# **Properties of APCVD Aluminum Coatings - an Environmentally Acceptable Replacement for Electroplated Cadmium Coatings**

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A physical vapor deposition process - known as ion vapor deposition - is used by USAF Air Logistics Centers to deposit aluminum as a replacement for cadmium coatings, because of the toxicity and regulation of cadmium. However, IVD aluminum coatings do not provide equivalent corrosion protection, or lubricity when used on fasteners. An atmospheric pressure, chemical vapor deposition method is being evaluated to provide coatings with acceptable performance. The properties of APCVD aluminum coatings on high-strength steel substrates are presented and compared to those for IVD aluminum, as well as electroplated aluminum coatings. The advantages and disadvantages of the different types of coating are discussed.

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### Introduction

Cadmium (Cd) has been widely accepted as the coating of choice on highstrength steels due to its excellent corrosion resistance, adhesion, and lubricity properties. However, Cd is a carcinogen and a toxic metal that can be leached easily causing potential contamination of the groundwater supply and food chain. Proposed replacements for Cd must, therefore, not only match or surpass its current performance, production throughput, maintainability, repairability, and cost, but also guarantee elimination of the current Cd related waste streams without generating secondary hazardous waste streams.

The U.S. Air Force has a mandate to eliminate the use of Cd coatings on aircraft and ground support systems. This mandate trickles down to the original equipment manufacturers and their suppliers. And taken in the contexts of ever increasing environmental standards and regulations worldwide, which also affect commercial aircraft, there is a significant driver to find one or more satisfactory alternatives. Any alternative coating must exhibit the following properties:

- Compatibility with substrate materials and working fluids used during manufacturing, maintenance, repair and overhaul (MRO) operations
- > Adequate galvanic (sacrificial) protection and corrosion resistance
- No adverse effect on substrate resistance to hydrogen embrittlement or re-embrittlement, or other forms of environmentally assisted cracking
- Low electrical contact resistance
- > Lubricity and acceptable torque/tension values for fasteners
- > Ability to be subsequently painted.

To address the need for a replacement, several technologies for applying alternative coatings to high strength steels have been evaluated, such as the use of electroplated zinc-nickel (Zn-Ni) and tin-zinc (Sn-Zn) alloys from aqueous plating baths<sup>1, 2</sup>, electroplated aluminum (Al) from an organic plating bath<sup>3</sup>, and ion vapor deposited (IVD) Al<sup>4, 5</sup>. However, no single candidate has emerged yet as the best alternative to cadmium.

The best approach to replacing Cd coatings appears to be to use an Al coating because this metal is environmentally friendly, non-toxic, and safe to handle<sup>5</sup>. In addition, these qualities eliminate some life cycle costs, such as those pertaining to reporting, medical monitoring, personal protective equipment, waste collection, storage, and disposal, which are typically associated with the handling and processing of hazardous materials.

Currently, Al coatings are being applied to high-strength steel parts by either ion vapor deposition (IVD), or to a more limited extent by electroplating.

However, there are several shortcomings. Because of inherent porosity in the IVD coatings, corrosion resistance has to be improved through post-treatments, such as glass bead peening and applying chromium-containing chemical conversion coatings. The introduction of another toxic metal (Cr) into the process is not acceptable to the U.S. Air Force. The IVD physical vapor deposition process also is unable to coat non-line-of-sight (NLOS) components, parts, and surfaces. The typical IVD "throwing power" (or conformal coverage) allows for Al coatings to be deposited inside a cylindrical shape only to a depth equivalent to its diameter. Because NLOS components and parts comprise up to 40% of the work load at an Air Logistics Center (ALC), this line-of-sight (LOS) limitation is a problem.

The electroplating process overcomes this LOS limitation, but requires the use of a flammable, toluene-based plating bath, which is considered by many to be too hazardous to operate in a typical working environment, such as a plating shop at an ALC where MRO operations are performed. The number of facilities that can coat parts by this process, and the size of parts that can be coated are limited at this time, and outsourcing is not a preferred option for the Air Force.

