NANO-PARTICLE COMPOSITE PLATING AS AN ALTERNATIVE TO HARD CHROMIUM AND NICKEL COATINGS

M.L. Klingenberg, Concurrent Technologies Corporation, Johnstown, PA, USA
E.W. Brooman and T. A. Naguy, Air Force Research Laboratory (MLSC), Wright-Patterson Air Force Base, OH, USA

ABSTRACT

As part of an effort to evaluate alternatives to electroplated hexavalent chromium coatings, screening tests were performed on numerous nano-structured coatings or amorphous coatings containing nano-particles or micro-particles. The objective was to determine if improvements in performance could be obtained with decreasing grain and/or particle size. Electrodeposited, nanocrystalline cobalt, with and without tungsten carbide particles, and electroless, mid-phosphorous nickel (ENi-P) coatings with various sizes of diamond particles (150, 1,000, 2,000 and 150+1,000 nm) were selected for investigation. Preliminary results suggested that additional electroless composites should be investigated. These coatings included nickel-cobalt phosphorous (ENi-Co-P), cobalt phosphorous (ECo-P), and nickel boron (ENi-B) - all with and without codeposited diamond particles. For baseline comparisons, electrodeposited polycrystalline cobalt and electroless nickel coatings were deposited without occluded particles.

This paper discusses the results obtained from the screening tests, which included adhesion, thickness analysis, hardness, and abrasive wear resistance. The results suggested that all of the ENi-P, ENi-Co-P, and ECo-P processes with occluded diamond particles have the potential to impart the required adhesion, hardness and tribological properties, while reducing the environmental impact of chromium plating processes.

For more information contact:
Melissa Klingenberg
Concurrent Technologies Corporation
100 *CTC* Drive
Johnstown, PA 15904
Telephone: (814) 269-2545/6415
Facsimile: (814) 269-6847
E-mail: klingenb@ctcgsc.org

BACKGROUND AND OBJECTIVE

Hexavalent chromium is used extensively to finish surfaces within the Department of Defense (DoD) and private industry due to its properties and decorative appeal. However, the environmental, health and safety (EHS) issues that are associated with hexavalent chromium have led to stringent regulations regarding its use. Reductions in permissible exposure limits and public owned treatment works discharge limits have escalated the burdens associated with using hexavalent chromium. Therefore, the search for viable alternatives to electroplated hard chromium (EHC) has become a high priority. In response, various DoD agencies have directed efforts towards identifying and evaluating viable alternative processes. The Hard Chrome Alternatives Team (HCAT) and the Air Force Research Laboratory (AFRL) are addressing near-term solutions to replacing EHC for both line-of-sight (LOS) and non-line-of-sight (NLOS) applications, respectively.

For many years, the HCAT has been investigating and validating high-velocity oxygen fuel (HVOF) technology as a potential EHC alternative. While HVOF technology may be able to meet the required performance characteristics of EHC, it cannot replace EHC in all applications because it is a LOS process. Therefore, even with the implementation of HVOF coatings, users would need to use EHC for some components. (For example, NLOS requirements comprise about 20-40 % of all EHC applications within the Air Force)

To address the NLOS need, the AFRL and Concurrent Technologies Corporation (*CTC*) established the “NLOS Hard Chromium Alternatives” project. This project established EHC needs and requirements per Air Force Air Logistic Center (ALC) operations and identified over one hundred possible alternatives. Included among these were electrochemical deposition processes that enabled the production of nano-structured coatings, as well as processes that produced amorphous structures and enabled the co-deposition of nano-particles. Inclusion of nano- or micron-sized particles into a metal matrix is sometimes called composite plating, and is a type of occlusion plating.

Nano-structures have been shown by many to exhibit interesting properties. Typically, as the grain size of a material decreases, its hardness, fracture toughness, and yield strength increase. This effect is known as the Hall-Petch effect [1-4]. Because nano-structured coatings offer the promise to improve the hardness and wear properties of conventional, softer, protective coatings, the AFRL established an effort to investigate the suitability of nano-particle composite plating processes as long-term replacements for EHC [5].

