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Evaluation of Alternatives to Electrodeposited Cadmium for Threaded Fasteners Applications

--Phase IV and V Test Results

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1. Introduction

Cadmium (Cd) plating is used for corrosion inhibition on diverse items such as aircraft components, locks, and fasteners. However, Cd electroplating is coming under increasing pressure due to both environmental and worker safety issues. The use of cadmium and hexavalent chromium on vehicles and electrical equipment is restricted by the regulations of European ELV, WEEE, and RoHS. For aircraft applications, the replacement of Cd with a less or non-hazardous material is necessary in order to avoid worker exposure and environmental pollution. To comply with the regulations, several types of technology were developed for aircraft applications. They include coatings by vacuum processing, aqueous electroplating, non-aqueous electroplating, powder spraying, as well as use of alloys which do not need protection by Cd plating.

Since 2005, Alcoa Fastening Systems (AFS) and Lockheed Martin have been conducting a collaborative research program to identify the most appropriate fastener coating materials for a Cd plating replacement. Phase I, II and III studies revealed that the Elisha Zinc-Nickel (Zn-Ni) and the AlumiPlate coatings seemed to mimic the overall characteristics of fasteners coated with cadmium. Additionally, a second zinc-nickel process, Coventya Zinc-Nickel (Zn-Ni2) was introduced into the testing. However, analysis of the Phase III results using open market fasteners NAS1580A3T14 revealed an off-set drive concentricity issue, meaning the center line of off-set drive does not coincide with that of fastener. This significantly impacted mechanical performance of all Cd alternatives, especially fatigue properties. Therefore, it was decided to perform the tests again with fasteners made by AFS. NAS4452 fasteners were also manufactured to check the candidate coatings performance on a different fastener type.

Phase IV efforts consisted of the manufacture of the NAS1580 and NAS4452 fasteners by AFS. Phase V involved testing of these fasteners. Evaluations focused on more detailed characteristics of the three candidate platings, along with the reference Cd plating. Similar to the previous study, all testing was designed to simulate the typical use of threaded fasteners. Detailed, carefully controlled experiments and microscopy studies were conducted, including coating thickness, mechanical properties, stress corrosion, salt spray (fog) tests, torque-tension relationship, locking and breakaway torque measurements, and push-in and interference tests. The work presented here, which was carried out under Lockheed Martin Aeronautics Purchase Order numbers 7168673 and 7175968, summarizes our findings during the Phase IV and V stages.

2. Test Program

2.1 Fasteners

In Phase IV, NAS1580A3T8 and NAS4452S06-08 fasteners were manufactured at AFS City of Industry (COI) and Carson facilities, respectively, for testing in Phase V. The base material was a low strength 8740 alloy with an Ultimate Tensile Strength (UTS) of 160 ksi. The fasteners were mistakenly processed through the Cd plating and chromate conversion coating line at AFS. As a result, all fasteners were stripped of the Cd and chromate conversion coating, followed by a baking cycle. After random selection and split, fasteners were then sent out for the application of the Cd alternative coatings and the control Cd plating.

It is unknown whether the extra Cd plating and stripping process was detrimental to the mechanical properties of the fasteners, but all fasteners were subjected to the same process, ensuring the validity of the candidate comparison.

2.2 Zn-Ni and AlumiPlate Coatings

In this investigation, two candidate coatings were downselected from Phase I: Electrodeposited Zinc-Nickel (Zn-Ni) and Electrodeposited Aluminum (AlumiPlate). A second zinc-nickel system by Coventya (Zn-Ni2) was added during the Phase II and III testing. For Zn-Ni plating, there are basically acidic and alkaline Zn-Ni plating. Acidic Zn-Ni plating was developed and is covered by aerospace specification SAE AMS2417G [1] or Boeing BAC5637 [2]. Acidic plating, however, is not applicable to steels above 220ksi strength due to hydrogen embrittlement. Development of alkaline Zn-Ni plating using Dipsol of America IZ-260 formula is reported by Boeing [3]. In the study, 5 to 8% Ni formula, 12 to 15% high Ni content formula, and low hydrogen embrittlement formula are evaluated. The currently selected electroless Coventya Zn-Ni (PERFORMA 280-5) used a higher Ni content with trivalent chromium post treatment that used in the automotive industry and AFS St Cosme facility.

Detailed information on how the various coatings were applied to the fasteners was provided in the Phase I report. Table 1 lists properties for each of the coatings tested.

Table 1. Summary of Coating Information.

Coatings	**Specification**	**Conversion coating**	**Base coating target thickness (inch)**	**Lubrication**	**Coating approach**
Cd	QQ-P-416B Type II Class 2	Chromate	0.0003-0.00045	Cetyl alcohol lube	Barrel
Coventya Zn-Ni (Zn-Ni2)	AMS 2417 and QQ-P-416B	Cr^{3+} Passivation	0.0003-0.00045	FINIGARD 111 top coat	Barrel
Elisha Zn-Ni (Zn-Ni)	AMS 2417 Type II	Surface mineralization	0.0003-0.00045	SCS Clear Seal 400 (Sharperize 0121)	Barrel
AlumiPlate	MIL-DTL-83488D Type II, Class 3	per MIL-DTL-5541F Type I Class 1A	0.0003-0.00045	Everlube 620C per MIL-L-46010E Type I.	Rack

2.3 Test Requirements

Table 2 lists the engineering and testing requirements for evaluating alternatives to Cd coatings used for corrosion protection and lubricity on threaded NAS1580A3T8 and NAS4452S06-08 fasteners. The listings also include acceptance criteria and references used for developing the tests. Each test consisted of ten specimens for each of the selected candidate coatings, in addition to Cd plated fasteners. Except salt-spray tests, all testing was conducted at Alcoa New Product Development at AFS. The salt-spray test was conducted at Lockheed Martin.

Cross-sectional optical microscopy was performed on sample fasteners using a Nikon optical microscope (Model EPIPHOT 200, Japan). A portion of each sectioned specimen was mounted in diallyl phthalate powder (LECO Corporation, MI). The specimens then were mechanically polished to a 0.05 μm (alumina powder) surface finish using standard metallographic polishing techniques. During the evaluations, all testing machines and load cells were well calibrated.

Table 2. Critical test and performance requirements for corrosion protection and lubricity on threaded parts NAS1580A3T8 and NAS4452S06-08 fasteners. Each test consists of 10 threaded fasteners for each selected coating: Coventya Zinc-Nickel, Elisha Zinc-Nickel, and AlumiPlate, in addition to Cd plating.