Electroplated Zn-Ni and Sn-Zn alloys from commercial, aqueous plating baths have received considerable attention, and the latter alloys appear to be more acceptable overall. However, there are problems with controlling coating composition to obtain predictable and reproducible properties, and with hydrogen embrittlement in high-strength steels. The latter might be mitigated by using a "hydrogen relief bake" after deposition, as is used for electroplated Cd coatings.

Chemical vapor deposition (CVD) can offer a solution to the problems associated with the IVD process for producing Al coatings. A CVD Al process - using the thermal decomposition of a tri-isobutyl aluminum (TIBA) precursor - has been extensively studied by many researchers<sup>6-10</sup>. TIBA has been used because of its tendency to dissociate at relatively low temperatures and produce a low carbon content in the coatings. Reports indicate that "low pressure" CVD Al deposited below about 325°C contains low carbon, while at higher temperatures (above 375°C) carbon incorporation (contamination) is significant<sup>9</sup>.

The simplest CVD process is atmospheric pressure CVD (APCVD). A single or multiple reactant gases are introduced in the reaction chamber at normal atmospheric pressure. Energy is supplied by heating the substrate to the temperature required to initiate and maintain the chemical reaction. Deposition temperature, reactant flow rate, and gas composition constitute the three principal variables that determine the rate of coating deposition. The advantages of APCVD include the simplicity of the technique, and the fact that no vacuum pumps and associated vacuum monitoring apparatus are required, as is the case with PVD. This paper describes some of the work performed to evaluate the use of APCVD to produce high quality, Al coatings for high-strength steel parts and components for U.S. Air Force and other applications<sup>11</sup>. This APCVD process has been studied at the New Jersey Institute of Technology, initially for semi-conductor applications, but more recently to apply coatings to gun barrels; and developed independently by Akzo Nobel Chemicals Division<sup>12</sup>. The latter is commercializing the process for coating discrete small parts with coatings, such as Al, for clients in the automotive and other industries<sup>\*</sup>.

## **Experimental Methods**

*Coating Deposition:* The substrates used for APCVD Al coatings included AISI 4130 and 4340 steels, and AerMet  $100^{TM}$ . Coupons, cylindrical tubes, fasteners, and standard specimen configurations were used for the tests performed. Prior to deposition, the substrates were cleaned using heptane and acetone followed by acid etching, alkaline neutralization, and drying in an inert atmosphere to obtain clean, oxide-free, and textured surfaces. After loading in a bench-scale, rotary APCVD reactor (Figure 1), Al deposition was performed using pure TIBA at 275 or 300°C, or blended TIBA at 300°C. Nitrogen was used as a carrier gas. A 20 kW induction heating system was used to heat the substrates. After deposition, the Al coated parts were cooled in an inert atmosphere and rinsed to remove any excess reactant. The details of the set-up and process have been reported elsewhere [12].



Figure 1. Photograph of Akzo Nobel Chemical's Bench-scale Rotary APCVD Reactor

<sup>\*</sup> Their FUZEBOX<sup>®</sup> technology is an aluminizing process based on the thermally induced decomposition of various precursors, including industrial-grade aluminum alkyls.

*Test Methods:* The surface morphology of APCVD Al coatings was examined using field emission scanning electron microscopy (FE-SEM). The crystallographic structure of the Al coatings was determined by x-ray diffraction (XRD) with Cu Kα radiation operated at 45 kV and 40 mA.

Compositional chemistry of the coatings was investigated using X-ray photo-electron spectroscopy (XPS) with a X-ray source of monochromatic Al K $\alpha$  operating at 15 kV and 100 W over an analytical area of 400 x 400  $\mu$ m<sup>2</sup>. Survey and profile pass energies were 300 and 100 eV, respectively. Argon ion etching [at 4 nm (SiO<sub>2</sub>)/min] was performed over a rastered area of 3 x 3 mm. Nuclear reaction analysis using <sup>1</sup>H(<sup>15</sup>N,  $\alpha\gamma$ )<sup>12</sup>C resonance nuclear reaction method was used to determine hydrogen incorporation in the Al coatings. Each sample was loaded in the analysis chamber at room temperature and bombarded with ~20 nA of <sup>15</sup>N ion. The ion beam energies used for depth profiling were 7.0 MeV (0.38  $\mu$ m), 7.3 MeV (0.57  $\mu$ m), 7.6 MeV (0.76  $\mu$ m), and 7.9 MeV (0.95  $\mu$ m). The measurement at 7.0 MeV was repeated to check the reproducibility of the data.