PROOF-OF-CONCEPT STUDY

A Proof-of-Concept study was conducted to identify and evaluate commercially available, or near commercial, nano-composite coatings. A literature search, vendor search, and personal contacts were used to identify processes that could be used to create nano-crystalline matrices, or to co-deposit nanoparticles within a metal matrix (microcrystalline, nano-crystalline, or amorphous) [6]. Information regarding these processes and the testing performed on the coatings for the proof-of-concept study are outlined in the following sections.

Coatings Selected

A vendor ("A") of nano-crystalline electrodeposits suggested that their nano-crystalline cobalt coating be tested. They also recommended that a second coating be developed to incorporate tungsten carbide (WC) particles within the nano-crystalline cobalt (Nano-Co) matrix. However, they were unable to obtain WC particles less than 2,000 nm in diameter. Consequently, they focused their attention on producing coatings with the nano-structured grains rather than occluded nano-particles, but did produce a set of samples with the 2,000 nm WC particles embedded in the cobalt matrix.

A second vendor ("B") was found that had the ability to either deposit nano-crystalline coatings or co-deposit nano-particles within a microcrystalline, nano-crystalline, or amorphous matrix. This company was selected because of its existing knowledge of occlusion plating, its willingness to accommodate special processing requests based on their commercial baths, and its willingness to adapt their process to accommodate smaller particles than what they currently used
(i.e., 2,000 nm). The coating matrix selected was based on an electroless nickel, mid-phosphorous (ENi-P) process. Diamond particles (2,000 nm, 1,000 nm, and 150 nm in diameter) were selected to be occluded in this matrix. In addition, samples with electroless nickel-cobalt-phosphorous (ENi-Co-P), electroless cobalt-boron (ECo-B), and electroless cobalt-phosphorous (ECo-P) coatings, with and without occluded, 1,000 nm diamond particles were prepared.

Baseline data were established with polycrystalline cobalt (Poly-Co) and ENi-P coatings, both without occluded particles, to try to determine the level of improvement imparted by nano-structured grains and particle incorporation, respectively. A third company ("C") provided the Poly-Co coatings, and Company ("B") provided the mid-phosphorous ENi-P baseline coatings. Data from previous studies were used to provide the electrolytic hard chromium (EHC) benchmark for comparison. A summary of the various coating system(s) selected for study is presented in Table 1.

Table 1. Proof-of-Concept Coatings Evaluated

Category	Coating(s) Applied†	Vendors
Baselines	EHC ENi-P (mid-phosphorous) Nano-Co without particles Poly-Co without particles	- - B A C
Nano-structured Matrix and Occluded Micro- and Nano-Particles	Nano-Co with 2,000 nm tungsten carbide particles ENi-P with 150, 1,000, 2,000 and 150 + 2,000 nm diamond particles ENi-Co-P with 1,000 nm diamond particles ECo-P with 1,000 nm diamond particles ECo-B with 1,000 nm diamond particles	A B B B B

† Company B heat treated their coated samples at 350^{o}C for two hours.

Coating Application

The vendors prepared nine, flat, 1010 cold-rolled steel (CRS) panels (3 each with dimensions of 4 x 4, 1 x 4, and 1 x 1 inches), and then applied their coatings (see Table 1). The requested target coating thickness was a minimum of 0.002 inch (2 mil). Company B used a heat treatment (350^{o}C for two hours) for all their coated samples to improve their properties. However, Companies A and C did not use a heat treatment, but supplied their samples “as plated”. Once vendor processing was complete, the panels were returned for inspection, testing, and evaluation.

Coating Testing

The testing that was performed on the coatings is outlined in Table 2. In some instances, the vendors performed additional characterization of their coatings. These data have been incorporated into the discussion of the results, where appropriate.

Table 2. Evaluation Test Matrix

Test	Test Method	Panel Sizes (inches)	No. of Panels per Test
Metallographic Thickness	ASTM B487	1 x 1	3†
Bend Adhesion	ASTM B571	1 x 4	3
Microhardness	ASTM B578	1 x 1	3†
Taber Wear Resistance	ASTM D4060	4 x 4	3

† The same panels were used for both these tests.

