AIR FORCE HARD CHROMIUM COATINGS REPLACEMENT EFFORTS

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ABSTRACT

The U.S. Air Force Research Laboratory (AFRL) has been working with Concurrent Technologies Corporation (*CTC*) to evaluate alternatives to hexavalent chromium electroplating. Initially, efforts focused on the demonstration/validation of commercially-available electrochemical alternatives for use in non-line-of-sight (NLOS) applications. A multi-phase approach was used in the initial project, through which the requirements of the Air Force Air Logistics Centers (ALCs) were identified and compared to the material properties of the available alternatives. In searching for potential alternatives, many alternatives in the development or research phases were identified and appeared to have technical as well as economic and environmental merit. One emerging technical area with great potential was that of nanocomposite plating. Because of the potential improvements in coating performance based on theory and laboratory-scale testing, the Air Force initiated a second project to characterize the potential of these coatings and obtain state-of-the-art information on the processes.

As a result, the "Non-Line-of-Sight Hard Chromium Alternatives" and the "Nanoparticle Composite Plating as an Alternative to Hard Chromium and Nickel" projects are being conducted in parallel in an effort to implement short-term and mid-term hard chromium plating alternatives. This paper summarizes the test results obtained for the short-term (NLOS) alternatives as well as the test results obtained from proof-of-concept studies conducted on nanocomposite plating.

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Introduction

Hexavalent chromium is used extensively to finish surfaces within the Department of Defense (DoD) and private industry due to its physical properties and decorative appeal. However, the environmental, health and safety (EHS) issues associated with hexavalent chromium has lead to stringent regulations regarding its use. Reductions in permissible exposure limits (PELs) and public owned treatment works (POTWs) 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 higher 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 replacements for EHC for both line-of-sight (LOS) and non-line-of-sight (NLOS) applications, respectively.

For many years, 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 will not be able to 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 to finish their NLOS components, which comprise about 20-40 % of EHC activities within the DoD.

To address the NLOS need, the AFRL and Concurrent Technologies Corporation (*CTC*) established the "Non-Line-of-Sight (NLOS) Hard Chromium Alternatives" project. The focus of this NLOS effort is to identify EHC alternatives that can be used for NLOS applications. The NLOS project has established EHC needs and requirements per Air Force Air Logistic Center (ALC) operations and identified over one hundred potential alternatives. Currently, six nickel-based processes are undergoing demonstration and evaluation. The processes under investigation are viewed as short-term solutions because they contain nickel. Pending regulations threaten the long-term use of nickel due to its hazardous nature; therefore, additional technologies are required to provide substantial material property improvements while reducing or minimizing risks to workers.

The findings of the NLOS project have identified a type of electrodeposition process, called composite plating, that has the potential to offer performance improvements and reduce EHS risks. Specifically, nano-composite plating processes seem to offer great potential as a long-term replacement for EHC. The AFRL has initiated the "Nanoparticle Composite Plating as an Alternative to Hard Chromium and Nickel" effort to pursue these processes. Under this project, *CTC* will investigate electrolytic and electroless processes that either produce nanocrystalline matrices or utilize nanocrystalline particles for inclusion in a polycrystalline or amorphous matrix. Although some of these processes being evaluated utilize a nickel matrix, the goal is to validate the potential improvements obtained with reduced coating grain and particle size. Upon successful demonstration of the improvements, Phase II studies will concentrate on identifying more environmentally benign alternative matrices.

The Air Force NLOS and nanoparticle composite plating efforts are ongoing and expected to result in the identification, validation, and implementation of EHC alternatives for near-term and long-term strategies, respectively. Discussed below are the current goals, activities, and findings to date for these efforts.

Non-Line-of-Sight Hard Chromium Alternatives

The NLOS project has been detailed in various other technical papers [1]; therefore, only a brief update of its activities and results is discussed here.