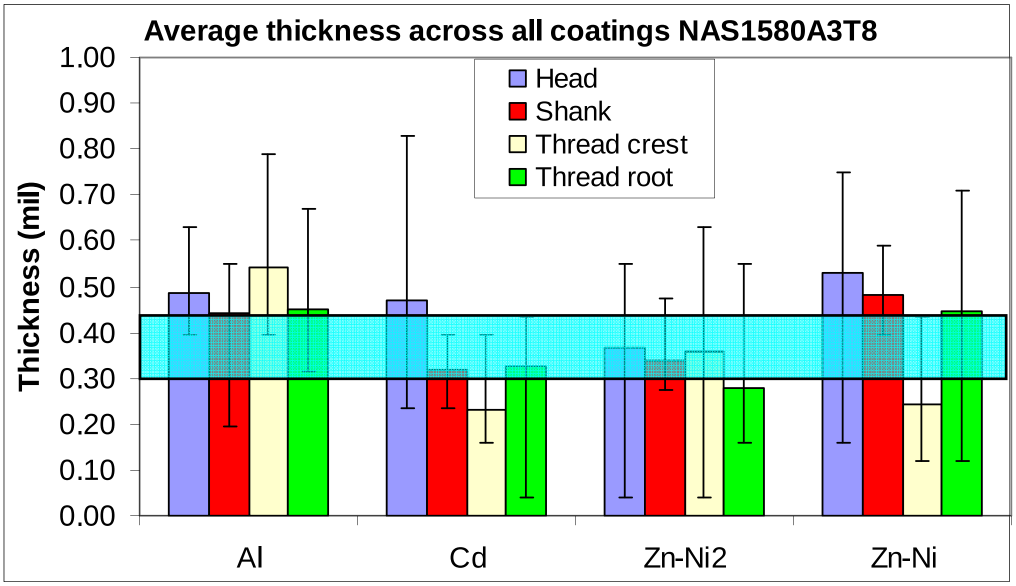
Engineering Requirement	Test Type	Reference Specification	Evaluation Criteria
General properties	Appearance	AMS-QQ-P-416, NAS4002 &, NAS4444	Coating is continuous, smooth, uniform in appearance, free from blisters, pits, nodules, and other apparent defects.
General properties	Quick Dimensional and metallurgical check	AMS-QQ-P-416, NAS4002 &, NAS4444	General requirement, including thread geometry, microstructure, untempered martensite, grain flow, stays within the process specification.
General properties	Thickness	AMS-QQ-P-416, NAS4002, NAS4444 & MIL-STD-1312-12	Thickness stays within the requirements.
General properties	Hydrogen content	AMS-QQ-P-416, NAS4002 &, NAS4444	Hydrogen content stays within the process specification.
Lubricity	Torque-Tension	NASM1312-15 NASM25027	Torque-tension for candidate material is within the range for Cd-plated fasteners. Fastener does not yield or fracture, threads do not strip.
Vibration resistance	Multi-cycle Run-on and Breakaway Torque	NASM1312-15 NASM25027	During installation, the maximum locking torque shall not exceed 18 in-lb requirements. During removal, the minimum breakaway torque shall not be less than requirements 2 in-lb. After 5 cycles of the locking torque test, nut and bolt threads shall remain in serviceable condition; when examined at high magnification, thread peel, cracks, galling, or splits are unacceptable.
Tensile property	Tensile strength	MIL-STD-1312- 8	Tensile strength values to be comparable to cadmium plated fasteners. • Minimum requirement of NAS4452S06-08: 2800 pounds • Minimum requirement of NAS1580A3T8: 3180 pounds
Double shear property	Double shear strength	MIL-STD-1312-13	Double shear strength values to be comparable to cadmium plated fasteners. • Minimum requirement of NAS4452S06-08: 108 ksi shear or 6124 pounds. • Minimum requirement of NAS1580A3T8: 95 ksi shear or 5380 pounds
Fatigue Resistance	Standard Fastener Fatigue Tests	MIL-STD-1312-11 and ASTM- E466	1. Fatigue values to be comparable to cadmium plated fasteners. Under specification required loads of 1190/119 and 860/86 pounds for NAS1580A3T8 and NAS4452S06-08 fasteners, respectively • Average life cycle shall be over 30,000 with minimum individual cycle over 15,000.

			- 60,000 cycles shall be maximum magnitude and no need to test further beyond. 2. Based on MIL-STD-1312-11, fastener fatigue properties, including the S-N curves, a plot of stress against the number of cycles to failure N, will be evaluated and compared to Cd plated bolts under the same conditions.
Resistance to Embrittlement	Stress durability test	MIL-STD-1312-105 and ASTM F 519-93 NAS4000 and 4402	No test fastener fracture within the 1000 hour exposure time. The requirement is conventional sustained load test for 48 hours at 75-80% tensile strength.
Resistance to insertion & Interference	Adhesion and push-in test	ASTM B 571-91	1. Fastener surface separation (weight loss, flaking, or peeling) for candidate coating is within the range for cadmium plated fasteners. 2. No separation (flaking, or peeling) from the basis metal or from any underplating at the edge. 3. Evaluate force required to insert fasteners into aluminum structure with interference.
Corrosion Protection	Salt Spray (Fog)	NASM1312-1 and/or ASTM B117-03	The requirement is 96 hours without red rust, but the test was carried out to a 700 hours exposure.

3. Test Results

3.1 Appearance, microstructure and coating thickness

Plating was evaluated by observing color, texture, and uniformity of appearance by the unaided eye. All coatings were applied commercially and attempts were made to obtain a uniform coating thickness among all Cd alternatives. The target thickness was 0.3-0.45 mil, excluding any lubrication. Figure 1 shows the metallurgical cross-section determined total thickness at different fastener locations for various coatings. Please note the huge difference among different lubrications. This could potential affect fatigue and fastener torque performances. Additionally, a variation in plating thickness at different sections of the fasteners was observed. It is believed to be due to the presence of a voltage potential along the fasteners' length during the electroplating operation. In addition, metallographic cross-sections were prepared from each group. The microstructure of the substrate materials from each group consisted of fine-grained tempered martensite, which is typical for quenched and tempered 8740 steel. No microstructural anomalies were observed, indicating no observable microstructural changes occurred during plating.



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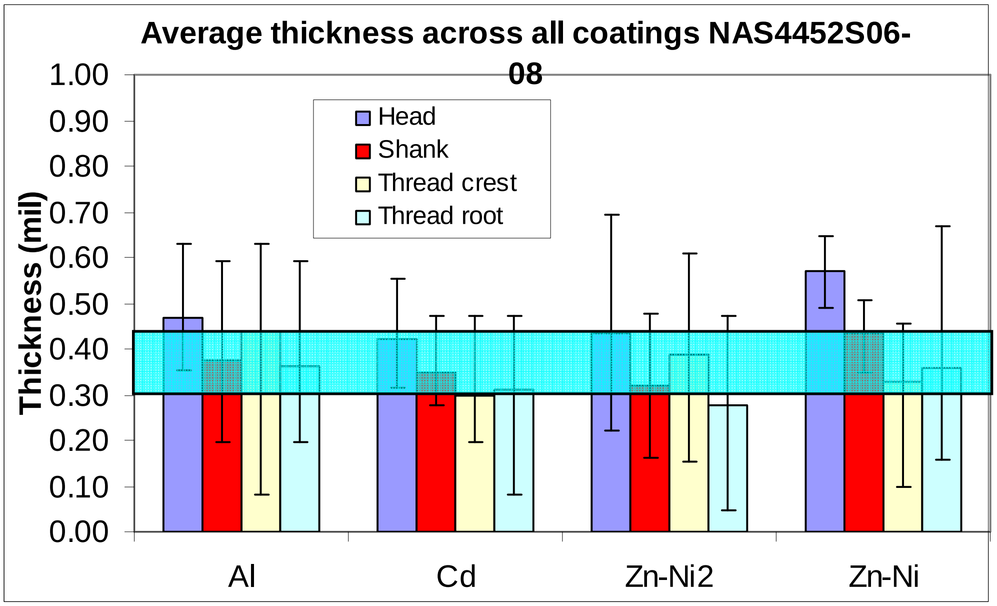