Test Results

A summary of the results of testing is given here, and correlations between composition, structure, and properties have been made, where possible, in the "Summary" section of this paper. Typical EHC data are included so that the alternative coatings evaluated may be compared to the currently used coating. A more detailed presentation and discussion of test results is given in Reference (5).

For any of the evaluated processes to be considered a viable alternative to EHC, it must meet or exceed various performance characteristics. Namely, the alternative processes must meet or exceed all guidelines outlined in "Federal Specification Chromium Plating (Electrodeposited) QQ-C-320B for Class II Engineering Plating". Table 3 provides the desired properties, per QQ-C-320B, for the tests conducted during proof-of-concept activities.

Table 3. Electroplated Hard Chromium Property Requirements

Parameter	QQ-C-320B Requirements
Quality	• Plating shall cover all specimen surfaces. • Plating shall be free from beads, nodules, jagged edges, and other irregularities. • Plating shall be smooth and uniform, dull matte or bright, as required. • Plating shall be smooth; fine-grained; free from blisters, pits, nodules, excessive edge build-up, contamination, excessive contact marks; and contain minimal staining or discoloration.
Thickness	For Class II Engineering Plating - a minimum of 0.002 inch (or as agreed upon by contract) shall be measured at several locations on accessible surfaces
Adhesion	At a magnification of 4X thickness, no separation of the plate from basis metal at interface shall be evident when using knife test or bend test.
Hardness	850 Vickers Hardness Number at 100-gram load, 10-15 seconds: measure each specimen at five locations and take the average of results.

Thickness Data

Coating thickness was measured in accordance with ASTM B487, "Standard Test Method for Measurement of Metal and Oxide Coating Thickness by Micro-scopical Examination of a Cross-section". Coated samples were mounted, ground and polished then inspected at a magnification of 100-200 times, using a metallographic microscope. The cross-sections of the ENi-P+diamond particles coatings were photographed. Company B used an instrument with commercial software to determine the approximate distributions of particles within the coating cross-sections.

Table 4 summarizes the thickness data obtained for the various samples.

Table 4. Thickness Measurement Test Results

Coating Type	Thickness, inch
EHC	**(0.0020)**
ENi-P (no diamond)	**0.0020**
ENi-P + 150 nm diamond	**0.0018**
ENi-P + 1,000 nm diamond	**0.0018**
ENi-P + 2,000 nm diamond	**0.0021**
ENi-P + 150 & 2,000 nm diamond	0.0017
Poly-Co	0.0012
Nano-Co	0.0016
Nano-Co + 2,000 nm WC (Sample Set #1)†	0.0014
Nano-Co + 2,000 nm WC (Sample Set #2)†	**0.0027**
ECo-P	0.0007
ECo-P + 1,000 nm diamond	0.0010
ECo-B	**0.0019**
ECo-B + 1,000 nm diamond	0.0010
ENi-Co-P	0.0016
ENi-Co-P + 1,000 nm diamond	0.0017

† The first set of samples contained approximately 10% WC by volume; the second set contained about 30% by volume.

Most of the ENi-P coatings supplied were of, or close to the required 2 mil (0.002 inch) thickness. The Nano-Co+2,000 nm WC, Set #2 and the ECo-B coatings also were close to the requirement. However, the ECo-P coating was only 0.7 mil thick, and several of the other coatings supplied were only about 1 to 1.5 mil thick (e.g., Poly-Co, ECo-P+1,000 nm diamond, ECo-B+1,000 nm diamond, and Nano-Co+2,000 nm WC, Set #1). The remainder of the coatings exhibited a marginally acceptable coating thickness. It should be noted that many of these plating baths were not yet in commercial production and that bath chemistry and operating parameters have yet to be optimized. Consequently, relatively less weight was placed at this time on the thickness data compared to the adhesion, hardness, and wear resistance data.