This project was initiated nearly four years ago and has resulted in the identification of ALC EHC NLOS requirements and numerous potential replacement processes. The goal of the NLOS project is to implement the most viable alternative at the ALCs in an effort to:

- Reduce worker health and safety risks by reducing, eliminating, or improving the control of hazardous materials
- Reduce or eliminate the generation of hazardous waste
- Reduce or eliminate the release of hazardous materials into the environment
- Maintain production rate and part quality while minimizing maintenance requirements
- Maintain or minimize life cycle costs as compared to current plating operations.

The NLOS effort is being completed using a four-phase approach, where Phase I has been completed and Phase II is ongoing. The six viable technologies selected for further consideration are being demonstrated and evaluated in Phase II activities. The following sections briefly describe the activities performed and results obtained during Phase I, as well as Phase II activities that have been completed, so far.

Requirements Task

CTC personnel conducted site surveys at Oklahoma City ALC (OC-ALC), Ogden ALC (OO-ALC), and Warner Robins ALC (WR-ALC) to identify NLOS chromium-plated parts, the coating requirements for those parts, and relevant processing methods for each part. Through these investigations, it was confirmed that 20-40 % of the chromium-plated parts were NLOS components, ranging in size, geometry, and substrate composition. All NLOS parts were catalogued and the processing methods and part characteristics and/or needs were defined for each component.

Most rework processes followed similar sequences, and the part met the requirements of the Federal Specification for Chromium (Electrodeposited) QQ-C-320B and the functional and production needs of the ALCs. The ALC production engineers and equipment operators identified additional functional and production needs or concerns as well as desired environmental benefits. Federal Specification QQ-C-320B is referenced by most process instructions at the ALCs; therefore, the criteria outlined in this specification were used to evaluate the alternative processes. Other requirements, identified by the NLOS team, included: (1) the ability to remove or grind the coating; (2) the reproducibility of the process; and (3) coating property data such as wear and corrosion resistance, coefficient of friction, and impact on fatigue life.

Alternatives Task

A market survey, including a literature search and discussions with vendors and researchers, was conducted to identify available alternatives to hard chromium plating. Alternative process information was obtained through discussions with the vendors, material safety data sheets, technical data sheets, and a survey requesting specific process and product data. Additional information was found in articles that focused on hard chromium alternatives, with each being reviewed for applicability to NLOS issues. Those articles that offered pertinent information were summarized and efforts to retrieve additional information from the authors were made.

After reviewing the potential alternatives, the alternative processes were separated into three categories: (1) commercially-available alternatives; (2) alternatives approaching commercialization, but requiring some development; and (3) alternatives in the research phase. Alternatives were categorized based on information obtained from the vendor/researcher of the process/coating. Information was gathered about each process/coating, the physical and mechanical properties of the coating, the environmental impacts of the process, ability of the coating to be reworked, the ability of the coating to restore dimensions, and the process limitations and/or advantages. Capital and operating cost information also was gathered when available.

Selection Task

The AFRL identified four primary requirements that each alternative process must meet to be considered for ALC use. They are as follows:

1. The alternative must be readily available and easily implemented at the ALCs
2. The alternative must adhere to steel substrates
3. The alternative cannot contain any form of chromium (e.g. trivalent chromium)
4. The alternative must be able to plate to a thickness of two mils or greater.

Any alternative that did not meet any one of these four requirements was eliminated from further consideration.
A decision tool was developed to analyze the remaining alternatives and determine the most viable alternative(s) for further investigation under this project. Decision criteria were based on input received by DoD personnel, HCAT members, members of the Propulsion Environmental Working Group (PEWG), and appropriate original equipment manufacturers (OEMs).
The NLOS Team selected seven processes for evaluation in Phase II, of which one was later eliminated due to proprietary issues. The processes selected, and ultimately demonstrated, in Phase II included two electroless nickel-phosphorous (ENP) processes, one ENP process that co-deposited boron nitride particles, one electrolytic nickel-tungsten (Ni-W) technology, one electroless nickel-silicon carbide (EN-SiC) composite, and one nickel-based, nanoparticle electrodeposition process.

