NICKEL- AND COBALT-BASED NANO-COMPOSITE AND NANO-STRUCTURED ALTERNATIVES TO CHROMIUM COATINGS

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The electrodeposition of chromium involves hazardous and/or toxic chemicals. With the proposed new OSHA exposure limit for hexavalent chromium, plating shops will find it harder to remain in compliance with the environmental, health and safety regulations. Consequently, cost effective alternatives with the ability to offer comparable performance, reduce compliance burdens, and address worker safety concerns are of considerable interest. This paper focuses on some of the nickel-based and cobalt-based coatings that have nano-scale grain sizes and/or particulate additives to improve properties such as deposit quality, surface finish, thickness, porosity, hardness, wear, and corrosion resistance. These alternatives are discussed and their properties compared to those for electroplated hard chromium (EHC). The effects of nano-scale particle dispersions on these properties also are reviewed to show any trends in the performance benefits obtained.

Based on this review, currently the best candidates to replace EHC are electrodeposited nano-Ni-Co, nano-Co-P, Ni-P+diamond or SiC particles, Ni-W-B with or without SiC particles, and electroless deposited Co-P+diamond particles. For touch up/repair, brush plated Ni-Fe-W-S coatings may be suitable.

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INTRODUCTION

In earlier papers (1-7), the corrosion and wear behavior of environmentally acceptable alternatives to cadmium, chromium and nickel coatings were discussed. The driving force for finding substitutes is the need to comply with occupational safety and health legislation, as well as federal, state and local environmental regulations and Executive Orders to reduce or eliminate emissions of, and exposure to hazardous materials in industry and the defense industrial base. Corrosion resistance is an important property to ensure that components, assemblies, and products have a useful life in service and maintain a pleasing appearance; however, published data on corrosion are not as plentiful as those for other properties, such as hardness and wear or abrasion resistance, which also are important for the products to function as designed.

The purpose of this paper is to update previous reviews of corrosion, hardness and wear data for alternative coatings to electroplated hard chromium (EHC), with an emphasis on electrodeposited or electroless plated nano-structured or nano-composite materials. This update is necessary because of the rapid increase in number of publications on candidate coatings in recent years. Alternatives to decorative chromium are not discussed in this paper. Published baseline property data for EHC coatings are summarized in Table 1.

Table 1. Baseline Property Data for Hard Chromium Coatings

Property	Value	Property	Value
Hardness		**Wear Resistance**	
• Knoop	• 900	Abrasive Slurry (ASTM G 75)	
• Rockwell	• 68-74	• Al_2O_3 particles	• 8.3
• Vickers	• 800-1,000	Block on Ring (ASTM G 77)	
Ductility		• Steel Ring (volume loss)	• 16.35
• %	• < 1.0	Pin on Disk (ASTM G 99)	
Coeff. of Friction		• Al_2O_3 ball (volume loss)	• 9.0-12.0
• 0.1 kg/cm^2 load	• 0.25	Taber Abrasive Wear Index (ASTM D 4060)	
• 0.3 kg/cm^2 load	• 0.40	• CS-10 wheel, 1 kg load	• 1.0-4.7
• 0.5 kg/cm^2 load	• 150.00	• CS-17 wheel, 1 kg load	• 3.2

There are four approaches to finding environmentally acceptable alternatives to EHC coatings:

- A - Alternative Substrate Material or Design (avoids need for a coating)
- B - Substrate Surface Modification (avoids need for a coating)
- C - Reduced Chromium Content Coatings (lowers emissions and exposure)
- D - Chromium-free Coatings (eliminates emissions and worker exposure).

This paper focuses on the last approach, where chromium is totally eliminated from the coating. Table 2 is an updated list of some of the possible alternatives that have been, or may be considered as replacements for EHC coatings. For convenience these have been divided into either nickel-based materials or cobalt-based materials.

Table 2. Possible Alternatives to Hard Chromium Coatings Found in the Open Literature

Nickel-Based Coatings		Cobalt-Based Coatings
• Ni + Al	• Ni-P + SiC + PTFE	• Co-B
• Ni + Al_2O_3	• Ni-P-Fe	• Co-B + diamond
• Ni-B	• Ni-P-W	• Co-Fe
• Ni-Co	• Ni + SiO_2	• Co-P
• Ni-Co-P	• Ni + TiO_2	• Co-P + B_4N
• Ni-Fe	• Ni + WC	• Co-P + diamond
• Ni-Fe-Co	• Ni-W	• Co-Sn
• Ni-Fe-W-S	• Ni-W + SiC	• Co-W
• Ni-Mo	• Ni-W-B	• Co + WC
• Ni + MoS_2	• Ni-W-B + ZrO_2, SiO_2 or TiO_2	
• Ni-P	• Ni-W-Co + SiC	
• Ni-P + diamond	• Ni-W-Mo	
• Ni-P + PTFE	• Ni-W-P	
• Ni-P + SiC	• Ni-W-P + SiC	

Hardness and wear resistance are often associated with each other in that harder coatings are usually considered more wear resistant. However, other factors may come into play, such as coating roughness, lubricity, or toughness. A coating that resists sliding wear is not necessarily the best to resist abrasive wear. Similarly, the presence of dispersed particulates in a coating may improve wear or have a detrimental effect depending on particle composition, size, and distribution. Data in the literature for alternatives to EHC usually focus on abrasive wear, and unless otherwise stated the wear data in this paper reflect this. However, when wear data are not available coefficients of friction may provide some insight to wear resistance, particularly for sliding wear, so these data also are provided when available.