Auger electron spectroscopy (AES) operating under a base pressure of  $<1.0 \times 10^{-9}$  torr, with a primary beam energy and current of 10 keV and 1.0 µA, respectively, originally was used to establish coating composition depth profiles. Argon ion etching was used at an etching rate of 20 nm (SiO<sub>2</sub>)/min over 2 x 2 mm area in order to create the depth profile. The samples for glow discharge, optical emission spectroscopy used later were cleaned with spectroscopically clean heptane prior to analysis using a LECO GDS750A instrument with "quantitative depth profiling". Certified analytical standards were run prior to this analysis in accordance with ISO 17025. The method used was validated with National Institute of Standards and Technology supplied standards.

Coating step coverage and throwing power were investigated. For the throwing power test, AISI 4130 steel tubes (50.8 mm length and 0.9 mm wall thickness) were used with different inner diameters (ID) of 3.0 and 6.0 mm. APCVD Al coatings were deposited on these tubes at  $300^{\circ}$ C using pure TIBA and blended TIBA precursors. After deposition, the Al coated tubes were crosssectioned lengthwise and radially, then mounted using epoxy, followed by mechanical polishing using a diamond suspension with particle size down to  $3\mu$ m. After measuring the coating thickness using field emission scanning electron microscopy, the throwing power (expressed by the ratio of inside to outside coating thickness) was calculated. The substrate used to evaluate the step (conformal) coverage of APCVD Al coatings was a hollow rivet sleeve with a step present on the inside surface.

Density of the Al coatings was determined by helium pycnometry, which uses a gas displacement technique to determine the volume of sample. The weight (Ws+c) and volume (Vs+c) of the Al-coated substrate were measured using a balance and a He pycnometer (AccuPyc 1330), respectively. After complete removal of the Al coating from the substrate using a 5 % NaOH solution, the weight (Ws) and volume (Vs) of the substrate were measured. Based on these measured values, the density of Al coating was calculated from the equation:

 $\rho c = (Ws+c-Ws)/(Vs+c-Vs).$ 

The adhesion test (pull test) to evaluate the adhesive bond strength between the Al coating layer and the steel substrate was conducted using a Sebastian Five-A instrument, which has the maximum load of 1,755 kg/cm<sup>2</sup> and an accuracy of  $\leq 1\%$  at 20 ±4°C.

Electrical resistivity was measured using a four-point probe (Veeco FPP-5000). Samples were prepared from of AISI 4130 steel coupons on top of which insulating silicon nitride layers (1 $\mu$ m thick) were deposited by plasma enhanced chemical vapor deposition (PECVD).

The anodic polarization behavior of APCVD Al coatings was determined from potentiodynamic experiments performed in 3.5 wt.% NaCl solution - with and without O<sub>2</sub> saturation - at room temperature using a Gamry Reference  $600^{\text{TM}}$ Potentiostat. Al coatings with a thickness of ~20 µm were deposited on AISI 4130 steel coupons at 300°C using pure TIBA. Al foils (99.99% purity) and bare AISI 4130 steel coupons were used as the baselines. A flat cell (Princeton Applied Research) was used with a three-electrode configuration (saturated calomel electrode, and platinum gauze reference and auxiliary electrodes). The specimen exposure area was 1 cm<sup>2</sup>. Potentiodynamic polarization was measured 1 hour after immersion, with a scan rate of

10 mV/min from -0.2 to +1.5 V versus the open circuit potential (OCP).