In Phase II, the vendors of the selected processes were asked to process samples to thicknesses of 2 mils and 20 mils, with each group being exposed to three heat treatment scenarios. Scenario one involved no heat treatment, scenario two involved a heat treatment of 375 °F for 24 hours, and scenario three involved the vendor-recommended optimum heat treatment to achieve the desired properties. *CTC* personnel visited each vendor between February and June, 2001 to observe the process and record optimization tactics. All processed panels were returned to *CTC* for independent testing and evaluation. Screening Level One testing, which included tests for adhesion, hardness, composition, thickness, quality, stress, and profile, were completed. However, the analysis of results was not completed at the time of writing this paper. It is expected that the results will be available for public dissemination at the Aerospace/Airline Plating & Metal Finishing Forum later this year.

Nanoparticle Composite Plating as an Alternative to Hard Chromium and Nickel Coatings

As noted previously, the NLOS project resulted in the identification of a wide array of potential EHC alternatives. Because the Air Force was primarily interested in those processes that were commercially available, the NLOS task only evaluated a small number of possibilities. There were a number of technologies that exhibited long-term potential, but were not investigated because they required further development.

Nanoparticle-composite plating – a form of occlusion plating - was one long-term alternative that showed potential and opened the possibility of modifying the existing chemistries to meet the escalating environmental regulations. Nanostructures have been shown by many to exhibit interesting properties. Specifically, as the grain size of a material decreases, increases in hardness, fracture toughness, and yield strength are experienced. This effect is known as the Hall-Petch effect(2-5). Because nanostructured coatings offered the promise to improve the hardness properties of typically softer coatings, the AFRL established the "Nanoparticle Composite Plating as an Alternative to Hard Chromium and Nickel" effort to investigate the ability of nanoparticle composite plating processes to be a long-term replacement for EHC. This project was initiated less than a year ago and has already resulted in an open exchange of data concerning nanomaterials and initial proof-of-concept testing and evaluation activities.

The goal of the Nanoparticle task is to evaluate the potential of nanostructured coatings or coatings incorporating nanoparticles, as deposited by electrochemical methods, as replacements for chromium and nickel electrodeposits. The requirements information obtained from the NLOS project is being utilized as the baseline, and the approach was designed to compliment the NLOS task, ensuring no duplication of effort. The activities of the multi-phase Nanoparticle project are separated into a number of tasks. An Information Exchange and Proof-of-Concept Studies are included in Phase I, leading to a determination of the validity of this approach for developing hard chromium and nickel alternatives. Phase I is progressing and the details of each task are presented below.

Information Exchange

Thus far, an Information Exchange focusing on nanomaterials was organized and hosted in December, 2001. Experts from industry, academia, national laboratories, and the government attended the event, representing the areas of nanopowders, nanostructured coatings, and nanocomposites. The AFRL and *CTC* personnel gained important information related to the efforts being made in the nanomaterial arena through both government and industry efforts. This information is being leveraged for task activities and analysis of results, as well as planning future work.

Proof-of-Concept Studies

Initial proof-of-concept testing was completed for commercially –available, composite coatings. The AFRL and *CTC* worked with the providers of nanodeposited coatings to identify the most appropriate system (or systems) with which to conduct initial, proof-of-concept studies. Electroless nickel-phosphorus and electrodeposited cobalt coatings were selected for investigation. The ENP coating is assumed to have an amorphous structure, while the cobalt coating has a nanocrystalline structure (average grain sizes ranging from 10 to 100 nm).

Coating Compositions

After selecting these coating systems, the AFRL and *CTC* personnel worked with the developers/providers to alter the size of the co-deposited particles from the micron-range into the nano-range (that, although conventionally is considered to be ≤ 100nm, is being defined on this project as ≤ 250 nm to provide the coating developers more flexibility). The objective is to determine the impact of particle size on hardness and wear resistance. Ultra-fine diamond particles with diameters of 150 nm, 1,000 nm, and 2,000 nm were co-deposited with the nickel independently, or in one instance both 150 nm and 2,000 nm particles were co-deposited. Tungsten carbide (WC) particles, 2,000 nm in diameter, were occluded in one set of nanocrystalline cobalt coatings, while a second set was coated with pure nanocrystalline cobalt. Originally, the WC particles were to be 500 nm in diameter; however, difficulties with agglomeration precluded the vendor from using particles less than 1,000 nm in diameter. Due to schedule constraints, the vendor decided to substitute the 2,000-nm particles for the 500-nm particles rather than continue efforts to reduce submicron particle agglomeration. The coatings were deposited to a target thickness of 2 mils on 1010 steel panels and returned to *CTC* for analysis.

