrosion products showed no iron, which indicated that pitting did not reach the steel interface. The structure of each bi-layer coating was the same as that of the single layer deposit, with the same composition as the top of the two layers.



Fig. 4—Scanning electron micrograph of surface of high-P electroless nickel after removal of corrosion products.

Conclusions

The mechanical properties of Ni-P deposits depend on their structure. Those with both crystalline and amorphous constituents have the highest tensile strengths and moduli of elasticity. Each has a low ductility. Corrosion resistance tends to increase with increasing phosphorus content. The resistance to the development of pits that penetrate to the substrate can be improved with hi-layered deposits with a top layer having a lower phosphorus content than the bottom. The layer with the lower phosphorus content acts as a sacrificial anode.

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