Less corrosion resistance information was found in the recent, open literature. It is sometimes presented as electrochemical polarization resistance or linear polarization data, where open circuit potential (OCP), passivation potential and current, and corrosion potential provide information about susceptibility to corrosion. There is inherent difficulty in evaluating these data because of the different corrosive media used, experimental parameters employed, and the different types of reference electrode used to measure potentials (voltages). Corrosion resistance also is presented as chemical immersion or salt fog exposure (ASTM Method B 117) data, where the latter is useful only for comparison purposes. Again, different test media and parameters can make comparisons among candidate alternative coatings difficult.

NICKEL-BASED COATINGS

The published properties of nickel-based, chromium-free coatings applied by either electrodeposition or by electroless plating techniques are discussed below. Examples of these alloys, mixtures, and composite coatings are listed in Table 2.

Electroplated Nickel Alloy Coatings

Ni Co Alloys

Nano-crystalline Ni-Co alloys, in the as deposited condition, give micro-hardness values of 820 to 900 VHN (8); however, when heat treated, precipitation hardening occurs (much like that found with electroless Ni-P or Ni-B coatings) and micro-hardness values of 1,000 to 1,150 VHN have been obtained. The abrasive wear resistance - as measured by the Taber Wear Index (TWI) (for a CS 17 wheel) - is in the range of 10.0 to 11.0 as deposited, and 8.0 to 9.0 after heat treatment compared to about 3.2 for EHC (Table 1). Thick coatings may be obtained (up to 380µm) which is an advantage for engineering or functional applications.

Ni-Co alloys electroplated on a steel substrate, and heat treated for 24 hours at 190^{o}C, were subjected to salt fog testing (ASTM B 117 Method). The results indicated that this alloy coating performed better than EHC without a nickel underlayer (9). Electrochemical polarization and impedance measurements also were made on this alternative coating and the results are summarized in Figure 1. The Ni-Co alloy did not perform well. [Note that relative rankings are shown where 1 is the best and 9 the worst ranking of the candidate alternatives tested.]

Ni-Fe-W-S Alloys

A brush plated Ni-Fe-W-S coating on a die steel was said to have a hardness after heat treatment of about 900 VHN and “better” wear resistance than EHC under dry, ambient conditions and also high speed, heavy load, lubricated conditions (15, 16). For the former conditions of sliding wear, the Ni-Fe-W-S coating showed only a small increase in wear rate (~0.5 to ~1.7 x 10^{-17} m^3/Nm volume loss) as the load was increased from 20 to 100 N. In contrast, an EHC coating showed a rapid increase in wear rate above 60 N applied loading (from about 2 to 15 x 10^{-17} m^3/Nm). The corrosion resistance said to be “superior” to EHC. No details were provided (15).

Ni-Mo Alloys

Nickel itself is not a hard material (~230 VHN as deposited); however, coatings with a nano-crystalline structure have exhibited higher micro-hardness values of 600 - 640 VHN as plated, and 500 - 550 VHN after heat treatment (8). To obtain higher hardness values alloying has been tried, especially with molybdenum and tungsten additions. For example, a Ni-Mo(0.5%) alloy coating had a hardness of 528 VHN (11), but this was still well below the minimum value for EHC given in Table 1.

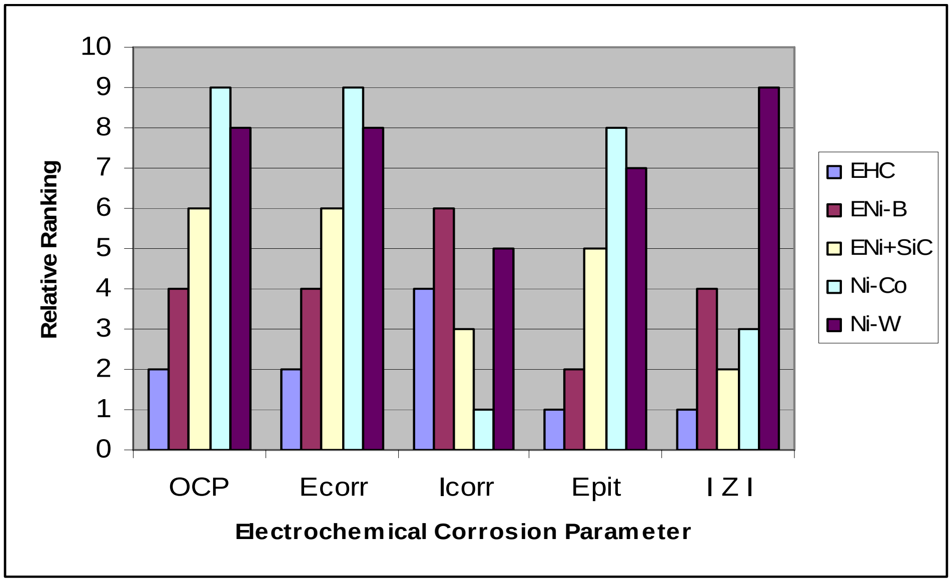

Figure 1. Corrosion Related Performance Data for Nickel-based Alternative Coatings
[Note: See text for explanation of the corrosion parameters measured.]