Deposit Testing

CTC performed thickness, adhesion, hardness, and Taber wear tests, as well as optical microscopy on all panels. Thickness tests were performed using a slightly modified version of ASTM B 487 *Standard Test Method for Measurement of Metal and Oxide Coating Thickness by Microscopical Examination of a Cross Section*. Table 1 shows the average coating thickness for all specimens.

Table 1. Nanocomposite Coating Thickness

Coating	Thickness (mils)
ENP + 150 nm diamond	1.8
ENP + 1,000 nm diamond	1.8
ENP + 2,000 nm diamond	2.0 – 2.1
ENP + 150 & 2,000 nm diamond	1.7
Cobalt	1.6
Cobalt + 2,000 nm WC	1.0 – 1.8

It can be seen that the ENP coatings, regardless of the size of the occluded particles, were slightly thicker and closer to the specified coating thickness than the cobalt coatings. It should be noted that the pure cobalt coatings were very level across the surface; however, the cobalt coatings containing the WC particles were very uneven with voids present in some instances. Such non-uniform coating thicknesses were not observed in the ENP coatings.

In terms of coating adhesion, all specimens passed the ASTM B571 *Standard Test Methods for Adhesion of Metallic Coatings* bend test.

Hardness tests were performed on cross-sections of the coatings per ASTM B578 *Standard Test Method for Microhardness of Electroplated Coatings*. At the discretion of the laboratory analyst, nanohardness tests could be performed if microhardness results appeared to be suspect; however, no issues arose with any particular coating that could not be resolved. As a result, only microhardness tests were performed. To obtain a clear indent, loads ranging from 50g to 300g were used. The results reported in Table 2 account for the different loads that were used.

Table 2. Nanocomposite Coating Hardness

Coating	Hardness (VHN)
ENP + 150 nm diamond	903
ENP + 1,000 nm diamond	1,070
ENP + 2,000 nm diamond	1,161
ENP + 150 & 2,000 nm diamond	884
Cobalt	468
Cobalt + 2,000 nm WC	500

As expected, the ENP coatings were substantially harder than the cobalt coatings, regardless of whether WC particles were present or not. It was anticipated that the smaller particles would provide harder surfaces; however, the reverse was true in the case of the ENP samples. For the cobalt specimens, the inclusion of WC particles provided only a modest increase in hardness using the microhardness test. As a benchmark, the microhardness of EHC coatings is typically in the range of 900-1,100 VHN.

Although hardness provided valuable information, wear data were crucial to the evaluation. Abrasive wear tests were performed according to ASTM D4060 *Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser*. ASTM D4060 was devised for use with organic coatings; however, industry, particularly the OEMs involved with the NLOS effort, also use this method with electrodeposited coatings. The test is conducted using a CS-10 wheel and a 1,000-g load. The coating weight loss was measured every 1,000 cycles, up to and including 5,000 cycles. The final measurement then was taken after the completion of 10,000 cycles. Table 3 lists the average weight loss for each coating type.

