Cadmium Coating Alternatives for High-Strength Steels - An Update

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DoD-selected cadmium coating alternatives were evaluated in accordance with the DoD-approved Joint Test Protocol (JTP) for both traditional and brush plating of high-strength steel parts. A two-phased approach was followed:

- Phase I: hydrogen embrittlement and adhesion testing - allowing best coating down-selection
- Phase II: JTP testing - resulting in alternative coating recommendations.

Three primary and three repair coatings were tested. Mid way through Phase II, the results indicate that electroplated and sputtered aluminum primary coatings show the most promise. Also, all three repair coatings are showing promise. This paper discusses the Phase II experimental results from completed tests.

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Introduction

Cadmium electroplating is widely used by the U.S. Air Force (USAF) and Department of Defense (DoD) to coat various metal substrates in weapons systems due to cadmium's exceptional performance characteristics, such as sacrificial corrosion protection, lubricity, galling prevention, and good torque-tension properties. Additionally, cadmium electroplating is a relatively simple and cost-effective process to operate and maintain. Cadmium is also used as a protective (sacrificial) metal coating under painted surfaces. Unfortunately, cadmium is easily removed during depainting operations resulting in costly disposal of large volumes of waste, and concerns with cadmium dust generation (as is the case with mechanical removal). Therefore, despite cadmium's performance characteristics, low processing cost, and versatility, the environmental, health, and safety issues associated with its use are significant, and various current and forthcoming regulations have been imposed on its use and disposal. Specifically, cadmium is known to be a carcinogen, a toxic heavy metal, and, when used in electroplating, has an associated hazard related to the cyanide chemicals in the plating bath. Due to the health concerns associated with its use, the Occupational Safety and Health Administration (OSHA) imposed a permissible exposure limit (PEL) to cadmium dust[1], leading to increased compliance costs. In response, the DoD has initiated efforts to search for alternative coatings and coating processes to cadmium plating.

Project Background

Ion vapor deposited aluminum (IVD-Al) is one suitable cadmium replacement for many applications, but it does not provide the lubricity of cadmium, nor does it always provide sufficient corrosion protection due to coating porosity. Additional post processing steps are required, such as labor-intensive glass bead peening, to further densify the coating for improved corrosion protection and adhesion to the substrate material. Furthermore, a "chromate" chemical conversion coating still must be applied to increase corrosion resistance, improve lubricity and provide a surface amenable to painting. These chromating solutions contain hexavalent chromium, a class one carcinogen. Due to the environmental, health, and safety problems and compliance costs associated with its use, alternative chromium-free pretreatments also have been investigated, but with limited success.

To date, other alternatives have been proposed to replace cadmium electroplating and IVD-Al. However, performance testing is needed to verify whether the alternative(s) can impart the required characteristics for weapons systems applications. To address this need, the U.S. Air Force Research Laboratory (AFRL) contracted Concurrent Technologies Corporation (*CTC*), in cooperation with The Boeing Company (Boeing), to develop a Joint Test Protocol (JTP). The purpose of the JTP was to design and outline a single suite of performance requirements and test methods that can be used to fully assess the fundamental capabilities of alternative cadmium plating processes in accordance with DoD-wide requirements and acceptance criteria. This JTP focused on high-strength steel

[1] The OSHA PEL established for cadmium dust is five micrograms per cubic meter of air (5 $\mu g/m^3$), calculated as an eight-hour, time-weighted, average exposure.

(HSS) applications, specifically landing gear components. To support JTP development and ensure accuracy and effectiveness, *CTC* and Boeing worked with the Joint Services (Air Force, Army, and Navy) and original equipment manufacturers (OEMs) to determine the necessary test information (i.e., common and Service-specific needs). The JTP provides a means of confirming vendor performance claims, allowing for Joint Service analyses, and outlining the requirements for coating developers to qualify new materials and processes to replace cadmium.

In addition to the JTP, the USAF and *CTC* developed the Environmental Security Technology Certification Program (ESTCP) "High Strength Steel (HSS) Cadmium Alternative Test Plan". This test plan organizes the required testing into sequential phases, and describes the logistics, roles, and responsibilities that are involved with the execution of the JTP. As outlined in this plan, Phase I test activities have commenced under the supervision of the Naval Air Systems Command (NAVAIR) for both primary and repair coatings identified as potential replacements for cadmium and IVD-Al.