Ni-W Alloys

In contrast, nickel alloyed with 24-45% tungsten gave hardness values up to 1,000 VHN after heat treatment (11, 12). Adhesion was excellent, but wear resistance data for these alloys were not reported. A similar brush plated, nickel alloy coating containing 35% tungsten exhibited a hardness less than that for EHC, but a sliding wear resistance equal to that for EHC, and an abrasive wear resistance about three times that of EHC (13). Ni-W alloys electroplated on a steel substrate, and heat treated for 24 hours at 190^{o}C, were subjected to salt fog testing (ASTM B 117 Method). The results indicated that this alloy coating performed better than EHC (without a nickel underlayer) and was better than the Ni-Co alloy discussed above (9). Electro-chemical polarization and impedance measurements also were made on this alternative coating, and the results also are summarized in Figure 1. The performance was similar to that of the Ni-Co alloy, and worse than that for an EHC coating.

Electrodeposited N-W-B alloy coatings also have been investigated (10, 14) and appear to have better wear properties than EHC. Although their hardness as plated was only about 650 VHN, after heat treating at 400^{o}C for two hours a hardness of 1,132 VHN could be achieved. These alloy coatings have better corrosion properties than EHC in a 3.5% sodium chloride solution and in a hydrogen sulfide gas environment (10). In the salt fog test, after 168 hours exposure, the Ni-W-B coating showed no signs of corrosion, but the EHC coating exhibited staining and some localized attack. Similar results were obtained in the H_2S exposure test after 168 hours, except the EHC coating showed signs of corrosion from the first day. Depending on the pH of the environment, different types of nickel or tungsten oxide containing protective oxide film are formed.

Electroplated Nickel Composite Coatings

Ni + Al_2O_3 Coatings

The addition of 1.5^{w}/o nanometer-size particles of α-aluminum oxide to a Watt's nickel matrix did not improve hardness or wear resistance according to the data listed in Reference (6). Only a slight increase in hardness was found and the sliding wear resistance was not as good as that exhibited by EHC (17). More recent data on brush plated Ni + Al_2O_3 coatings on a 1045 steel substrate are more promising (18). These coatings incorporated about 2.6^{w}/o alumina particles (with a size range of 20-40 nm) and displayed a micro-hardness in the range of 600 - 700 VHN compared to 440 VHN measured for pure nickel. The coefficient of friction was 0.11 compared to 0.16 for pure nickel; and the wear resistance (under abrasive lubrication conditions) was one third better than that for pure nickel. Comparable data for EHC were not provided.

Pulse plating of nickel with 5,000nm alumina particles gave coatings 15-25μm thick on copper that were harder than those obtained by conventional (dc) plating techniques. The micro-hardness of these coatings depended on the duty cycle and frequency, with greater hardness values at lower frequencies and lower duty cycles (19). Even so, values of only 400 - 440VHN were obtained for coatings containing about 40^{v}/o alumina particles. The wear resistance followed a similar trend, with best results obtained for the lower duty cycles and frequencies of pulse plating. Using a stainless steel pin on disc apparatus, the wear resistance was improved over that for pure nickel by about 25%. Comparable data for EHC were not provided.

Ni + SiC + PTFE Coatings

The properties of two nano-crystalline nickel coatings and a Ni + SiC + PTFE composite coating (3.1^{w}/o inclusions) have been measured (20). The hardness of the composite coating was the greatest (766 VHN) compared to 235 and 695 VHN for the nano-crystalline nickel coatings deposited from different plating baths. However, the wear properties of the latter were very similar (16.1 - 16.7 μm wear depth using a ball on disc method with no lubrication, and a load of 1.3 N for 60 minutes). In contrast the composite coating exhibited a wear depth of only 1.6 μm. When the corrosion resistance of the nano-crystalline nickel coatings is considered, it becomes apparent that they are not good candidates to replace EHC coatings (20). Overall, the composite coating has better properties.

The corrosion resistance of nano-crystalline nickel coatings and Ni + SiC + PTFE composite coatings (3.1^{w}/o inclusions) was measured by a voltammetric method in 0.5M NaCl solution (20). The corrosion current (I_{corr}) was the lowest for the composite coating (0.38 $\mu A/cm^2$). The nano-crystalline nickel coatings, in comparison, gave values of 0.45 and 0.81 $\mu A/cm^2$ depending on bath composition and deposition parameters. The hardness of the composite coating was the greatest (766VHN) compared to 235VHN and 695VHN for the nano-crystalline nickel coatings. However, the wear properties of the latter were very similar (16.1 - 16.7μm wear depth using a ball on disc method with no lubrication, and a load of 1.3 N for 60 minutes). In contrast the composite coating exhibited a wear depth of only 1.6μm.

