The Effect of Heat Treatment Upon the Hardness and Abrasion Resistance of EN Coatings

by Ronald N. Duncan

For many applications, two of the the most important properties of electroless nickel coatings are hardness and wear resistance. These properties, in turn, are dependent upon the phosphorus content of the deposit, the support provided by the substrate, and most importantly upon the heat treatment given to it.

This paper describes the results of tests conducted to quantify the effect of different heat treatments upon the hardness and abrasive wear resistance of a high phosphorus, electroless nickel deposit. It also discusses why changes occur and how the period and temperature of the treatment may be varied to suit the intended application.

PROCEDURE

The samples for this study were plated from a malate/citrate solution of the type used to obtain deposits containing approximately 11% phosphorus. The solution was prepared and maintained using commercially available concentrates in an air agitated, 200-liter polypropylene tank. The solution was operated at a temperature of 88 ± 1°C and a pH of 4.8 ±0.1. Its plating rate was 12 µm/hr.

The specimens plated for microhardness testing were single-edge razor blades of high carbon steel. Those for abrasive wear tests were the standard mild steel panels available commercially. For both, the coating thickness was 75 µm. After plating, the specimens were heat treated in air in an electric convection oven whose temperature was controlled within ± 5°C. After heating, they were removed from the oven and allowed to cool in still air.

For comparison, hardness and Taber wear specimens plated in hard chromium were also obtained. These were plated in a commercial facility, using a standard 100:1 sulfate catalyzed solution, to a thickness of 75 µm.

Prior to hardness testing, the specimens were coated with a thick layer of copper to help support the coating. The microhardness tests were conducted as described by ASTM standard B-578, using a Vickers diamond indentor and a 100 gram load.

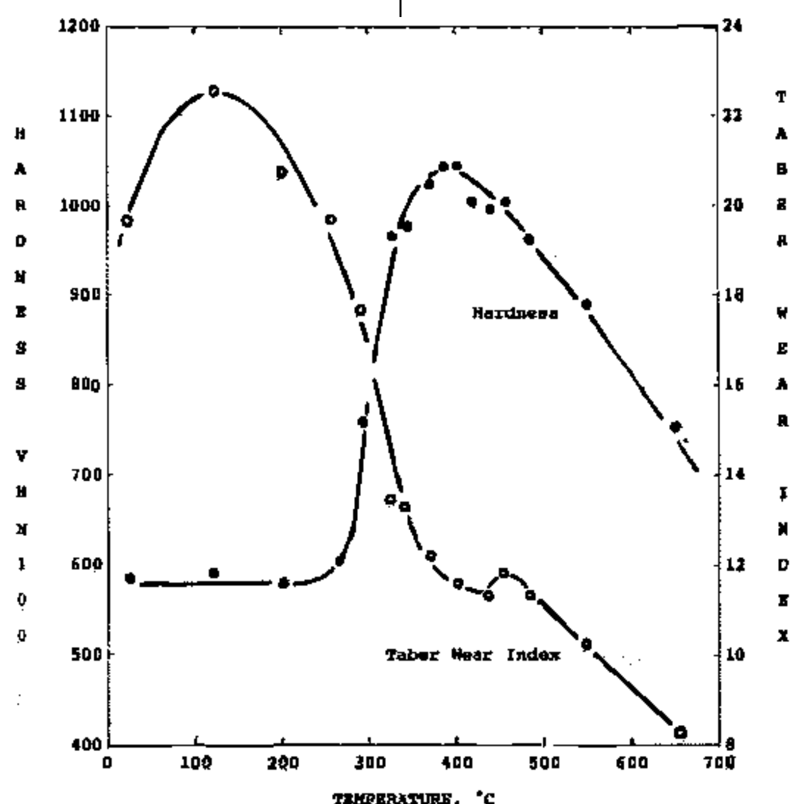
The Taber wear tests were conducted in duplicate in accordance with industry standards. The panels were abraded w ith bonded wheels, under a 1000 gram load, for six 1,000-cycle periods. The wheels were cleaned and redressed between each segment. The panels were weighed to the nearest 0.1 mg, before and after each increment, so that their weight loss and Taber Wear Index could be determined.

RESULTS

The effect of one hour treatments at temperatures between 120 and 650°C upon the hardness and wear resistance of the electroless nickel deposit is shown in Table I and is summarized in Fig. 1.

For one-hour periods, no change in hardness occurs, until the temperature exceeds 260°C. At higher temperatures, the hardness of the alloy increases rapidly, as its structure begins to change. First, very hard, intermetallic particles of nickel phosphide (Ni jP) start to form within the amorphous nickel-phosphorus coating, causing it to precipitation harden. Increased time or temperature produces more particles and more hardening; After 34(FC is exceeded, the remaining amorphous material crystallizes, providing additional sites to restrict deformation and to strengthen the deposit.