Phase I testing consisted of hydrogen embrittlement (HE), re-embrittlement(HRE), and stress-corrosion cracking (SCC) analysis of the selected coatings to ensure that potential replacement processes had no detrimental effect on the steel substrates. Likewise, bend adhesion testing was performed for each process to determine whether the deposited coating was capable of adequately adhering to the substrate materials. Data generated during Phase I testing[2] was reviewed with the Joint Cadmium Alternatives Team (JCAT). The team down-selected the coatings and processes for testing and evaluation in Phase II. An electroplated aluminum coating outperformed all other primary coatings, including cadmium, in Phase I evaluations, while the tin-zinc (Sn-Zn) primary coating and an acidic zinc-nickel (Zn-Ni) coating were dropped from the study due to poor performance. Results for the repair coatings were mixed, with brush plated Sn-Zn performing the best, though there was considerable interest in the other repair coatings, and all three were continued to Phase II testing.

The information contained within this paper reflects the current status of Phase II testing of cadmium and IVD-Al replacement coatings.

Primary Coatings

Based on the results from Phase I testing, three alternative coatings were selected to undergo a suite of performance tests for further evaluation of the ability of these coatings to meet the requirements of a cadmium replacement process. The primary coatings selected were Low Hydrogen Embrittlement (LHE) Zn-Ni, electroplated aluminum, and sputtered aluminum. LHE-cadmium and IVD-Al coated panels and components were selected as baselines for comparison when evaluating the Phase II data. The tests for

[2] Beck, Erin N., "Joint Test Report for Execution of Phase I of High Strength Steel Joint Test Protocol for Validation of Alternatives to Low Hydrogen Embrittlement Cadmium for High Strength Steel Landing Gear and Component Application – of July 2003", Naval Air Warfare Center Aircraft Division Technical Report NAWCADPAX/TR-2006/164, 10 January 2007.

primary coatings under Phase II, as well as the specific testing facility used, as outlined in the JTP, are listed in Table 1.

Table 1. Phase II Testing and Facilities for Primary Coatings

Test Category	Test	Testing Facility
General Properties	Appearance	*CTC*
	Throwing power and alloy composition uniformity	*CTC*
	Strippability	NAVAIR
	Galvanic potential	Army Research Laboratory (ARL)
Adhesion	Bend adhesion	NAVAIR
	Paint adhesion	NAVAIR
Corrosion	Unscribed NSS* (bare)	ARL
	Scribed NSS* (bare)	ARL
	Galvanic corrosion resistance	ARL
	Fluid corrosion resistance	ARL
	SO_2 salt fog	NAVAIR
Lubricity	Run-on/Break-away torque	Westmoreland Mechanical Testing and Research (WMTR)
	Torque-tension	WMTR
Quality Assurance	Hydrogen embrittlement – notched bar	NAVAIR

* NSS = neutral salt spray (fog).

Repair Coatings

While identifying a primary coating capable of replacing cadmium and IVD-Al is one goal of the current project, identifying a coating capable of replacing brush plated cadmium for touch up and/or repair applications is essential for the total systems approach to the replacement of cadmium. The selected repair coatings were a brush plated Zn-Ni, a brush plated Sn-Zn, and a sprayed aluminum-ceramic. Brush plated LHE cadmium was selected as the baseline repair coating. While repair coatings are typically used to deposit a protective layer on areas where the primary coating has been damaged or compromised, Phase II testing focuses on evaluating the performance of repair coatings that have been deposited on bare substrates, in accordance with the JTP. The tests to be performed on the candidate repair coatings as well as the testing facility used are listed in Table 2.

Table 2. Phase II Testing and Facilities for Repair Coatings

Test Category	Test	Testing Facility
Reparability	Appearance	*CTC*
	Bend adhesion	ARL
	Paint adhesion	ARL
	Unscribed corrosion resistance	ARL
	Scribed corrosion resistance	ARL
Quality Assurance	Hydrogen embrittlement – notched bar	NAVAIR

Summary of Phase II Results

Several performance tests are currently in progress or pending evaluation for both primary and repair coatings. However, the following sections summarize the results obtained from tests that have been completed.