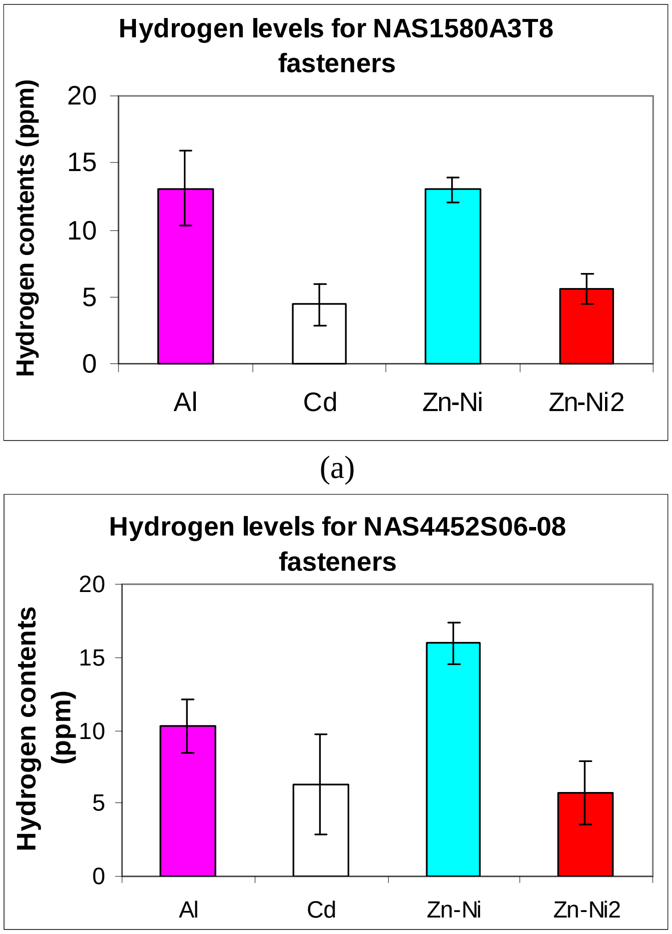
(b)

Figure 1 Variation in plating thickness at different locations of the NAS1580A3T8 (a) and NAS4452S06-08 (b) fasteners via optical microscope approach with target thickness 0.3-0.45 mil, excluding any lubrication. The blue box shows the target base coating thickness.

3.2 Hydrogen and stress durability test

Hydrogen embrittlement test was one of the most important tests for Cd replacement evaluation. Direct hydrogen content and stress durability tests were conducted. Hydrogen quantity measurements revealed zero or minimum hydrogen pick-up during plating (Figure 2). For comparison, bare fasteners after Cd stripping were measured as the control.

In addition, stress durability tests were conducted to determine the capability of externally threaded fasteners to withstand high stress load conditions. Based on the fastener torque-tension relationship, a torque method was used. Test fasteners were assembled in a test block (Figure 3). Per NASM 1312-5, fasteners were tightened with a torque wrench to a torque equivalent of 75-80% of the minimum ultimate tensile failure load specified in specification NAS4002 (for NAS1580 fasteners) and NAS4444 for NAS4452 fasteners). All fasteners assemblies were to remain in a torqued condition at room temperature for more than 1000 hours. No yielding or further elongation occurred; indicating load of 75-80% of ultimate strength is still below fastener yielding point.



(a)

(b)

Figure 2. Measured Hydrogen level after various coatings for NAS1580A3T8 (a) and NAS4452S06-08 (b) fasteners.

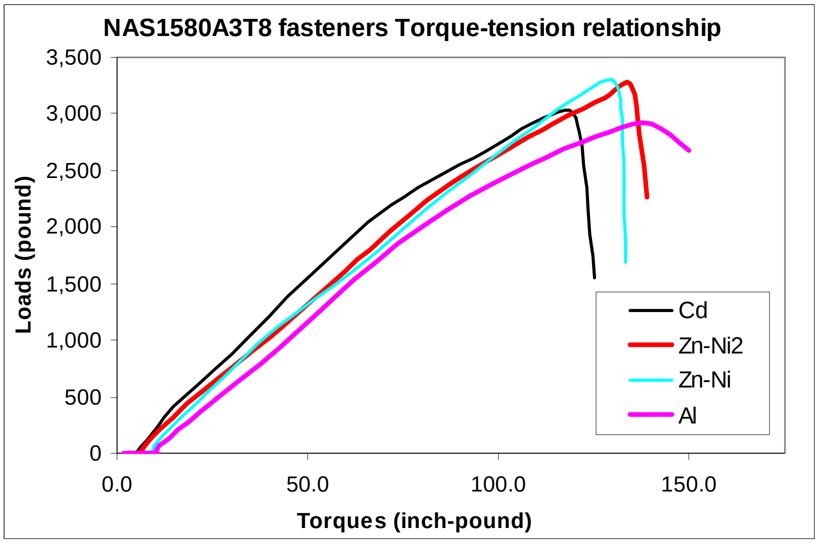
(a) (b)

Figure 3. Stress-durability test blocks for NAS1580A3T8 (a) and NAS4452S06-08 (b) fasteners.

3.3 Lubricity

3.3.1 Torque-Tension Properties

Relationship between tightening torque and tension was measured on NAS1580A3T8 and NAS4452S06-08 fasteners. An incremental tightening of Aerospace grade K-nuts (KFN541L-3F nuts with dry film lubrication) method was used to measure tension load as a function of torque. Each fastener was used one time only to simulate the assembly of factory new components. Measured torque-tension relationship is as plotted in Figure 4. The data shown are averages of 10 bolts per coating. It is desired that the candidate coatings mimic the torque-tension characteristics of bolts coated with cadmium. Please note that additional supplemental lubrications were used on all coatings. As expected, the lubricants had a significant effect on torque-tension characteristics, making the alternative coatings similar in performance to Cd plating. Due to surface lubrication, all Cd alternatives have similar torque to achieve the required tension for both for NAS1580A3T8 and NAS4452S06-08 parts.