Ni + TiO_2 Coatings

The addition of 1^{w}/o titanium dioxide to a Watt's nickel matrix was not successful either for improving hardness and wear resistance according to data given in Reference (6). Only a slight increase in hardness was found and the sliding wear resistance was not as good as that exhibited by EHC (17). Reference (21) however, does indicate that the hardness is dependent on the type of titania added. In general, anatase particles (~12nm diameter) gave better results than rutile particle (~1,000nm) additions. The hardness of the electrodeposited Ni + TiO_2 coatings increased as the amount of titania in the coating increased. With nano-structured nickel as a baseline (hardness ~5.5 GPa), the average hardness was about ~9% greater for a 4% TiO_2 addition; ~27% for an 8% addition; and ~36% greater for an 11% addition. Comparable wear data were not provided for EHC, so a direct comparison cannot be made.

Reference (21) indicates that their Ni + TiO_2 coatings exhibited a better corrosion resistance than nano-structured nickel when immersed in "acidic corrosive water" (1.0 g/L $CuCl.H_2O$ + 5% NaCl solution maintained at a pH between 3.1 and 3.3). With respect to the corrosion rate, the volume loss was about 16.8 g/m^2/h for nickel. In comparison, the volume loss was lowered by about 11%, 40%, and 64% for the 4%, 8%, and 11% titania additions, respectively. Like the hardness data presented above, the anatase additions gave better results than the rutile additions, and this may be related to the size of the added particles.

Ni + WC Coatings

Hardness and wear values for Ni + WC coatings are not available in the literature. Electrochemical polarization data for Ni + WC(19-37%) composite coatings on mild steel in a 0.1 M sulfuric acid solution have been reported (22). The open circuit potential and passivation properties varied depending on the concentration of the 5,000nm tungsten carbide particles occluded in the 35-50μm thick coatings; however, no consistent trends were observed. The tungsten carbide additions were said to decrease the stability of the passive film that forms on the nickel matrix.

Ni-Co + WC Coatings

Good results also have been obtained with 25-30 ^{v}/o nanometer-size particles of tungsten carbide added to a nickel-cobalt electroplated matrix (23). As deposited, the hardness measured was 850 VHN, and the coefficient of friction and sliding wear resistance compared very favorably with the baseline EHC coating data.

Ni-W-B- and Ni-W-P-based Coatings

Some limited micro-hardness and wear data have been published (24, 25, 26) on dc and pulse plated Ni-W-B-X and Ni-W-P-X coatings [where X = SiC, a rare earth (RE), ZrO_2, MoS_2, or poly(tetraf louroethylene)]. In general, the hardness values peaked at a heat treatment temperature of 400°C (exceeding that for an EHC control coating), or a duty cycle of 0.6 to 0.8, and a frequency of 50Hz. Values of 1,420 VHN and 1,650 VHN were obtained for the Ni-W-B(3.85 ^{w}/o) + SiC(12.3 ^{w}/o) and Ni-W-B(3.82 ^{w}/o) + SiC(15.4 ^{w}/o) + RE heat treated coatings (400°C for 1 hour), and 1,450 VHN for the Ni-W-P(9.75 ^{w}/o) + SiC(13.6 ^{w}/o) coating (24). As plated, these coatings had an amorphous or nano-structured microstructure. The harder composite coatings exhibited an order of magnitude lower wear loss (0.65 - 1.37 mg) compared to the EHC control coating (20.8 mg). Reference (24) contains data on the corrosion properties of a number of Ni-W-B coatings containing various added particles, such as silicon carbide and rare earths (RE). Tables 3 and 4 summarize these data for the coatings studied. The "self-corrosion potential" (E_{corr}) in a 5% sulfuric acid solution is expressed in volts (V) versus a standard calomel reference electrode (SCE).

Table 3. Corrosion Potential Data for Various Ni-W-B Based Composite Coatings

As Deposited Coating	E_{corr} (V vs. SCE)
Ni Control	-0.204
EHC	-0.489
Ni-W-B(2.75 ^{w}/o) + SiC(11.8 ^{w}/o)	-0.345
Ni-W-B(3.85 ^{w}/o) + SiC(12.3 ^{w}/o)	-0.341
Ni-W-B(3.82 ^{w}/o) + SiC(15.4 ^{w}/o) + RE	-0.333
Ni-W-P(9.75 ^{w}/o) + SiC(13.6 ^{w}/o)	+0.123

It was observed that the composite coatings exhibited a more noble (positive) potential than the EHC coating, meaning that they were more corrosion resistant.

Corrosion rate data obtained when the coatings were immersed in a 20% hydro-chloric acid solution showed that the phosphorus-containing coating was more corrosion resistant than the boron-containing coatings. The corrosion rates at room temperature of the as deposited coatings in this and other corrosive acidic solutions are listed in Table 4. The phosphorus-containing coating consistently performed better than the boron-containing coating.

Table 4. Corrosion Rate Data for Ni-W-P + SiC and Ni-W-B + SiC Coatings

	Corrosion Rate (10^3 mg/cm^{2}h)	
Corrosive Solution	**Ni-W-P + SiC**	**Ni-W-B + SiC**
10% Sulfuric Acid	2.17	9.53
16% Nitric Acid	4, 694.95	6,728.45
20% Hydrochloric Acid	66.72	97.32
85% Phosphoric Acid	0.36	0.57
10% Sodium Chloride	1.43	6.54
10% Cupric Chloride	182.51	432.83
10% Ferric Chloride	158.12	521.32

In a 20% sodium hydroxide solution at room temperature, as expected these two nickel-based composite coatings exhibited no corrosion weight loss. According to the polarization curves obtained (24) the "passivation causing" current densities (i_{pass}) were about 9.6 and 7.5 mA/cm^2 at about - 0.5 and - 035V vs. SCE, and the "minimum passivation maintaining" current densities were about 1.3 and 2.5 mA/cm^2 for the phosphorus- and boron-containing coatings, respectively.