Appearance

The vendor deposited coatings were visually inspected by *CTC* personnel and evaluated for color, texture, uniformity of appearance, and presence of defects such as pitting, blisters, or contamination. Per MIL-STD-870B and FED-STD-QQ-P-416F (*Plating, Cadmium, (Electrodeposited)*, issued October 1, 1991), cadmium plating is required to be smooth, adherent, uniform in appearance, and free from defects. The same requirements were used in the evaluation of candidate replacement coatings.

In general, the appearance of all primary coatings was determined to be acceptable, and all candidate coatings, as well as baseline cadmium and IVD-Al coatings, were given a "pass" rating for appearance. Results documented from the visual examination of the primary coatings are presented in Table 3.

Table 3. Appearance of Primary Coatings

Coating	Appearance Results
LHE Cd (Baseline) - Hill AFB	Coating is continuous but not uniform, showing some edge effect; coating is smooth, adherent, and free from blisters, pits, excessive powder, and contamination
IVD-Al (Baseline) - Hill AFB	Coating is continuous, uniform, smooth, adherent, and free from blisters, pits, excessive powder, and contamination
IVD-Al (Baseline) - Commercial Vendor	Coating is continuous, uniform, smooth, adherent, and free from blisters, pits, excessive powder, and contamination
LHE Zn-Ni - Commercial Vendor	Coating is continuous but not uniform, also containing a few spots of possible contamination; otherwise, the coating is smooth, adherent, and free from pits, blisters, and excessive powder
Electroplated Al - Commercial Vendor	Coating is continuous, uniform, smooth, adherent, and free from blisters, pits, excessive powder, and contamination
Sputtered Al - Commercial Vendor	Coating is continuous, uniform, smooth, adherent, and free from blisters, pits, excessive powder, and contamination

Repair coatings also were evaluated for appearance and held to the same requirements as the primary coatings. An OEM brush plated cadmium was selected as the baseline coating for comparison. Two of the three candidate repair coatings, as well as the baseline coating, were given a pass rating. The brush plated Sn-Zn coating was given a "fail" rating, due in part to the observation of a dark brown area through the center of the panel. The observations from the appearance evaluation of the repair coatings are located in Table 4.

Table 4. Appearance of Repair Coatings

Coating	Appearance Results
Brush Plated Cd (Baseline) - OEM	Coating is continuous but not uniform, showing swirls from processing; coating is smooth, adherent, and free from blisters, pits, excessive powder, and contamination
Brush Plated Zn-Ni - OEM	Coating is not continuous or uniform; coating is adherent, but rough, with excessive powder and possible rust spots
Brush Plated Sn-Zn - OEM	Coating is continuous but not uniform, with a dark brown area through the center of the panel; the coating is smooth and adherent, but has excessive powder
Sprayed Al-Ceramic - OEM	Coating is continuous and uniform, smooth, adherent, and free from pits, blisters, excessive powder, and contamination

Strippability

Strippability testing was performed by NAVAIR personnel for the primary coatings to evaluate the ability to remove and reapply the candidate coating, simulating typical maintenance and repair operations. To accomplish this evaluation, the coatings were removed following manufacturer specifications or MIL-S-5002D (*Surface Treatments and Inorganic Coatings for Metal Surfaces of Weapons Systems*, dated March 24, 1994) so as not to damage the substrate material. After stripping, a portion of the specimens was tested for HE, while the coatings were reapplied to the remaining specimens. To evaluate the effect of the stripping process, HE and bend adhesion testing were performed on the coated specimens. To achieve a pass rating, the coating must not separate from the substrate material during bend adhesion testing. Likewise, all four HE specimens tested per coating must sustain 200 hours at 75% of the notched fracture strength (NFS), while also exhibiting a NFS within 10 ksi of the specimen manufacturer's reported value. Alternatively, if one of the four specimens fractures during testing, the remaining three must sustain 90% of the NFS for one hour.

Though testing of the sputtered aluminum coating was incomplete, the stripped and recoated LHE Zn-Ni and electroplated aluminum coatings both passed HE testing. However, the LHE Zn-Ni coating failed adhesion testing, exhibiting coating failure in one to two bend cycles. The strippability results gathered to this point are presented in Table 5.