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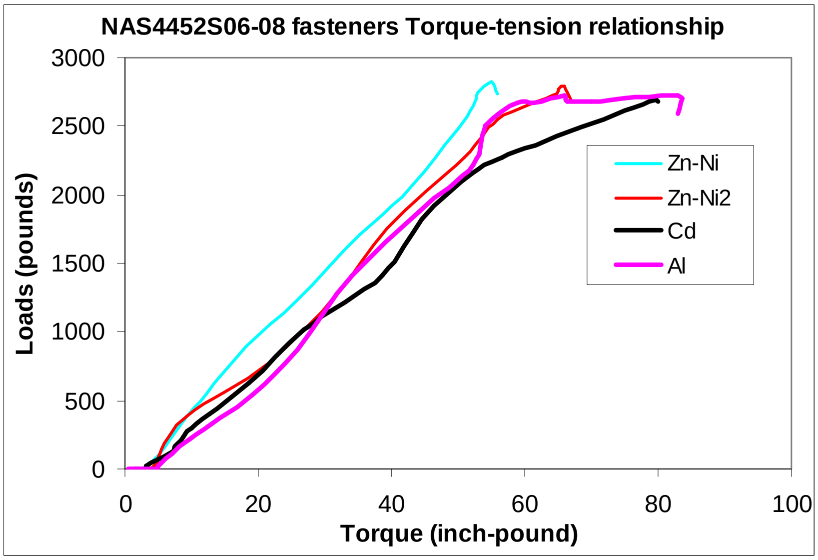


(b)

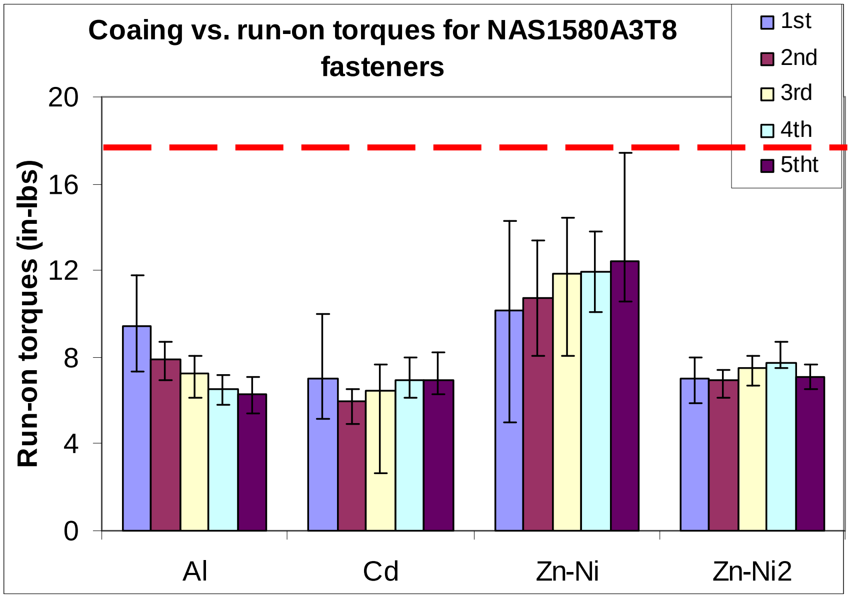
Figure 4. Relationship of torque and tension for NAS1580A3T8 (a) and NAS4452S06-08 (b) fasteners.

3.3.2 Run-on and Breakaway Torque

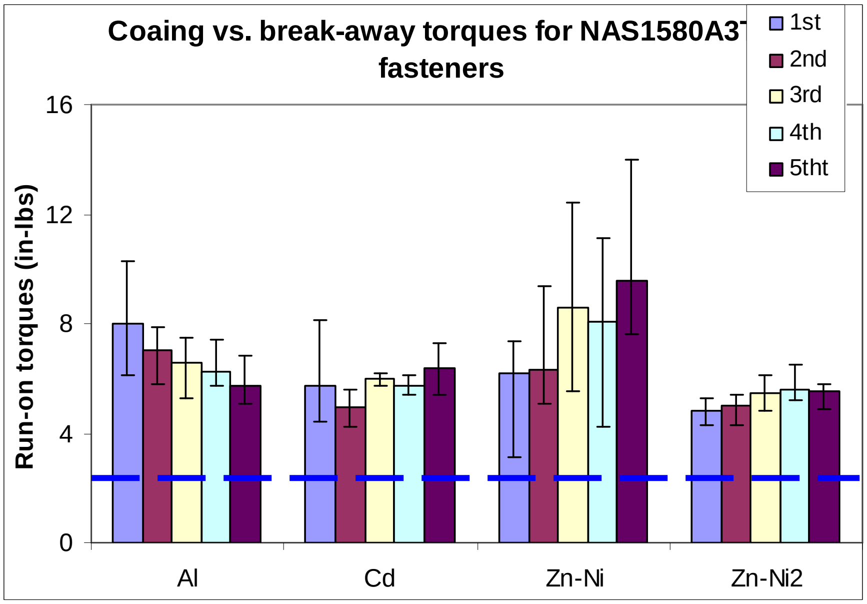
Multi-cycle run-on and break-away tests were conducted to evaluate the effects of coating and lubrication on maximum run-on and minimum break-away torque values. Unlike torque tension tests, the same bolt was used five times to measure run-on and break-away torque values using five new Aerospace grade K-nuts (KFN541L-3F nuts with dry film lubrication). These represent the performance at original manufacture for a reuse condition that might be encountered in field maintenance. An incremental tightening method was used that measured torque as a function of degrees of rotation. The results are shown in Figure 5. The data shown are averages of ten bolts per coating. It is desired that the candidate coatings have consistent and sustainable torque-tension characteristics.

All run-on torque values for both NAS1580A3T8 and NAS4452S06-08 fasteners meet the requirements of 18 inch-pounds of KFN541L-3F nuts during locking. Data for AlumiPlate showed a continuously dropping of torque values as the cycle numbers increase in all cases (Figure 5) On the other hand, Elisha Zn-Ni coating demonstrated increased values, especially for NAS1580A3T8 nut/bolt (Figure 5(a)(b)). While, Zn-Ni2 coating showed fairly stable values for both NAS1580A3T8 and NAS4452S06-08 fasteners, including variation from the cycle to cycle, and variation within each cycles. However, the break-away torque is slightly lower than specification requirement of 2.0 inch-pounds. This could be problematic, especially since subsequent cycles show a small ***decrease*** in break-away torque values for NAS4452S06-08 (Figure 5(d)).

As indicated in previous report [3-4], it is possible that Zn-Ni consistently demonstrated higher run-on and break-away torque values as the cycle number increases due to base coating galling. The higher strength metal or silica particles leftover between threads could increase the interference between nut and bolt, resulting in higher torque values. However, the AlumiPlate coating is very soft and could be compressed even after thread galling, leading to reduced run-on and break-away torque values as the cycle number increases. The data for the AlumiPlate nut/bolt samples show significant dropping after the first cycle. This may indicate that the AlumiPlate have overly thick coatings and lubricants and/or a lower inherent lubricity than the rest of the coatings.