Ni-W-Co-based Coatings

A Ni-W-Co + SiC composite coating applied by brush plating to a steel substrate provided a micro-hardness of 990 VHN (15). This coating was subjected to high speed, heavy load, lubricated conditions at temperatures in the range of 400°C to 600°C. The lowest coefficient of friction (0.58) and abrasive wear loss (3.5 x10^{-3} mg/m, plate on ring method with a 61 RC steel plate) was observed at a 500°C test temperature.

Electroless Nickel Alloy Coatings

A qualitative overview of the hardness and wear resistance of a wide range of electroless nickel alloy coatings is provided in Reference (27). Some published quantitative data are given in Reference (6) for the most common Ni-P and Ni-B "alloys", and others with metals such as cobalt or tungsten. The as deposited hardness of these coatings typically falls in the range of 500 to 800 VHN. When heat treated, most of the coatings are harder (900 to 1,200 VHN) because of a precipitation hardening mechanism.

Ni-B Coatings

The hardness depends on the composition and the type of heat treatment used. For example, Ni-B coatings, as deposited, are too soft, but when 5% thallium is added the hardness increases to 700 VHN as deposited and 1,200 VHN when heat treated (27). Ni-B alloy coatings, however, are less ductile than Ni-P alloys.

Additional coefficient of friction, wear and micro-hardness data are available for electroless Ni-B coatings (containing 6.5% boron, 0.3% thallium) on mild steel, copper and stainless steel substrates (28). To increase their hardness, the coatings were heat treated at temperatures between 200^{o}C and 600^{o}C for one hour. The results indicate that maximum hardness (905 VHN) was obtained at 450^{o}C, and there was a second peak at 350^{o}C (850 VHN). Both values are at the low end of the acceptable range for an EHC alternative.

The values obtained for the coefficient of friction and wear behavior of these Ni-B coatings depend on the applied load and heat treatment they received. Table 5 summarizes these data. A pin-on-disc apparatus with an unlubricated 63 RC steel pin at moving at 0.5 m s^{-1} was used for the wear testing. The test data indicated that the volume loss was mostly attributable to an adhesive wear mechanism.

Table 5. Summary of Coefficient of Friction and Wear Data for Ni-B Coatings as a Function of Heat Treatment

Applied Load, N	As Deposited, No HT	HT at 350^{o}C	HT at 450^{o}C
Coefficient of Friction			
20	0.74	0.71	0.68
30	0.77	0.73	0.70
40	0.78	0.75	0.71
Wear (volume loss x10^{-10} kg/$N^{-1}m^{-1}$)			
20	0.52	0.39	0.30
30	1.36	0.68	0.70
40	2.46	1.72	0.71

The corrosion behavior of an electroless deposited Ni-B coating on steel - heat treated at 190^{o}C for 24 hours - has been investigated (9) and the results are summarized in Figure 1. This coating performed better than the electroplated Ni-W and Ni-Co alloy coatings discussed earlier. In salt fog testing (ASTM B 117 Method) the results indicated that this coating performed better than EHC (without a nickel underlayer).

Ni-Co-P Coatings

Ni-Co-P(4-6%) coatings also exhibit equivalent or better hardness and abrasive wear resistance compared to EHC (29, 30). Thus electroless Ni-P or Ni-Co-P coatings may be candidates to replace EHC for some applications, especially as electroless plating is a NLOS deposition process. That is, complex shapes and internal diameters can be coated with a uniform thickness.

Ni-P Coatings

As the phosphorus content of electroless Ni-P coatings increases from 3 percent to 11 percent, the heat treated hardness values vary between about 877 and 1,050 VHN (6). These values compare favorably with the hardness for EHC; however, there is not a correlation between hardness and composition, although ductility tends to increase as the phosphorus content increases (42). In contrast, in the as deposited condition hardness decreases as the phosphorus content increases.

For a “mid-P” coating the TWI (CS-10 wheel, 1 kg load)) is reported as 11.6, compared to a value between 1.0 and 4.7 for EHC. Reference (31) also gives a value of 11.0 for a Ni-P (8.5%) alloy deposited from a cadmium and lead free plating bath, and compares this to TWI values of 18 and 24 for “conventional mid- and high-phosphorus” electroless deposited coatings.

Reference (27) provides a useful table of the resistance of electroless Ni-P coatings to a number of chemicals determined from simple immersion testing.

Ni-P-W Coatings

Some hardness data have been reported for electroless Ni-P-W coatings (19.6% P and 2.7% W) some 8 µm thick (32). These were heat treated at temperatures ranging from 400 ^oC to 550^oC and exhibited hardness values of about 12 GPa and 13 GPa at these temperatures. At 450^oC and 500^oC the hardness increased to almost 14 GPa. As a point of reference, nano-structured nickel coatings have a hardness of about 5.5 GPa (17).

Electroless Nickel Composite Coatings

Ni + B_4N Coatings

The hardness value for a Ni-P(10%) + 1% boron nitride coating was below what is considered the minimum for an alternative to EHC (27, 34).