Table 5. Strippability Results

Coating	Change in Hydrogen Embrittlement	Change in Bend Adhesion
LHE Cd (Baseline) - Hill AFB	Not required	Not required
IVD-Al (Baseline) - Hill AFB	Not required	Not required
IVD-Al (Baseline) - Commercial Vendor	Not required	Not required
LHE Zn-Ni - Commercial Vendor	Pass - average of 88.5% fracture strength for 200 hours (3 of 4 specimens)	Fail - coating failure in 1-2 bend cycles
Electroplated Al - Commercial Vendor	Pass - average of 93.6% fracture strength for 200 hours (4 of 4 specimens)	Pass - no coating failure before substrate rupture (12 cycles)
Sputtered Al- Commercial Vendor	Pending	Pending

Bend Adhesion

Bend adhesion testing was performed for primary coatings deposited on three substrates: 4130 steel, 17-4 PH stainless steel, and Ti 6Al-4V alloy. The purpose of adhesion testing is to evaluate the ability of candidate coatings to adhere to various substrates, and resist peeling or flaking. To accomplish this, the coated specimen is clamped in a vice and the projecting end is bent back and forth until the substrate and/or coating ruptures. The coating is then microscopically evaluated near the ruptured edge for peeling or flaking from the substrate. To achieve a pass rating, there must be no peeling, flaking, or blistering of the coating from the substrate at the rupture edge. Cracking is acceptable as long as the coating cannot be peeled away with a sharp instrument. All three candidate coatings passed bend adhesion testing for 4130 steel and 17-4PH stainless steel alloys, with only minor cracking exhibited in some cases. However, both the LHE Zn-Ni and the electroplated aluminum showed poor adhesion to the Ti 6Al-4V substrate. In these cases, spalling and edge buckling were detected, respectively. The results from the bend adhesion tests are contained in Table 6, with representative photographs of failed specimens displayed in Figure 1.

Table 6. Bend Adhesion Results

Coating	4130 Steel Substrate	17-4 PH Stainless Steel Substrate	Ti 6Al-4V Alloy Substrate
LHE Cd (Baseline) - Hill AFB	Not required	Pass	Pass
IVD Al (Baseline) - Hill AFB	Not required	Not required	Not required
LHE Zn-Ni - Commercial Vendor	Pass - cracking of coating up to 3/8”	Pass – no cracking or defect	Fail - during 1st bend cycle; spalling beyond 3/8”
Electroplated Al - Commercial Vendor	Pass - cracking of coating up to 1/8”	Pass - no cracking or defect	Fail - edge buckling to ½”
Sputtered Al - Commercial Vendor	Pass- no cracking or defect	Pass - no cracking or defect	Pass - no cracking or defect