Corrosion resistance in service was estimated by subjecting coated coupons to the GM 9540P cyclic immersion test protocol. This is an accelerated corrosion test that provides results that more closely simulate real life conditions than results obtained from the standard ASTM B 117 salt fog exposure test. AISI 4130 steel test panels and coupons were coated with APCVD Al. The coatings on the smaller coupons ( $2.5 \times 3.5 \text{ cm}$ ) were then scribed through to the substrate, while the coatings on panels ( $2.5 \times 5.0 \text{ cm}$ ) were not. One set of each were tested as deposited, and another set was tested after receiving a commercial, trivalent chromium post-treatment (TCP). The pass criterion was set at 80 cycles for the unscribed panels and 40 cycles for the scribed panels.

The relative sliding friction of coating samples was measured using the ASTM G 99 "Pin-on-Disk" technique. Samples consisted of Cd-coated mild steel,

and APCVD Al-coated AISI 4340 steel substrates nominally 2.54 cm diameter round flats, 0.635 cm thick (initial RC hardness = 52). APCVD Al coatings were deposited at ~300°C using a blended TIBA precursor. No post-treatment was performed. The control samples were mild steel panels, with electroplated Cd per SAE AMS QQ-P-416, Class II, Type 2. The initial friction of each coating was measured, then the samples were placed in a salt fog chamber. Samples were removed from the chamber for observation and friction measurement at intervals of 3, 51, and 75 hours. After removal from the chamber, the samples were rinsed in deionized water and allowed to dry in ambient conditions for at least 2 hours before testing. Different wear tracks were used for each test. All friction measurements were conducted dry (i.e., without lubrication).

Hydrogen embrittlement (HE) testing was conducted in accordance with ASTM F 519. Testing was performed on APCVD Al-coated, notched round bars without and with baking at 190°C for 23 hours immediately after deposition. The notched round bars used in this test were Type 1a.1 made from AISI 4340 steel (UTS  $\approx$  300ksi) per specification MIL-S-5000E. The bars were quenched and tempered to a hardness of 51-53 HRC per specification AMS-H-6875A. The pass criterion for this test was 200 hours before failure.

High cycle fatigue resistance was determined using the ASTM E 466 test protocol with three stress levels and two stress ratios. Al coatings were deposited on AISI 4340 steel and AerMet 100 smooth round test bars using pure TIBA at 275 or 300°C. The coated bars were given a hydrogen relief bake at 190°C for 23 hr immediately after deposition. Bare steel and AerMet 100 and Cd-plated bars were used as controls. The pass criterion was a fatigue debit equal to or less than that exhibited by the Cd plated and heat treated control.

#### **Results and Discussion**

Figure 2 illustrates a typical surface morphology. The Al coatings are continuous, with a roughness of about 900 nm (rms) compared to about 150 nm (rms) for the surface of the steel substrate. This small amount of roughening may be beneficial if the coating subsequently is to be painted. The Al coatings - regardless of deposition conditions - were found to be polycrystalline, with a face centered cubic structure and a (111) preferred orientation, similar to the Al powder reference (Figure 3).

The chemical composition of the coatings evaluated by AES and XPS revealed that, regardless of deposition temperature, the Al coatings exhibited a similar composition (Figure 4).



Figure 2. Typical FE-SEM Image Showing the Surface Morphology of an APCVD Aluminum Coating on a Steel Substrate



Figure 3. X-ray Diffraction Patterns of Coatings Deposited at 275 and 300°C Compared to an Aluminum Powder Reference Material



Figure 4. AES Depth Profiles of APCVD Aluminum Coatings Deposited Under Different Conditions

The carbon present in the Al coatings appears to exist mostly in elemental form near the surface (<25 nm). The carbon impurity concentration in the blended TIBA Al coating was found to be lower than that in the pure TIBA coatings.

As expected, the AES analysis of the Al coatings deposited using the pure TIBA precursor identified an oxide film naturally formed on and near the surface (less than about 50 nm). However, the blended TIBA precursor produced coatings with an oxygen concentration not dropping to a relatively low level until a depth of ~350 nm from the surface. A higher level of oxygen was anticipated because of the chemical composition of the proprietary precursor blend used; however, it is worthwhile to note that because of the rough surface of the Al coatings, Ar etching used for depth profiling was not able to remove the coatings uniformly, layer by layer. For this reason, it could be implied that the some or all of the oxygen detected in the "deep" region also was attributable to aluminum oxide that was present on the lower surfaces of the facets of individual grains, shown in Figure 2.