Coaing vs. run-on torques for NAS1580A3T8 fasteners
Run-on torques (in-lbs)
0
4
8
12
16
20
Al
Cd
Zn-Ni
Zn-Ni2
1st
2nd
3rd
4th
5tht

(a)


Coaing vs. break-away torques for NAS1580A3T fasteners
Run-on torques (in-lbs)
0
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12
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Al
Cd
Zn-Ni
Zn-Ni2
1st
2nd
3rd
4th
5tht

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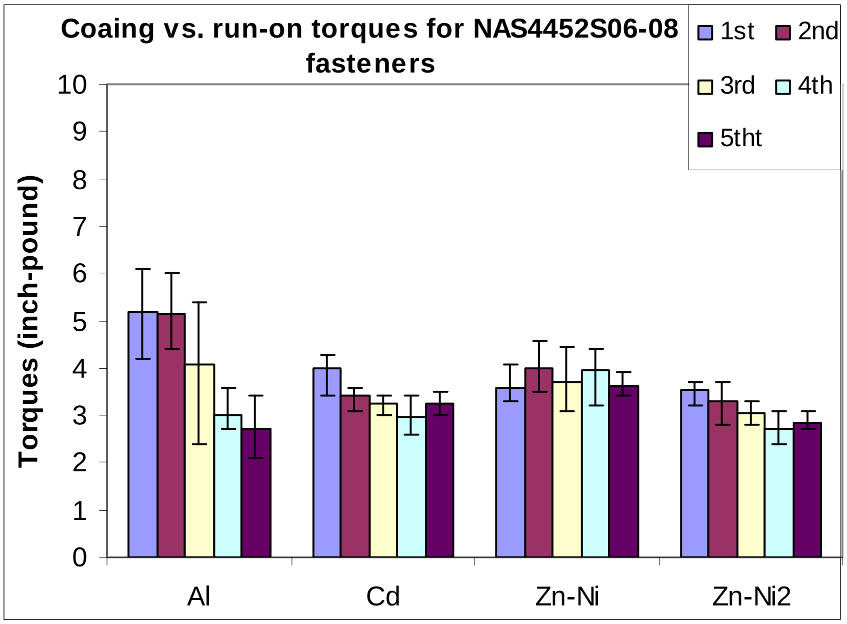

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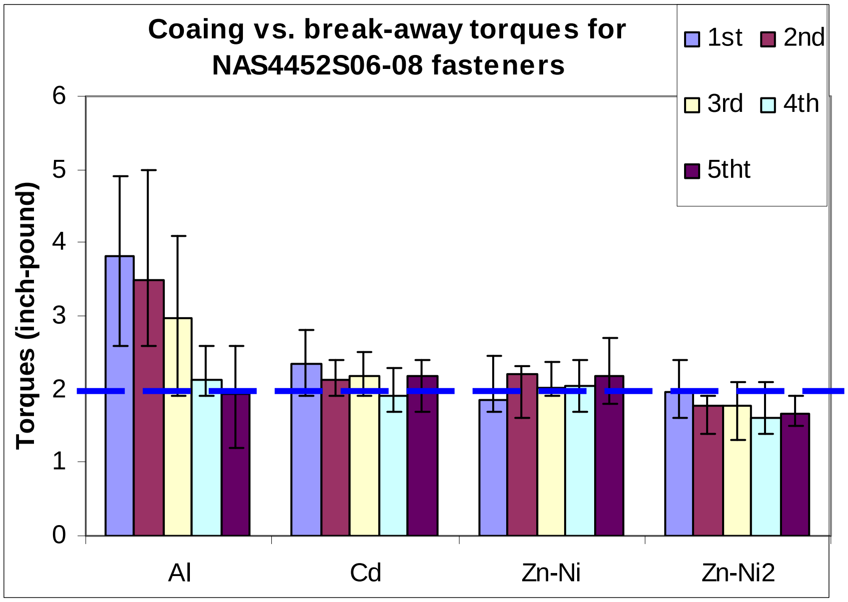


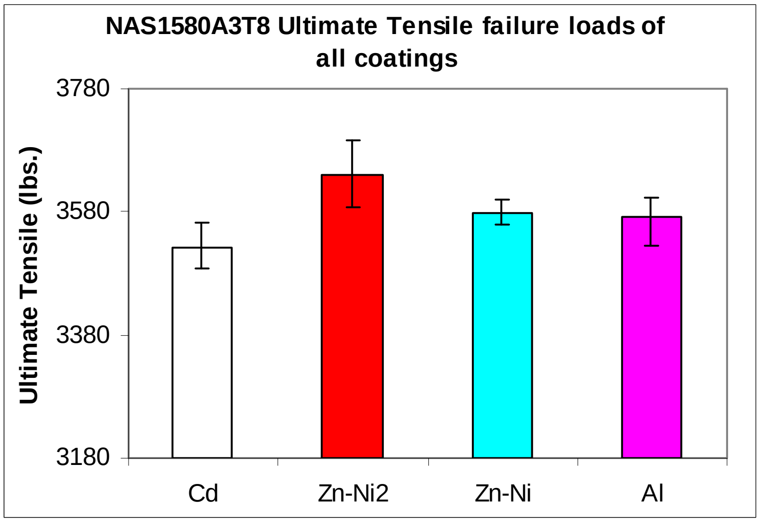
(d)

Figure 5 shows the 5-cycle maximum run-on (a) and minimum break-away values (b) for all NAS1580A3T8. The NAS4452S06-08 fasteners run-on (a) and minimum break-away was shown in graphs values (c) for (d), respectively. The red and blue lines represent maximum of 18 in-pounds run-on torque during locking and a minimum 2 in-pounds break-away torque.

3.4 Mechanical properties

3.4.1 Ultimate tensile load and double shear strength

Tensile and double shear testing in accordance with NASM 1312-8 and NASM 1312-13 were conducted using a Universal Testing machine. The failure mode of all tensile-tested parts was head tension failure at the fillet radius. The results are shown in Figure 6. The data shown are averages of ten bolts per coating. As expected, all candidates meet the tensile specification requirement of minimum 3180 and 2800 pounds for NAS1580A3T8 and NAS4452S06-08 fasteners, respectively. In addition, all coated bolts met the shear strength specification requirement minimum 95 and 108 ksi for NAS1580A3T8 and NAS4452S06-08 fasteners, respectively. As is well known, shear testing inherently involves a number of variables. The test parts' surface tribology, including friction coefficient, roughness, coating thickness, etc. could have a significant effect on the final shear strength value. Thus, it was expected to see different double shear strength values among the various coatings due to different surface tribology.