Maximum hardness occurs with treatments between 380 and 400° C. Within this range, values of 1040



Fiq. 1. Hardness arid abrasive wear resistance of electroless nickel containing 11%P after one-hour heat treatment.

Table I. The Effect of Various One-Hour Heat Treatments Upon the Hardness and Wear Resistance of 11 %P Electroless Nickel Deposits

Temperature °C	*Hardness* HV_{100}	*Taber Wear index* *mg/1000cycles*
As deposited	580	19.7
120	590	22.6
200	580	20.6
260	600	19.7
290	750	17.6
320	960	13.4
340	970	13.3
370	1020	12.1
385	1040	
400	1040	11.5
415	1000	—
430	990	11.2
450	1000	11.8
460	960	11.2
540	890	10.1
650	750	LI
Chroriiium	1020	1.5

HV_{100} were obtained. At higher temperatures, the coating begins to soften, as the nickel phosphide particles conglomerate, reducing the number of hardening sites. This process also removes phosphorus from the alloy producing a separate phase of soft nickel in the Ni_3P matrix, and further reducing the bulk hardness of the coating.

The abrasive wear resistance of the coating follows a different pattern. Initially, the Taper Wear Index (TWI) increases with temperature, as stress and hydrogen are relieved from the deposit. Then, as the coating begins to harden at about 260°C, abrasive wear resistance starts to increase and the TWI begins to decline. This trend continues Until the phosphides conglomerate and the coating softens, when a small reduction in resistance is observed.

Above 450°C, the TWI again declines as large particles of Ni_3P form, providing hard Mounds to protect the surface from contact with the abrasive. Maximum resistance is obtained at temperatures of 650°C and above. Even after these extreme treatments, however, the resistance of electroless nickel is still significantly less than that of hard chromium, which was found to have a TWI of 1.5 mg/1000 cycles at a microhardness of 1020 HV_{100}.

For some applications, higher temperature treatments are not possible because of part warpage or because of their effect upon the strength of the substrate. For these cases, it is sometimes possible to use lower temperatures and longer times to obtain the desired hardness. This is illustrated by the results listed in Table II, which shows the effect of different treatment periods upon the hardness and wear resistance of the coating.

At 400°C, hardening occurs very rapidly, and 1020 HV_{10o} is obtained within about 30 minutes. As the temperature is reduced, however, much more time is required for the hardening reactions to reach completion. For example, at 340 and 290°C, 4 and 10 hours respectively are needed to provide maximum hardness, although values greater than 950 HV_{100} are obtained in one or two hours. At 26OT, the coating will also come to full hardness, but only after 12 days of heating. Accordingly, treatments at temperatures below 290°C are normally only used for hydrogen embrittlement relief or adhesion improvement.

The abrasive wear resistance of coatings heat treated for longer periods at lower temperatures is like that of those hardened for one hour to a similar hardness. Typically, coatings at 950 to 1050 HV_{100}, have a Taber Wear Index of 11.5 to 13.5 mg/1000 cycles, irrespective of their heat treatment.

CONCLUSIONS

In the as deposited condition, electroless nickel is one of the harder coatings available, and its hardness may be increased to even higher levels by heat treatment. The coating also offers good resistance to abrasion, and is frequently used to mitigate the effects of wear. The temperature and period of heat treatment may be varied over wide limits to suit individual conditions, while still providing the same level of hardness and wear resistance.

For purely abrasive conditions, however, hard chromium does provide superior performance, and should be considered the coating of choice. For other applications, especially those where corrosion may occur, the resistance of electroless nickel often exceeds that of chromium and is the preferred coating. For adhesive wear, the resistance of the two coatings is Usually similar.

Table K. The Effect Sf Different Heat Treatments Upon the Hardness and Wear Resistance of 11%P Electroless Nickel Deposits

Temperature °C	*Period hours*	*Hardness* HV_{i00}	*TeberWaar Index mglitjOOcycles*
As deposited		580	19.7
200	1	580	20.6
	8	560	—
	24	590	...
260	1	600	19.7
	2	580	
	4	890	
	8	910	—
	16	990	—
	24	940	13.4
	48	970	—
	96	960	—
	288	1000	—
290	1	750	17.6
	2	960	—
	4	1000	13.4
	8	1010	
	10	1050	13.6
	24	970	—
340	1	970	13.3
	2	980	
	4	1020	11.6
	6	1000	12.7
	8	1O00	▪▪
	24	960	12.0
400	0.2	970	—-
	0.5	1020	—▪
	1	1040	11.5
	24	970	11.9

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.