Ni + PTFE Coatings

The N-P+20-25% PTFE coatings are too soft (≤ 500 VHN) but they do exhibit good sliding wear resistance, as might be expected because of the relatively high concentration of the dry lubricating particles (33). The coefficient of friction of these coatings is in the range of 0.1 to 0.3 vs. steel. Ni + PTFE coatings - 15 to 25µm thick - exhibit good corrosion resistance in the salt fog test. Between 500 and 1,000 hours exposure have been recorded before corrosion was observed (35).

Ni + Diamond Coatings

In contrast, a harder Ni-P(6-8%) + diamond particles coating showed a better abrasive wear resistance than EHC (294, 30). Coatings - 25 µm thick - of 4-8 nm diameter diamond particles in a Ni-P matrix on a medium carbon steel substrate also have been investigated in some detail (36). As deposited, the micro-hardness was 615 VHN, and was a maximum (1,316 VHN) when the coating was heat treated at 400°C for two hours. At 300°C the measured micro-hardness was only 983 VHN. Wear resistance was comparable to EHC for these coatings with dispersed nano-diamond particles. Table 6 lists the measured wear and coefficient of friction values as a function of heat treatment temperature. A ball-on-disc method was used for the wear measurements, with an unlubricated, 62 RC steel ball. Both the coefficient of friction and the wear resistance was optimum when the heat treatment was 400°C for two hours. Of interest is the observation that the composite coatings were smoother and had a smaller grain size than equivalent Ni-P coatings.

Table 6. Summary of Coefficient of Friction and Wear Data for Ni-P + Diamond Composite Coatings as a Function of Heat Treatment

Coating	As Deposited, No HT	HT at 200°C	HT at 400 °C	HT at 500°C
Coefficient of Friction				
Ni-P	0.58	N/A	N/A	N/A
Ni-P + diamond	0.46	0.47	0.36	0.39
Wear (volume loss x$10^{-4}$$mm^3$)				
Ni-P	10.2	N/A	N/A	N/A
Ni-P + diamond	5.6	5.8	3.4	3.9

In general, diamond particle size can have an effect on hardness, (29, 30). The larger the particle size, the greater the hardness value obtained (43). However, it is likely that the concentrations of particles were not the same for all the coatings tested, and this variable needs to be investigated for any composite coating before any rigorous comparisons may be made.

Similarly, there seems to be a correlation between particle incorporation and abrasive wear resistance (29, 30). The Ni-P(6%) alloy has a relatively low TWI of about 15, but when the harder diamond particles are added the TWI drops to below 2, which is equivalent to, or better than that for EHC.

Ni + MoS_2 Coatings

The hardness value for a Ni-P(7-10%) + <50% molybdenum disulfide coating, was below what is considered acceptable for an alternative to EHC (27, 37). Although the Ni-P+MoS_2 coatings had a low coefficient of friction, they were not as wear resistant as EHC coatings.

Ni + SiC Coatings

An electroless Ni-P + SiC coating on a steel substrate exhibited relatively good corrosion behavior when compared to an EHC coating (9). The results of the test performed are shown in Figure 1 above. This type of electroless plated coating performed better than the Ni-Co and Ni-W electrodeposited alloys, but not as well as an EHC coating. In salt fog testing the results (9) indicated that this coating performed better than an EHC (without a nickel underlayer).

COBALT-BASED COATINGS

Examples of the cobalt-based alloys and composite coatings found in the open literature are listed in Table 2 and their published hardness, coefficient of friction, and wear properties are discussed below.

Electroplated Cobalt Alloy Coatings

Co-Fe Coatings

Only a few cobalt alloys have been investigated. Cobalt alloyed with "high" iron content produces coatings with hardness values that only approach the minimum for EHC, namely 850 VHN (38). The hardness is lower for lower iron contents. The reported abrasive wear resistance (TWI = 3.0 and 5.0 for the high and "low" iron content alloys, respectively) is comparable to that of EHC coatings.

Co-P Coatings

Electroplated, nano-structured Co-P(2-5%) "alloy" analogs of electroless plated coatings exhibit more promising behavior, with hardnesses up to 1,000 VHN after heat treatment, compared to only about 730 VHN in the as plated condition (43). Hardness of these coatings increased as the phosphorus content was increased. A TWI value of about 11, or a sliding wear loss of 5.5 x 10^{-6} mm^3/Nm has been reported (38). The coefficient of friction of these alloys also was in the acceptable range. Some more recent hardness, coefficient of friction, and wear data (39) are summarized in Table 7 and compared to data for EHC coatings.

For nano-Co and nano-Co-P coatings approximately 50 µm thick, Reference (39) provides both salt fog (1,000 hour exposure) and corrosion rate (linear polarization resistance in 3.5% sodium chloride solution) data. The ASTM B 537 rating system was used for the salt fog exposure results where 10 represents the best resistance and 1 the worst corrosion resistance. Both the nano-Co and nano-Co-P coatings performed well in the salt fog test, with ratings of 9 to 10 compared to 1.5 for an EHC coating. Also tested were two Co-Fe-P coatings with "low" and "high" iron contents. Both exhibited much worse corrosion resistance than an EHC coating in the salt fog testing (39). In the linear polarization resistance tests, the corrosion rate (expressed as mils per year, mpy) was found to increase as the phosphorus content was increased in the nano-Co-P "alloy" coatings. All of the alloy coatings had a worse corrosion resistance than the EHC baseline used for comparison. These results are summarized in Table 8.