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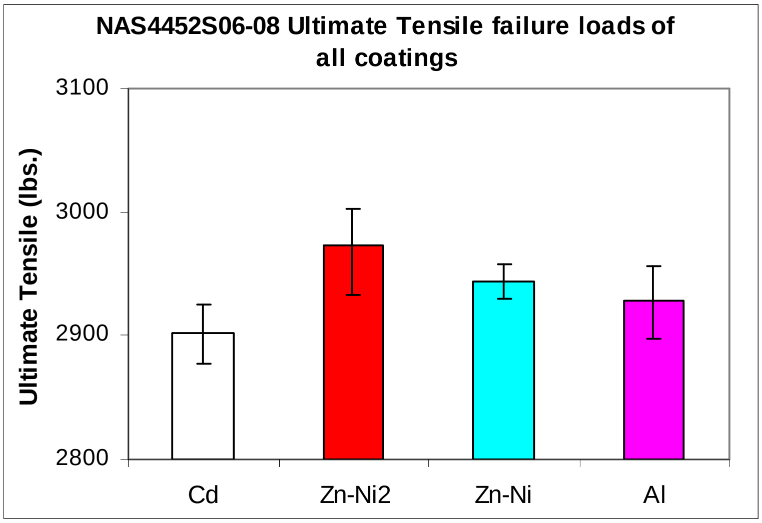

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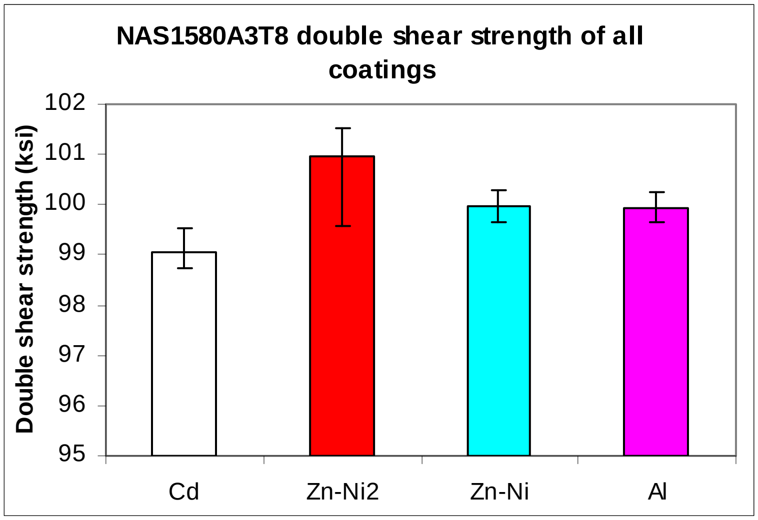

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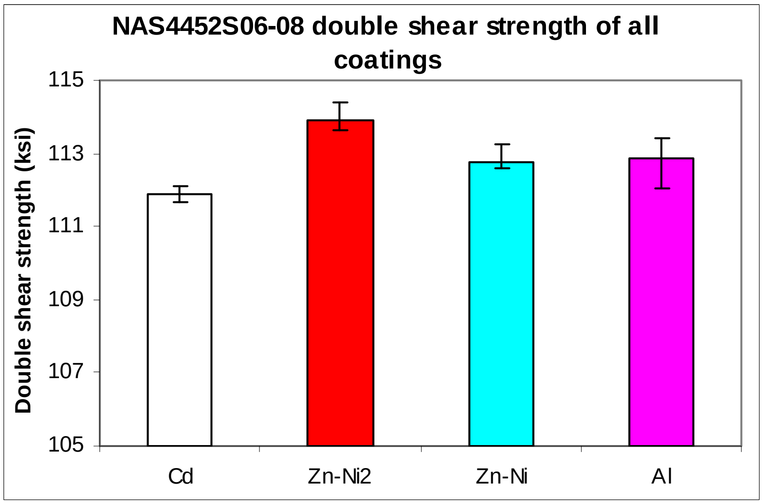


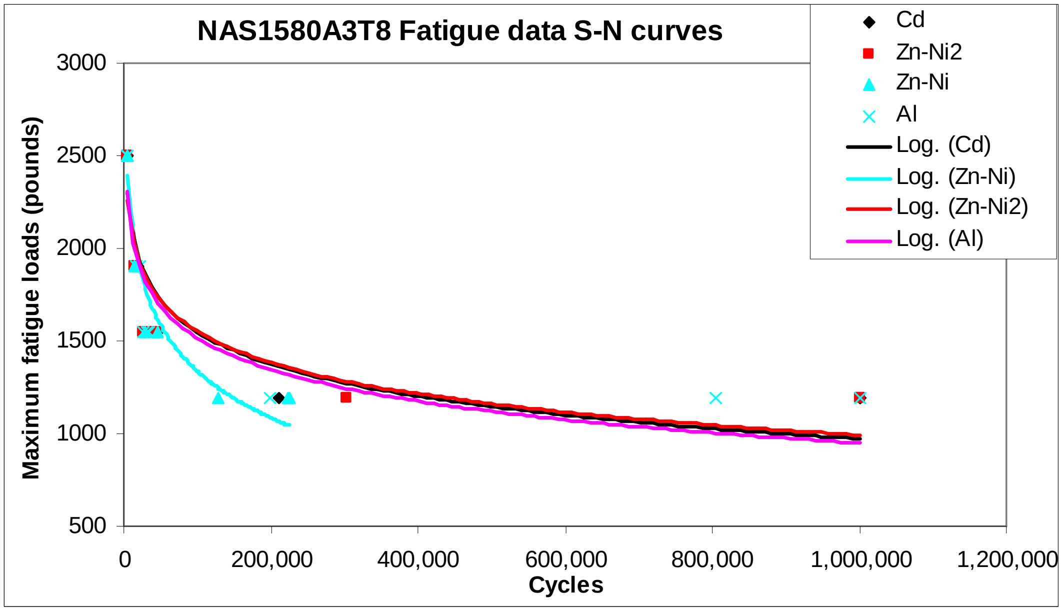
(d)

Figure 6. Effects of various coatings on tensile properties for NAS1580A3T8 (a) and NAS4452S06-08 (b), and double shear strength for NAS1580A3T8 (c) and NAS4452S06-08 (d), respectively.

3.4.2 Fatigue properties

It is well-known that the fatigue life of a component could be affected by surface quality features, such as surface hardness, plating and lubrication thickness, nature and structure of coating, oxidation resistance, surface roughness, scratches, etc. A previous report [3-4] indicated that Zn-Ni coated fasteners exhibited a lower fatigue life relative to Cd. The reason could relate to the higher surface hardness of Zn-Ni coating. The fatigue testing was accomplished on 9 kip Static Testing machine. The testing produces a stress ratio of R=0.1 at a nominal frequency of 30 Hz. In addition to specification required loads, additional tests loads that corresponded to 37.5%, 45%, 60% and 79% of the minimum ultimate tensile failure load were carried out to generate S-N curves. The 37.5% ultimate tensile failure load corresponds to the NAS4002 specified load. As expected, all coatings meet specification limits.