Adhesion Data

Coating adhesion was analyzed in accordance with ASTM B571, "Standard Practice for Qualitative Adhesion Testing of Metallic Coatings." The findings of the adhesion testing are shown in Table 5 for each coating type.

Of all the specimens tested, only the ECo-B coatings (with and without particles) did not meet the requirements. However, the panels used for this coating were coated once, stripped and etched, and then recoated by the vendor. Such operations may have contributed to the lack of adhesion. In addition, Company B believes that these films are highly stressed, leading to reduced adhesion. However, stress was not measured for these films in this study.

Table 5. Adhesion Test Results

Coating Type	Adhesion
EHC	**Pass**
ENi-P (no diamond)	**Pass**
ENi-P + 150 nm diamond	**Pass**
ENi-P + 1,000 nm diamond	**Pass**
ENi-P + 2,000 nm diamond	**Pass**
ENi-P + 150 & 2,000 nm diamond	**Pass**
Poly-Co	**Pass**
Nano-Co	**Pass**
Nano-Co + 2,000 nm WC (Sample Set #1)†	**Pass**
Nano-Co + 2,000 nm WC (Sample Set #2)†	**Pass**
ECo-P	**Pass**
ECo-P + 1,000 nm diamond	**Pass**
ECo-B	Fail
ECo-B + 1,000 nm diamond	Fail
ENi-Co-P	**Pass**
ENi-Co-P + 1,000 nm diamond	**Pass**

† The first set of samples contained approximately 10% WC by volume; the second set contained about 30% by volume.

Microhardness Data

Coating hardness was measured in accordance with ASTM B578, "Standard Test Method for Microhardness of Electroplated Coatings," using the Knoop hardness test. Various loads were used depending on the coating thickness. Table 6 provides the results of the average hardness for each coating type.

Upon comparing the test results to the accepted value for EHC, it is clear that most electroless deposited films met the requirement. However, none of the electrodeposited coatings, or the ECo-B - with or without particles - coatings, achieved the required hardness. It does appear that phosphide formation, whether in a cobalt or nickel matrix, is instrumental in improving hardness.

Taber Wear Resistance

Wear testing was performed on the vendor-coated, 4 x 4-inch panels using a Taber Wear apparatus in accordance with modified ASTM D4060, "Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser". A CS-10 wheel and a 1,000-gram load were used over 10,000 cycles.

Table 6. Microhardness Results

Coating Type	Hardness, VHN
EHC	**(850)**
ENi-P (no diamond)	**940**
ENi-P + 150 nm diamond	**903**
ENi-P + 1,000 nm diamond	**1,070**
ENi-P + 2,000 nm diamond	**1,161**
ENi-P + 150 & 2,000 nm diamond	**884**
Poly-Co	343
Nano-Co	468
Nano-Co + 2,000 nm WC (Sample Set #1)†	500
Nano-Co + 2,000 nm WC (Sample Set #2)†	346
ECo-P	**883**
ECo-P + 1,000 nm diamond	**948**
ECo-B	716
ECo-B + 1,000 nm diamond	723
ENi-Co-P	**924**
ENi-Co-P + 1,000 nm diamond	**1,135**

† The first set of samples contained about 10% WC, the second set about 30% WC by volume.

The Taber wear data are presented as a "wear index" in Table 7. Lower weight loss (Taber Wear Index) indicates a more wear resistant coating material.

Typically, Taber wear evaluations do not include the initial 1,000 cycles as part of the final analysis. This is largely because nodules and other surface imperfections (loosely bound particles, etc.) are removed during the initial 1,000 cycles and can provide seemingly large wear loss. Consequently, Table 7 also includes the index values calculated by subtracting the weight losses in the first 1,000 cycles from the 10,000 cycle total weight loss data.