Table 7. Hardness, Coefficient of Friction and Wear Data for Nano-Co-P Coatings as a unction of Heat Treatment

Coating*	**Hardness** (VHN)	**Coefficient of Friction**	**Wear Resistance**** (vol. loss, 10^{-6} mm^3/Nm)
EHC	1,200	0.70	11.9
Nano-Co	500	0.35	10.7
Nano-Co-P (4%)	745	0.48	6.4
Nano-Co-P (4%) **HT**	1,010	0.44	5.3
Nano-Co-P (>10%)	720	0.50	6.2
Nano-Co-P (>10%) **HT**	904	0.63	0.40

*** HT** = Heat treated, typically at 350 - 400°C for 10 - 15 minutes: other coatings as plated values.
****** For the adhesive/sliding wear measurements an alumina ball-on-disc method was used.

Table 8. Corrosion Rate Data for nano-Co-P Coatings

Coating	**Corrosion Rate** (mpy)
EHC Control	~ 0.02
Nano-Co (no P) Control	~ 0.50
Nano-Co-P(1.5%)	~ 0.07
Nano-Co-P(2.5%)	~ 0.15
Nano-Co-P(3.5%)	~ 0.60
Nano-Co-P(4.5%)	~ 0.65

Co-W Coatings

Amorphous or nano-structured Co-W alloys are too soft as deposited (10, 11) but heat treatment of alloys containing 25-45% tungsten does increase the hardness to acceptable values (e.g., 1,000 VHN). Brush plated Co-W alloys exhibited about three times the abrasive wear resistance compared to an EHC coating, and an equivalent sliding wear resistance (13).

Electroplated Cobalt Composite Coatings

Table 2 indicates that additions of diamond, boron carbide, and tungsten carbide particles to an electroplated cobalt, Co-B, or a Co-P matrix have been evaluated.

Co-P + B_4C Coatings

The as deposited hardness (700 VHN) of a Co-P + B_4C(22%) composite coating is below the criterion for an EHC replacement, but the abrasive wear resistance (TWI = ~1.0, CS-10 wheel and 1 kg load) is better than that for EHC (40).

Co + WC Coatings

A composite coating of cobalt and 10% tungsten carbide exhibited an as deposited hardness of only about one half that for EHC, and a TWI = 21.5 (CS-10 wheel and 1 kg load) that is unacceptable for an EHC replacement coating. Thermal spray applied WC-Co coatings provide much better properties (41) probably because of the much higher concentration (83%) of the harder WC particles. Hardness values >1,050 VHN can be obtained, along with reasonable values for the coefficient of friction (0.6 - 0.9) and better wear resistance than EHC.

Electroless Cobalt Alloy Coatings

Co-B and Co-P Alloys

A few cobalt-boron and cobalt-phosphorus "alloy" coatings have been studied. As deposited Co-B(~1%) coatings do not have the required hardness, and their abrasive wear resistance is too low for to be a candidate for an EHC alternative (12, 30). In contrast, heat treated Co-P(4-6%) alloy coatings may be hard enough to qualify as an alternative, but no wear data are available (29, 30).

Electroless Cobalt Composite Coatings

Like electroless nickel composite coatings, property values measured depend on composition, concentration of the reducing agent element incorporated (i.e., P or B), type of heat treatment, and the size and concentration of particulate additions (43). While the nano-structured coating offers some improvement over the conventional electroplated coating, electroless deposition and the incorporation of diamond particles provides even further improvements in hardness. A similar trend is found for abrasive wear resistance (24, 25, 43).

Co-B + Diamond Coatings

Electroless Co-B(~1%) coatings containing dispersed diamond particles have been investigated (29, 30). While the abrasive wear resistance is acceptable (i.e., TWI = 3.0, CS-10 wheel, 1 kg load) the hardness (723 VHN) falls below the criterion for EHC (Table 1).

Co-P + Diamond Coatings

In contrast, the Co-P(4-6%) coatings with diamond particles (29, 30) exhibit equal or better performance than EHC when heat treated (hardnesses of about 948 VHN and TWIs of about 2.6 were reported).

DISCUSSION

The reported properties of the candidate electrodeposited and electroless plated EHC alternatives discussed in this paper are summarized in Table 9 for the nickel-based coatings, and Table 10 for the cobalt-based coatings. The former outnumber the latter by a factor of two, probably because there is a greater history of developing nickel-based coatings than cobalt-based coatings. More attention has been paid to the latter only recently because of concerns that nickel may become as heavily regulated as chromium.

In the two summary tables, the information for the coatings has been entered as follows:

- Green indicates that it performs as well as or better than EHC
- Green/yellow indicates that optimized coatings may be acceptable
- Yellow indicates that the performance is marginally acceptable
- Red indicates that the coating is unacceptable for an EHC replacement.

In general, although there is no direct correlation between hardness, coefficient of friction, and wear resistance, high hardness and low coefficient of friction often are indicators of good wear resistance. Acceptable alternatives to chromium usually are said to require comparable hardness as well as exhibit acceptable sliding or abrasive wear resistance.