Table 3. Nanocomposite Coating Abrasive Wear Test Results

Coating	Weight loss (g)	Taber Wear Index
ENP + 150 nm diamond	0.0126	1.3
ENP + 1,000 nm diamond	0.0072	0.7
ENP + 2,000 nm diamond	0.0172	1.7
ENP + 150 & 2,000 nm diamond	0.0151	1.5
Cobalt	0.2381	23.8
Cobalt + 2,000 nm WC	0.2145	21.5

It is clear that the ENP coatings performed better (lower Taber Wear Index) than the cobalt coatings, with or without WC particles. Because cobalt is a relatively soft coating by nature, and Co-WC composites cannot be age-hardened like ENP deposits, the results are not surprising for an abrasive wear test. However, it should be noted that higher hardness does not necessarily lead to improved wear properties. This is exemplified by comparing the data in Tables 2 and 3. Although there is not an extremely large difference in hardness between the different varieties of ENP coatings, a difference in weight loss through wear is still obtained. The hardest of the ENP coatings, ENP + 2,000 nm diamond particles, displayed the greatest wear loss, whereas the coating of slightly lower hardness (e.g., ENP + 1,000 nm diamond particles) displayed the best abrasive wear properties. Similarly, the least hard of the coatings (ENP + 150 & 2,000 nm diamond particles) displayed abrasive wear properties comparable, albeit intermediate of the coatings produced with 150 nm and 2,000 nm particles, respectively. Although the cobalt coatings did not perform as well as the ENP coatings, it appears that the addition of the WC particles slightly enhances the wear resistance of the coating.

At the time this paper was written, *CTC* had not performed coating characterization using atomic force microscopy (AFM). It is anticipated that these data will be provided at the time of presentation. However, the provider of the cobalt coatings performed some independent testing on their coatings. Using x-ray diffraction (XRD) and analyzing line broadening, they determined that the approximate grain size for both the pure cobalt and cobalt with WC particles was 13-15 nm. Their independent analysis of hardness also showed the pure cobalt coating to be harder than that with the WC particles at 500 VHN versus 450 VHN, the opposite of what was observed in *CTC*'s laboratory. Using SEM analysis, they found that the cobalt coatings with WC contained approximately 10 % by volume WC particles. Because the vendor had obtained much higher content (up to 28 % by volume) in a previous experiment, they agreed to produce another set of samples, targeting greater incorporation of WC. Although these samples have not yet been received and tested by *CTC*, it is anticipated that the results will be available at the time the presentation is made.

The results obtained in *CTC* testing do not demonstrate improved performance with smaller particle sizes, but do show that an appropriate choice of particle size can greatly improve the performance of the coating. It should be noted that the comparison of properties for smaller grain size (i.e., nanocrystalline cobalt) to larger grain size coatings (conventional polycrystalline cobalt) has not been made through this study. The AFRL currently is considering funding additional studies on polycrystalline cobalt. Previous studies conducted by the vendor have shown increases in hardness with decreased grain size, until a minimum threshold is reached where a reverse Hall-Petch effect was observed. Hardness values up to 620 VHN were reported with grain sizes down to 8 nm versus 270 to 360 VHN for coatings with grain sizes of 1 and 10 µm, respectively(5). The team believes that reduced grain size, in conjunction with increased WC content, will provide further improvements in performance. It is also interesting to note that, analogous to the age hardening possible with ENP coatings, the hardness of Co-P alloys can be increased by age hardening to about 1,100 VHN(6).

Based on the overall outcome of Phase I efforts, the AFRL and *CTC* will determine whether Phase II efforts are justified. Phase II activities are expected to focus on selecting appropriate materials for composite coating optimization and production and performing laboratory/bench scale testing and analysis. Phase II activities may continue regardless of whether the improvements are due to grain size or particle size; i.e., studies may pursue the development of successful, alternative coatings, even if they are not considered nanomaterials.

Summary

The AFRL expects the outcomes of the NLOS and Nanoparticle efforts to greatly aid in the implementation of short-term and long-term solutions for replacing EHC operations at the ALCs. The results of these efforts are expected to meet the Air Force's internal goals of chromium elimination by implementing NLOS findings. Further, the Nanoparticle task has allowed the Air Force to be ahead of anticipated regulations that may require the elimination of nickel plating within the near future. By establishing these efforts, the AFRL has worked to maintain the Air Force's high environmental and performance standards. It also is expected that the outcomes of these efforts will be employed throughout the DoD; therefore, providing benefits to the overall defense industrial base, as well as industry in general.

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