Table 7. Average Abrasive Wear Resistance

Coating Type	Taber Wear Index	
	0 - 10,000 Cycles	**1,000 - 10,000 Cycles**
EHC	**(4.0)**	**(< 4.0)**
ENi-P (no diamond)	11.6	11.4
ENi-P + 150 nm diamond	**1.3**	**1.2**
ENi-P + 1,000 nm diamond	**0.7**	**0.6**
ENi-P + 2,000 nm diamond	**1.7**	**1.3**
ENi-P + 150 & 2,000 nm diamond	**1.5**	**1.3**
Poly-Co	31.1	29.4
Nano-Co	23.8	23.4
Nano-Co + 2,000 nm WC (Sample Set #1)†	21.5	16.2
Nano-Co + 2,000 nm WC (Sample Set #2)†	37.9	18.1
ECo-P	13.7	12.5
ECo-P + 1,000 nm diamond	**2.6**	**2.2**
ECo-B	49.4	39.4
ECo-B + 1,000 nm diamond	**3.0**	**2.1**
ENi-Co-P	13.3	12.7
ENi-Co-P + 1,000 nm diamond	**2.1**	**1.7**

† The first set of samples contained about 10% WC, the second set about 30% WC by volume.

There were no dramatic differences in Taber Wear Indices for these coatings when comparing the data after 10,000 cycles or 10,000 cycles minus the first 1,000 cycles, with the exception of the Nano-Co+2,000 nm WC sample that contained the greater amount of occluded WC particles. This observation might be attributed to the removal of a relatively larger number of WC particles at the beginning of the test.

EHC displays a weight loss of between 0.004 and 0.021 gram over 1,000 cycles, and it was decided to use the lower value for a more rigorous comparison in this evaluation of alternative coatings. The 0.004 gram loss was extrapolated over 10,000 cycles to give an estimated wear loss of approximately 0.04 gram (equivalent to a Taber Wear Index value of 4.0).

As can be seen from Table 7, none of the electrolytically deposited (electroplated) cobalt coatings (with or without particles) or the electroless deposited coatings without particles provided adequate wear resistance. However, all of the electroless deposited coatings with diamond particles, regardless of their diameter, exhibited wear properties superior to those of EHC.

SUMMARY OF FINDINGS

The performance data that were obtained for the various coatings supplied by the three companies that participated in this study are summarized in Table 8 in the context of whether or not the requirements criteria - based on the performance of electrolytic hard chromium coatings (see Table 3) - were met.

As mentioned earlier, note that the coatings applied by the three companies have not been optimized; consequently, the performance data obtained may not represent the best that may be obtained. However, these data represent the only information upon which to base the conclusions at the present time.

The coatings that were studied represented a mixture of matrices with and without occluded micro- and nano-size particles. The types of matrices studied were as follows:

- Amorphous and pseudo-amorphous matrix - electroless nickel-phosphorous, electroless nickel-cobalt-phosphorous, electroless cobalt-phosphorous, electroless cobalt-boron
- Nano-crystalline matrix - cobalt
- Micro- and macro- polycrystalline matrix - cobalt.

Table 8. Summary of Coating Performance Data

Coating Type	Heat Treated	Thickness	Adhesion	Hardness	Wear Resist.
EHC	No	**Pass**	**Pass**	**Pass**	**Pass**
ENi-P (no diamond)	Yes	**Pass**	**Pass**	**Pass**	Fail
ENi-P + 150 nm diamond	Yes	Marginal	**Pass**	**Pass**	**Pass**
ENi-P + 1,000 nm diamond	Yes	Marginal	**Pass**	**Pass**	**Pass**
ENi-P + 2,000 nm diamond	Yes	**Pass**	**Pass**	**Pass**	**Pass**
ENi-P + 150 + 2,000 nm diamond	Yes	Marginal	**Pass**	**Pass**	**Pass**
Poly-Co	No	Fail	**Pass**	Fail	Fail
Nano-Co	No	Marginal	**Pass**	Fail	Fail
Nano-Co + 2,000 nm WC (Sample Set #1) †	No	**Pass**	**Pass**	Fail	Fail
Nano-Co + 2,000 nm WC (Sample Set #2) †	No	**Pass**	**Pass**	Fail	Fail
ECo-P	Yes	Fail	**Pass**	**Pass**	Fail
ECo-P + 1,000 nm diamond	Yes	Fail	**Pass**	**Pass**	**Pass**
ECo-B	Yes	Marginal	Fail	Marginal	Fail
ECo-B + 1,000 nm diamond	Yes	Fail	Fail	Marginal	**Pass**
ENi-Co-P	Yes	Marginal	**Pass**	**Pass**	Fail
ENi-Co-P + 1,000 nm diamond	Yes	Marginal	**Pass**	**Pass**	**Pass**

† The first set of samples contained about 10% WC, the second set about 30% WC by volume.