The fatigue test data were presented graphically in Figure 7. Typical the S-N curves were generated to determine if there was a fatigue penalty associated with any of the coatings relative to Cd. As expected, due to intrinsic nature of fatigue testing, actual fatigue testing data showed very large variation among different kinds of fasteners, or even within the same group. For NAS1580A3T8 fasteners, Elisha Zn-Ni coated fasteners exhibited a lower fatigue life relative to other coatings. However, For NAS4452S0608 fasteners, Coventya Zn-Ni2 demonstrated slightly lower fatigue life than others.



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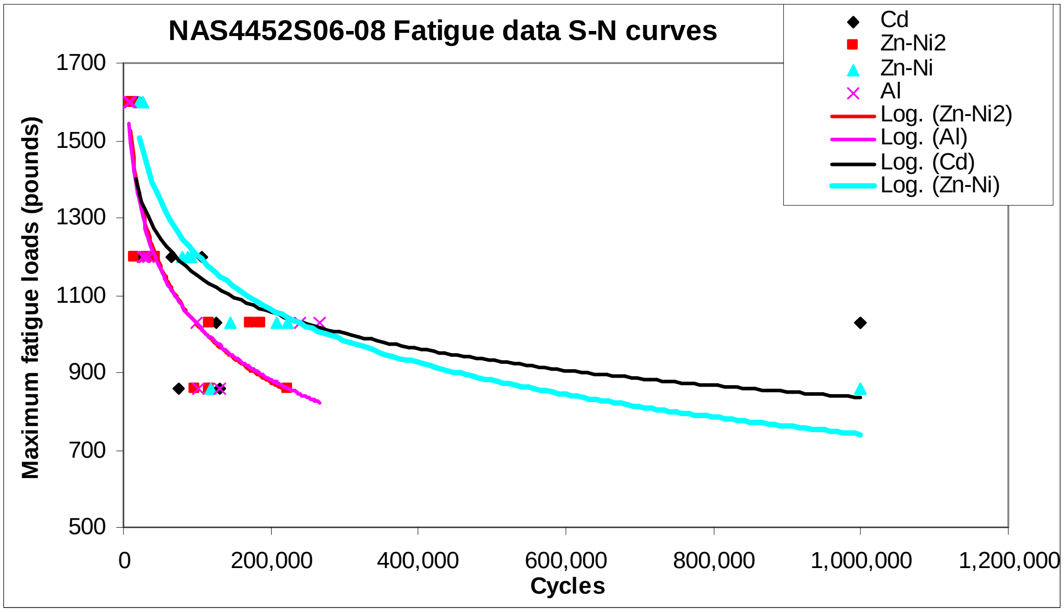
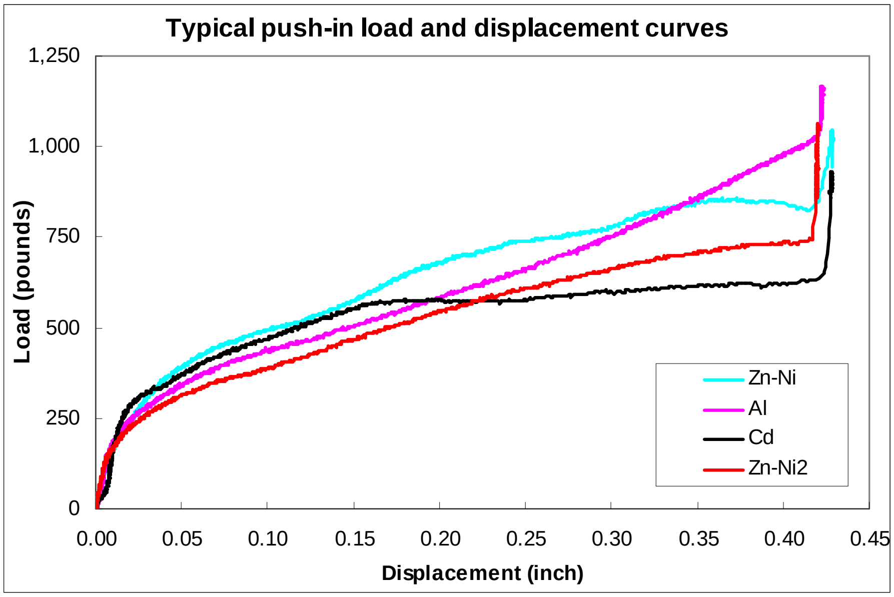


(b)

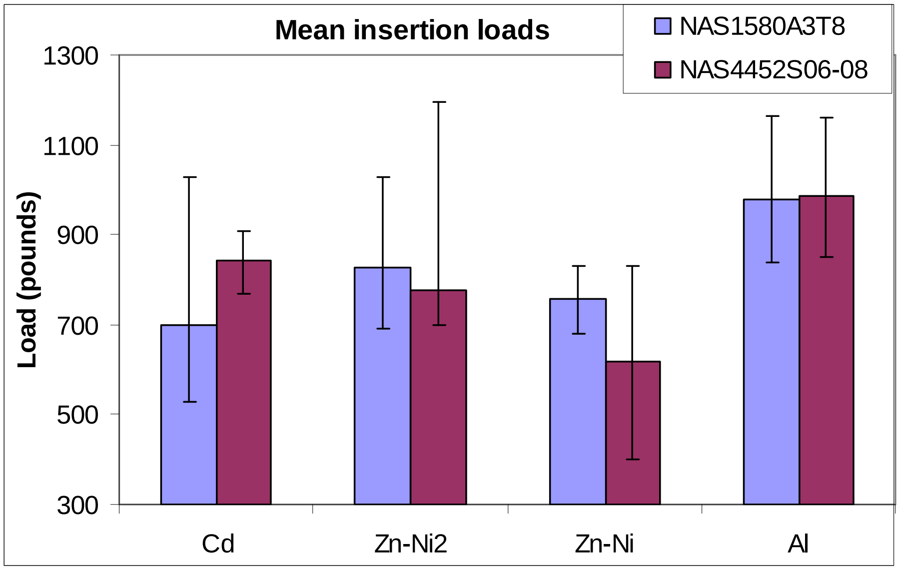
Figure 7. S-N plots for the various coated specimens

3.5 Insertion Testing

Insertion testing was conducted on 9 kip Static Testing machine. The detailed insertion testing description can be found in a previous report [3-4]. The desired maximum installation force was less than 2000 pounds. All the coatings examined resulted in average insertion load much less than the maximum load required due to surface lubrication (Figure 8). Typical load displacement curves are shown in Figure 8(b).



(a)



(b)

Figure 8. Typical push-in load and displacement curves (a) and (b) average push-in loads for both NAS1580A3T8 and NAS4452S06-08 fasteners (b).