Zinc-Nickel on Ti 6Al-4V


Electroplated Aluminum

Figure 1. Coatings Exhibiting Failed Adhesion to the Ti 6Al-4V Substrate

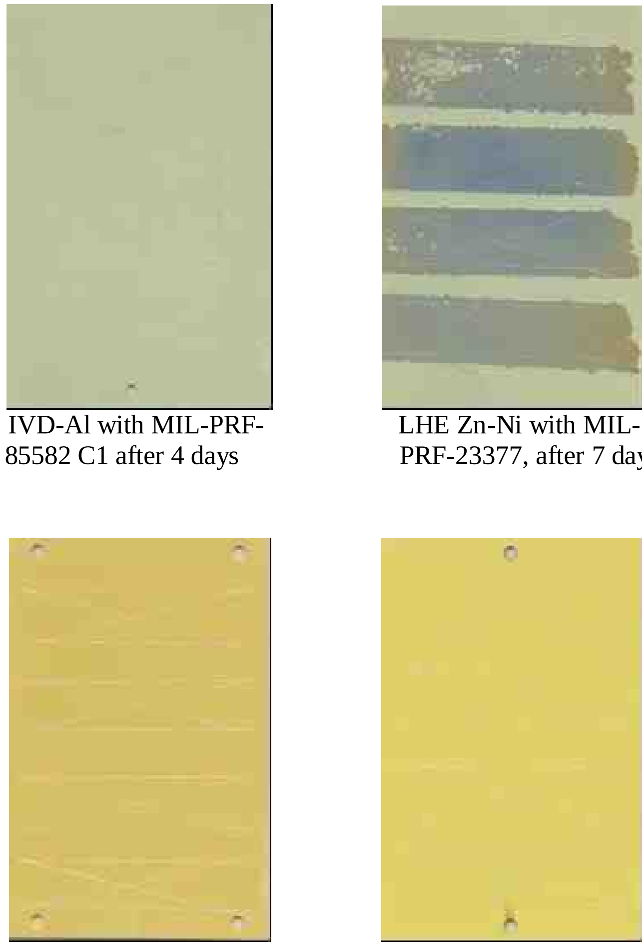
Wet Tape Paint Adhesion

Each candidate primary coating was tested for paint adhesion following ASTM D 3359 Method B (*Standard Test Methods for Measuring Adhesion by Tape Test*). This method involves applying a layer of primer to coated test specimens, allowing it to dry in air for 14 days, and then immersing the specimens in distilled water for a specified amount of time. Three primers were tested, corresponding to a MIL-PRF-85582 Type I, Class C1 waterborne epoxy primer, a MIL-PRF-85582 Type I, Class N non-chromated waterborne epoxy primer, and a MIL-PRF-23377 Type I, Class C solvent borne epoxy primer. Testing was conducted on panels immersed for 24 hours at 23°C, 96 hours at 49°C, and 168 hours at 65°C. Once removed from the distilled water, the panels were wiped dry with a cloth. Within one minute of removal, the panels were scribed with a grid pattern and an adhesive tape was applied uniformly to the scribed regions. The tape was then removed from the panels and examined for adhesion of the primer layer.

To receive a pass rating, the primary coating must achieve a primer adhesion ranking not less than 4B, as defined in ASTM D 3359, for specimens immersed for 24 hours at 23°C. Adhesion results from other immersion times and temperatures are for reference only. The candidate primary coatings received ratings of 4B or higher for all primer and immersion time/temperature combinations with two exceptions. The LHE Zn-Ni coating performed poorly when the MIL-PRF-85582 Type I, Class C1 waterborne epoxy primer was tested under the 96 hours at 49°C and 168 hours at 65°C conditions. The full set of results from paint adhesion testing is given in Table 7. Likewise, Figure 2 contains photographs of representative panels that have been tested under various conditions.

Table 7. Wet Tape Paint Adhesion Results

Primer application →	**MIL-PRF-23377, Class C2**			**MIL-PRF-85582, Class C1**			**MIL-PRF-85582, Class N**		
Test Duration (Days)→	**1**	**4**	**7**	**1**	**4**	**7**	**1**	**4**	**7**
Coating	**Test Results (average of 12 measurements)**								
IVD Al (Baseline) Hill AFB	5B	5B	5B	5B	5B	5B	5B	5B	5B
LHE Zn-Ni	5B	4B	4B	5B	1B	1B	5B	5B	5B
Electroplated Al	5B	5B	5B	5B	5B	5B	5B	5B	5B
Sputtered Al	5B	5B	5B	5B	5B	5B	5B	5B	5B



IVD-Al with MIL-PRF-85582 C1 after 4 days

LHE Zn-Ni with MIL-PRF-23377, after 7 days

Electroplated Al with MIL-PRF-23377, after 7 days

Sputtered Al with MIL-PRF-23377, after 7 days

Figure 2. Photographs of Test Panels After Paint Adhesion Testing

Locking and Breakaway Torque

The purpose of this test is to measure the maximum torque value required during the assembly of a nut on a bolt (locking torque), and the torque required to initiate removal of a threaded part (breakaway torque). This is required to determine the lubricity of the candidate primary coatings on threaded components. The candidate coatings were applied to bolt/nut fasteners NASM21250-06032 / NAS1804-6 (0.375 in) and NASM21250-10032 / NAS1804-10 (0.625 in) according to the manufacturers' instructions for coating threaded components. The nuts were then lubricated with SAE AMS 2518 (*Thread Compound, Anti-Seize, Graphite-Petrolatum*, revised July 2001) prior to testing. Next, the nuts were installed at room temperature using a torque measuring device in order to record the maximum locking torque. Once installed, the nuts were removed using a torque measuring device to determine the minimum breakaway torque. This cycle was repeated 15 times for each coated fastener, and once testing was completed, the threads were examined microscopically for damage. To achieve a pass rating, a coated 0.375 in fastener must not exceed a maximum locking torque of 80 in-lb or exhibit a minimum breakaway torque less than 9.5 in-lb. Likewise, a coated 0.625 in fastener must not exceed a maximum locking torque of 300 in-lb or exhibit a minimum breakaway torque of less than 32 in-lb. At the conclusion of testing, the threads for both nuts and bolts must not show damage such as peeling, missing segments, cracks, galling, or splits.