There are two relationships that can provide some guidance in the selection of suitable candidates based on hardness. One is Archard's Law relating to wear resistance, and the other is the Hall-Petch Law relating to hardness, as applied to nano-structured materials. A discussion of how these laws may be applied is given in Reference (7). Based on these two relationships, when optimizing material compositions and properties, changing the deposition parameters to give smaller grain sizes and greater hardness can be beneficial. In addition, whereas electroless deposited coatings are usually amorphous, a subsequent heat treatment to precipitation harden the coating, also can cause the grain structure to change to nano-crystalline, which can be beneficial. Similarly, any heat treatment used to remove hydrogen (to prevent hydrogen-related failures in service) can result in a more desirable average grain size in the coating.

Table 9. Summary of Property Data for Nickel-based, Chromium-free Candidates to Replace EHC

Coating	Application Method	Hardness	Coeff. of Friction	Wear Resistance	Corrosion Resistance	Comments
Ni-B-Tl	Electroless Plating	√	?	?	√	Contains thallium; heat treated
Ni-Co	Electroplating	√	?	(√)	√	Nano-structured matrix
Ni-Co-P	Electroless Plating	√	?	√	?	Pseudo-amorphous matrix; heat treated
Ni-Co + WC (25-30%)	Electroplating	(√)	√	√	X	Nano-sized WC particles
Ni-Fe-W-S	Electroplating	√	?	√	√	Brush plated
Ni-P (5-10%)	Electroless Plating	√	?	√	?	Pseudo-amorphous matrix; heat treated
Ni-P + B_4N	Electroless Plating	X	?	?	?	Pseudo-amorphous matrix; heat treated
Ni-P + diamond	Electroless Plating	√	(√)	√	?	Pseudo-amorphous matrix; heat treated
Ni-P + MoS_2	Electroless Plating	X	√	X	?	Pseudo-amorphous matrix; heat treated
Ni-P + PTFE	Electroless Plating	X	√	√	(√)	Pseudo-amorphous matrix; heat treated
Ni-P + SiC	Electroless Plating	√	?	√	(√)	Pseudo-amorphous matrix; heat treated
Ni-P-W	Electroless Plating	√	?	?	?	Pseudo-amorphous matrix; heat treated
Ni/Sn	Electroplating	X	?	?	√	Multilayers, heat treated
Ni-W (25-45%)	Electroplating	√	?	?	(√)	Nano-structured matrix
Ni-W (35%)	Electroplating	X	?	√	?	Brush plated
Ni-W-B	Electroplating	√	?	√	√	Pseudo-amorphous; after heat treatment
Ni-W-B + SiC	Electroplating	√	?	√	√	After heat treatment
Ni-W-B + SiC + RE	Electroplating	√	?	√	√	After heat treatment
Ni-W-Co + SiC	Electroplating	√	√	?	?	Brush plated
Ni-W-P + SiC	Electroplating	√	?	√	√	Pseudo-amorphous matrix
Ni + Al_2O_3	Electroplating	X	√	X	?	Pulse plated; nano-particles best
Ni + SiC + PTFE	Electroplating	X	?	√	(√)	Nano-structured matrix
Ni + TiO_2	Electroless Plating	X	?	X	√	Pseudo-amorphous matrix
Ni + TiO_2	Electroplating	X	?	X	?	Properties depend on particle size
Ni + WC (10-37%)	Electroplating	?	?	?	X	Properties not dependent on composition

Table 10. Summary of Property Data for Cobalt-based, Chromium-free Candidates to Replace EHC

Coating	Application Method	Hardness	Coeff. of Friction	Wear Resistance	Corrosion Resistance	Comments
Co	Electroplating	X	√	(√)	√	Nano-structured matrix
Co-B	Electroless Plating	X	?	X	?	Amorphous matrix; heat treated
Co-B + diamond	Electroless Plating	X	?	√	?	Nano-structured matrix
Co-Fe	Electroplating	(√)	?	√	X	Nano-structured matrix
Co-P	Electroless Plating	(√)	?	?	?	Amorphous matrix; heat treated
Co-P	Electroplating	√	√	√	√	Nano-structured matrix
Co-P + B_4C	Electroplating	X	?	√	?	Hardness may not be acceptable
Co-P + diamond	Electroless Plating	√	?	√	?	Amorphous matrix; heat treated
Co-Sn	Electroplating	X	√	X	?	Coating too soft
Co-W	Electroplating	X	?	√	?	Brush plated
Co-W (25-45%)	Electroplating	√	?	?	?	Heat treated
Co + WC	Electroplating	X	?	X	?	Thermal spray WC-Co better properties

CONCLUSIONS

An opportunity still exists to develop, characterize, and validate an acceptable alternative to EHC for applications where abrasion and sliding wear resistance is needed, and where corrosion will not be a problem in service. Electroless plating and electrodeposition techniques have the potential to provide thick coatings with no line-of-sight limitations if the coating compositions, deposition parameters and post-treatments are optimized. Based on this review, currently the best candidates are electrodeposited nano-Ni-Co, nano-Co-P, Ni-P + diamond or SiC particles, Ni-W-B with or without SiC particles; and electroless deposited Co-P + diamond particles. For touch up/repair, brush plated Ni-Fe-W-S coatings may be suitable.

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