3.6 Salt fog test corrosion resistance

Two samples of each coating system and fastener group were exposed to a continuous salt spray exposure, per ASTM B117. The total exposure period was 700 hours. Figure 9 shows the appearance of the fasteners after 700 hours of salt spray. All replicates looked essentially similar. There was a bit of red rust on the head of one of the AlumiPlate pins, but it was generating from a flawed area of the coating at the sharp corner of the head. In general, all of the coated fasteners looked very good without any evidence of a “structural” corrosion behavior, e.g., in the form of pits or cracks.

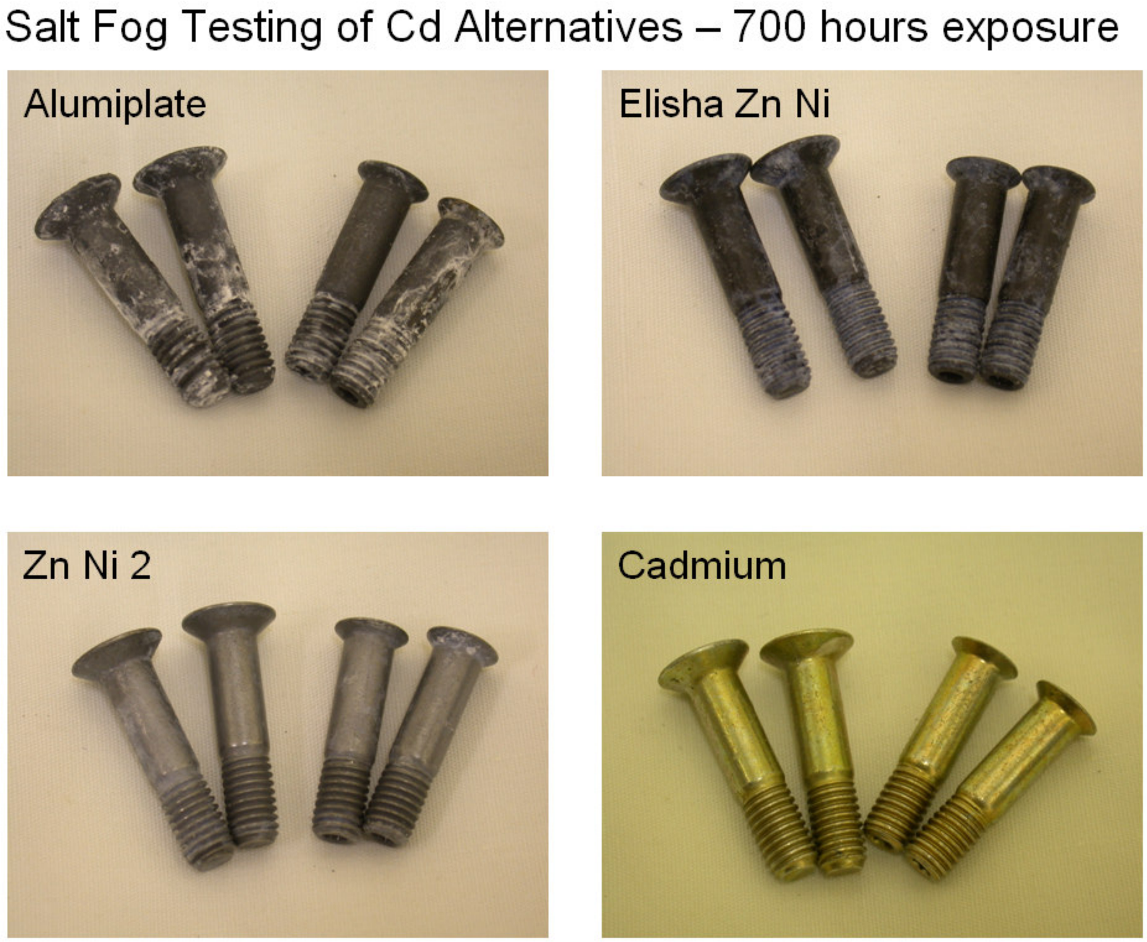


Figure 9 illustrates the appearance of the typical fasteners after 700 hours of salt spray test.

4. Discussion

The corrosion resistance of Zn-Ni plating is highly dependent on its Ni content. In general, with a Ni content around 11 to 17% Ni, the Zn-Ni plating has the best corrosion resistance. At a lower Ni content, Zn-Ni demonstrates sacrificial corrosion-type protection. However, higher Ni content could lead to surface pit corrosion. Current Coventya and Elisha Zn-Ni have similar Ni contents, resulting in decent corrosion resistance. In addition, the electrochemical property of Zn-Ni plating is also highly dependent on its Ni content and surface treatment. Thus, the position of Zn-Ni in the galvanic electrochemical potential series of metals (Table 3) is not fixed and would depend on alloy composition. This could explain Coventya and Elisha Zn-Ni showing different corrosion potentials [3].

Hardness of the Boeing Dipsol IZ-250 Zn-Ni plating is reported at 350 to 450 Hv [5]. Although no hardness measurement was conducted in the current evaluation, it is expected that a similar hardness would be found for the evaluated Zn-Ni coatings, especially Elisha due to the hard mineralization silica layer. This high hardness could affect fatigue strength of plated fasteners, especially if the base material has lower hardness. This is consistent with current and previous report [3] that Zn-Ni generally showed slightly lower fatigue life than other coatings, while still meeting the specification requirements.

Table 3. Excerpt of the galvanic electrochemical potential series of metals [6-7].

Anodic ↕ Cathodic	Magnesium
	Zinc
	Pure Aluminum
	Aluminum 5000 series
	Cadmium
	Aluminum 2000 series
	Aluminum 7000 series
	Alloy steel 8740
	Stainless steel (active)
	Nickel (active)
	Nickel (passive)
	Stainless steel (passive)
	Graphite

5. Summary

It appears that all three coating candidates offer quite similar performances as Cd alternatives. However, no one coating offers the same broad range of properties as Cd plating. Table 3 presents a summary of the pass/fail test results for the three Cd alternatives and the baseline Cd process for each test. Green and red shading indicate positive and negative results, respectively, compared to Cd plated bolts.

Table 4. Test results positive/negative summary

Test Description	**Elisha Zn-Ni**	**Coventya Zn-Ni**	**AlumiPlate**
Appearance	+	+	+
Coating thickness	+	+	+
Microstructure	+	+	+
Hydrogen level	+	+	+
Torque Tension: NAS1580	+	+	+

Torque Tension: NAS 4452	+	+	+
Multi-cycle Run-on Torque: NAS1580	+	+	+
Multi-cycle Run-on Torque: NAS 4452	+	+	+
Multi-cycle Breakaway Torque: NAS 1580	+	+	+
Multi-cycle Breakaway Torque: NAS 4452	+	–	–
Tensile strength	+	+	+
Double shear strength	+	+	+
Fatigue: NAS1580	–	+	+
Fatigue: NAS4452	+	+	–
Sustained Tensile Load	+	+	+
Salt Fog test	+	+	+

References

[1] AMS2417 SAE Aerospace Material Specification "Plating, Zinc-Nickel Alloy"
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