The results gathered from these tests show that all tested coatings pass both the locking and breakaway torque requirements for the 0.375 in fasteners. Likewise, all tested coatings meet the maximum locking torque requirements for the 0.625 in fasteners. However, all tested coatings, including the cadmium baseline, failed the minimum breakaway torque requirements for 0.625 in fasteners. All results from the locking and breakaway torque tests are summarized in Figures 3 through 6. It is important to note that testing is currently in progress for the IVD-Al baseline fasteners coated by a vendor.

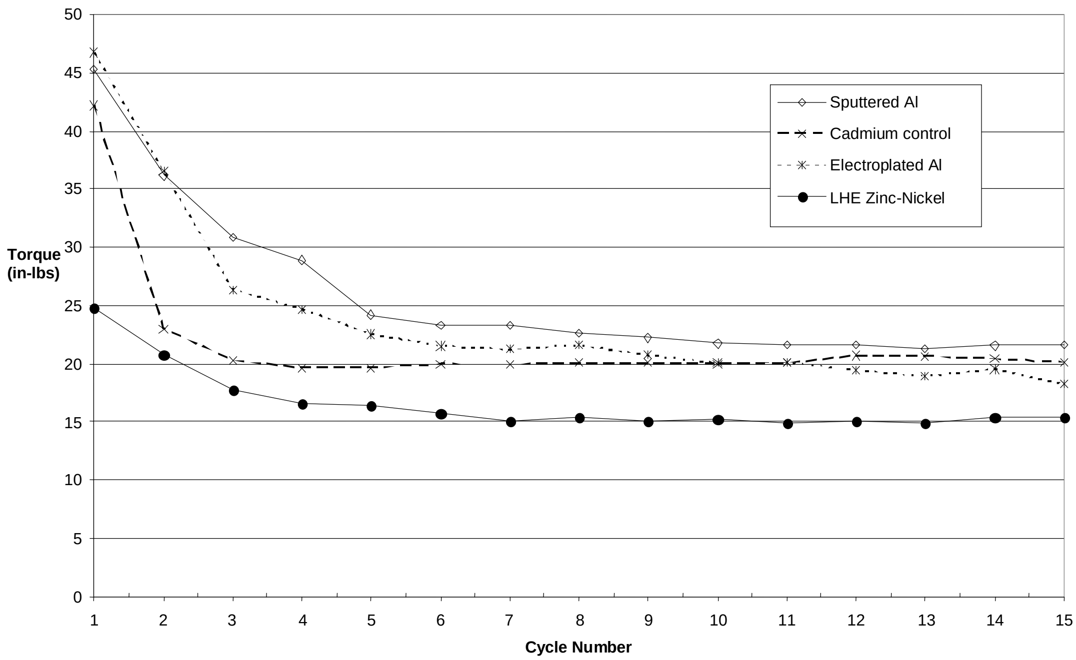


Figure 3. Maximum Locking Torque for 0.375-inch Fasteners

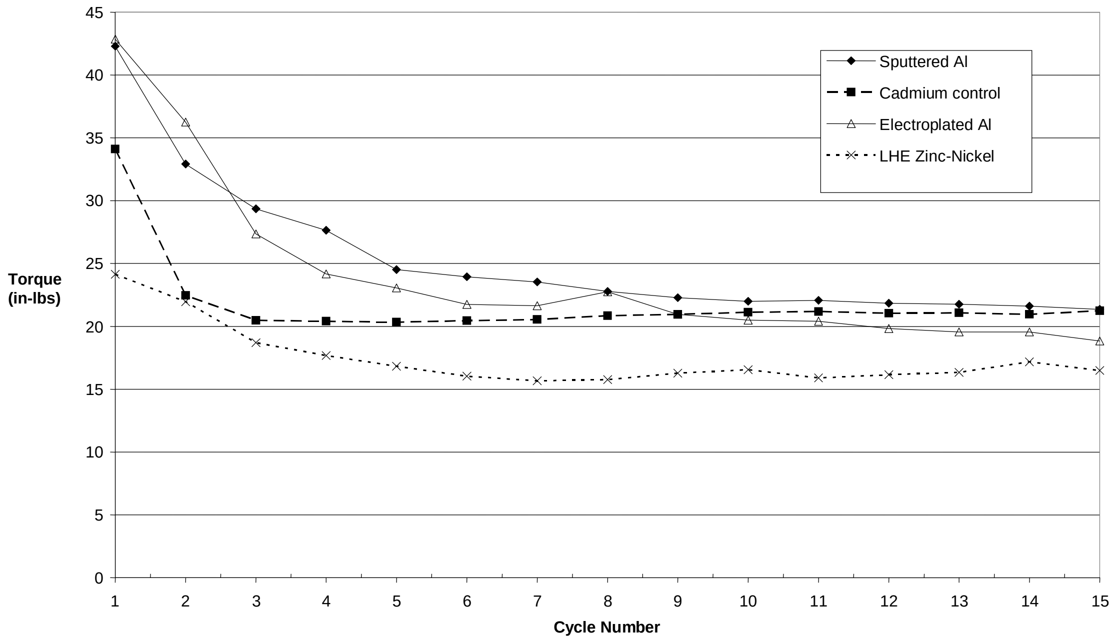


Figure 4. Breakaway Torque for 0.375- inch Fasteners

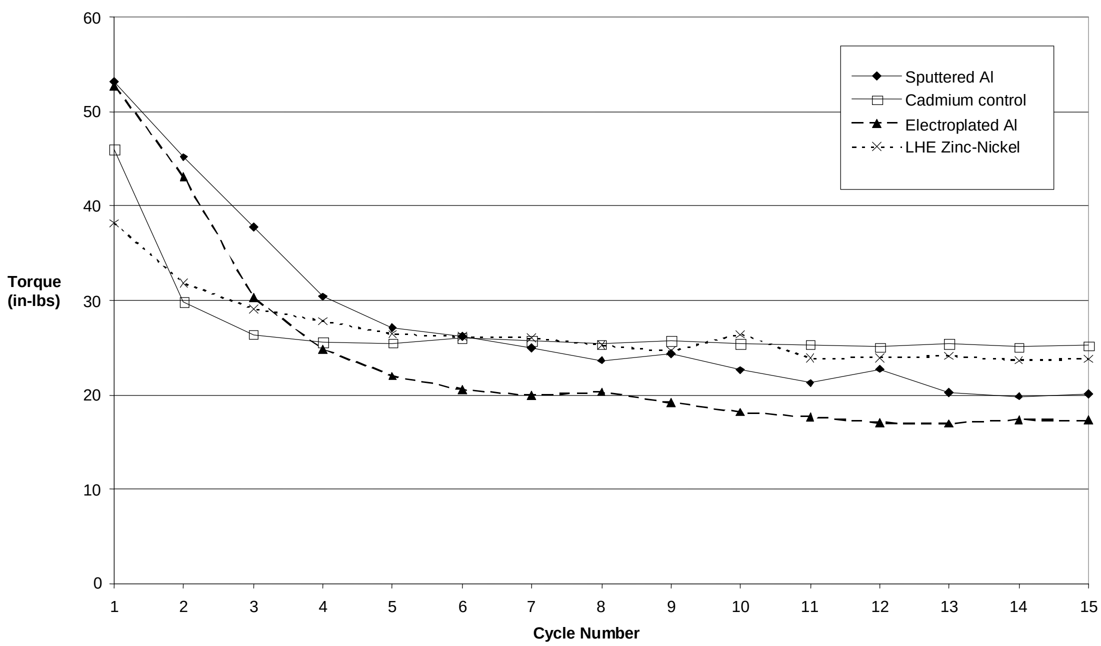


Figure 5. Maximum Locking Torque for 0.625-inch Fasteners

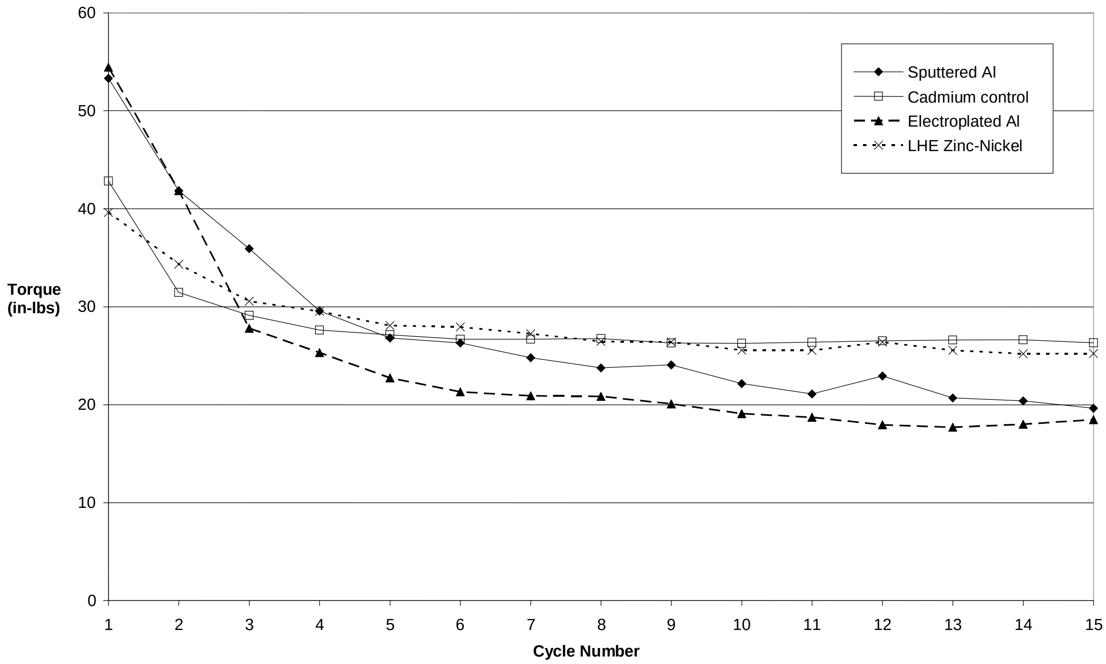


Figure 6. Breakaway Torque for 0.625-inch Fasteners

<u>Hydrogen Embrittlement – Quality Assurance</u>