Any EHC alternative used in aerospace applications must be able to: be deposited to the required thickness (typically 1-20 mil, depending on the application); adhere well; have high hardness; good corrosion resistance; good wear and abrasion resistance; and not cause a fatigue debit in the substrate material because of phenomena such as hydrogen embrittlement or hydrogen re-embrittlement. In the concept evaluation phase described here, some relatively low cost, preliminary screening tests were performed to identify candidates for further study. The results are summarized below.

Thickness [Table 4]

Based on the ability to deposit thick coatings, the electrodeposited coatings certainly have potential, but the electroless coatings, in general, are hampered either by a slow deposition rate or an inability to provide the required thickness. Nevertheless, the ENi-P coatings with diamond particles warrant further study to optimize the deposition parameters to obtain thicker coatings, as do some of the ENi-Co-P coatings. With the large WC particles, because of their mass it was difficult to keep them in suspension. As a result, there was some difficulty in obtaining a uniform concentration and distribution within the composite coatings. Further optimization efforts are required with this type of coating, and particles with smaller diameters might help to alleviate this problem.

Adhesion [Table 5]

Adhesion does not appear to be a limiting factor with any of the candidate coatings studied, with the exception of the ECo-B coatings. However, the company that applied the coatings experienced some problems with panel preparation and coating application and had to strip and recoat the panels. They felt that this could have contributed to the poor results. In addition, this type of coating may require the use of suitable bath additives to control internal stress. However, this type of coating did not meet all of the other property requirements, so further development work does not appear to be justified.

Hardness [Table 6]

In general, the nickel-based coatings had no problem in exhibiting the required hardness. In contrast, the Nano-Co and ECo-B-based coatings were much softer, and the lattice strain that was introduced by the occluded particles did not have sufficient effect on improving the hardness of the matrix materials. Company A indicated that heat treating the Nano-Co-based coatings would not significantly improve hardness and even could have a detrimental effect. Contrary to expectations, with the ENi-P coatings increasing the size of the occluded diamond particles increased the hardness values obtained; however, the volume percentage of the occluded particles was less for the nano-sized particles (~23%) compared with the micron-size particles (~35-40%). Therefore, lattice strain may have contributed to the observed results. Decreasing the grain size of the cobalt matrix did have the desired effect in making the coatings slightly harder (the Hall-Petch effect).

Wear Resistance [Table 7]

Generally, the nickel-based coatings exhibited a satisfactory wear resistance. The small differences observed in wear resistance may be attributed to non-uniformity of particle dispersion or the different percentages of occluded particles in the matrices. As expected, the softer, cobalt-based coatings failed this test unless they contained occluded 1,000 nm diamond particles.

CONCLUSIONS

The electroless nickel coatings with occluded diamond particles warrant further development and investigation. These coatings have the potential to meet the four criteria used in this proof-of-concept study and, as a group, they are the best understood in terms of commercial maturity. The electroless nickel-cobalt coatings did not perform as well in this study, suggesting that there was no benefit in substituting cobalt for some of the nickel. However, this observation needs to be investigated further with optimized coatings.

The electroplated, polycrystalline and nano-structured cobalt-based coatings, although they adhered well, in general failed the other requirements criteria.

The electroless cobalt-boron based coatings, like the electroplated cobalt-based coatings, also failed most of the requirements criteria.

The electroless cobalt-phosphorous based coatings exhibited mixed results. Although thick coatings were not deposited, when diamond particles were occluded in the coatings they provided satisfactory adhesion, hardness, and wear resistance.

Further development work and additional testing are required before any of the candidates evaluated can be considered as being robust enough to replace electroplated hard chromium coatings.

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