HE testing was performed in accordance with ASTM F 519 (*Standard Test Method for Mechanical HE Evaluation of Plating Processes and Service Environments E (1998)*, issued May 10, 1997) for each of the primary and repair candidate coatings and baselines. This series of HE testing served to replicate tests performed during Phase I in order to provide a comparison for quality assurance purposes. The same acceptance criteria outlined in the section discussing strippability testing was applied to the quality assurance HE testing. While some coatings are currently pending testing, those that have undergone HE analysis have all received a pass rating. A summary of the quality assurance HE test results is located in Table 8.

Table 8. Hydrogen Embrittlement Testing for Quality Assurance Results

Coating	Ave. Fracture Strength (%)	Time to Failure (200 hr test)	Pass/Fail Rating
LHE Cd (Baseline) - Hill AFB	93.7%	204 hours	Pass
IVD-Al - Commercial Vendor	Pending	Pending	Pending
Sputtered Al - Commercial Vendor	97.1%	204 hours	Pass
LHE Zn-Ni - Commercial Vendor	Pending	Pending	Pending
Electroplated Al - Commercial Vendor	Pending	Pending	Pending
Brush LHE Cd - OEM	96.3%	204 hours	Pass
Brush Sn-Zn - OEM	98.1%	205 hours	Pass
Brush Zn-Ni - OEM	93.8%	203 hours	Pass
Sprayed Al-Ceramic - OEM	96.0%	204 hours	Pass

Conclusion

While significant testing remains to be completed, some candidate coatings selected for Phase II evaluation under the JTP show potential as replacements for cadmium and IVD-Al based on current results. Specifically, the electroplated aluminum and sputtered aluminum coatings have exhibited the strongest performance in tests completed up to this point. Significant concerns exist with the LHE Zn-Ni coating after failing portions of the strippability, bend adhesion, and paint adhesion tests. Currently, all three brush plated, repair coatings are showing promise, although only a limited number of tests have been completed to this point. Once the complete set of tests has been finished and results are available for all coatings, the JCAT will meet to select the most promising coating(s) for the next step towards technology insertion.