Additional experiments conducted later with APCVD Al coatings about 25.4 mm thick using glow discharge, optical emission spectrometry (GD-OES) corroborated these general findings, as shown in Figure 5 (but note the difference in scale for the carbon and nitrogen concentrations).



Figure 5. GD-OES Depth Profiles of APCVD Aluminum Coatings Deposited Under Different Conditions

Figure 6 shows the concentrations of hydrogen incorporated in the APCVD Al coatings versus the coating depth on AISI 4130 steel. These results suggest that that there is an unstable H-containing compound in the Al coatings deposited using pure TIBA. And as the temperature is raised, more hydrogen is released. The blended TIBA precursor appears to give a lower concentration at the surface, but the concentration in the bulk (<0.5 - 0.6 at.% at >1  $\mu$ m) seems independent of the precursor or deposition conditions. Further experimentation is needed to explore this hypothesis.



Figure 6. Depth Profile of Hydrogen in Aluminum Coatings Deposited at 275 and 300°C

Figure 7 shows the dimensions used to evaluate the conformal coverage of the coatings on the outside and inside surfaces of a hollow steel rivet, along with a FE-SEM image of a cross-section showing the "steps" present on the inside surface. This figure also includes the formula for calculating the step coverage ratio "r" from the average thickness measurements. Note that the step height is only 0.5 mm with relatively sharp corners.



Figure 7. Diagram Showing Dimension of Cross-sectioned Hollow Rivet Used for Step Coverage Measurement and SEM images of Aluminum Coating

The step coverage ratio of the deposited Al coating was found to be 0.96, indicating that the APCVD Al process can provide excellent conformal coverage. In addition to the step coverage, the uniformity of the outside and inside coating thickness was examined as a function of length. The average thicknesses inside and outside were  $15.10 \pm 1.44$  and  $15.29 \pm 1.90 \mu m$ , respectively, and hence the ratio was 0.99. Both results are excellent when compared with what might be obtained with an electroplated Cd coating on the same rivet.

APCVD Al coatings were deposited at 300°C using a pure TIBA and a blended TIBA precursor on small AISI 4130 steel tubes with inner diameters of 3.0 mm and 6.0 mm. The throwing power measured for coatings on 6.0 mm ID tubes was  $0.93 \pm 0.07$  for blended TIBA and  $1.00 \pm 0.13$  for pure TIBA. There was no significant difference in throwing power when using pure or blended TIBA precursors. However, in the case of tubes with 3.0 mm ID, the throwing power values were lower (i.e.,  $0.73 \pm 0.09$  for blended TIBA,  $0.56 \pm 0.19$  for pure TIBA) probably due to the greater difficulty in maintaining adequate mass transfer inside the smaller diameter tubes during deposition. However, in both tubes, the Al coatings deposited using the blended precursor show less variation in throwing power along the tube length than those using pure TIBA (Figure 8).



Figure 8. Ratio of Inside  $(d_1)$  to Outside  $(d_2)$  Coating Thickness on AISI 4130 Tubes as a Function of Tube Length

The density measurements yielded an average value of  $2.60 \pm 0.04 \text{ g/cm}^2$ , which was similar to the earlier value calculated from weight and volume measurements (~2.69 g/cm<sup>3</sup>). Both density values are comparable to that reported for bulk Al (2.70 g/cm<sup>3</sup>).

The electrical resistivity of the APCVD Al coatings was found to be  $3.5 \pm 0.1 \mu$ ohm-cm, which is close to that of bulk Al (2.7  $\mu$ ohm-cm). The difference might be accounted for by the small amount of surface contamination described above. However, the result indicates that the Al coatings exhibit satisfactory electrical conductivity for the applications under consideration.

The adhesive strength of the Al coatings produced on AISI 4130 steel coupons, using pure and blended TIBA precursors, was found to be  $703 \pm 85$  and  $684 \pm 30 \text{ kg/cm}^2$ , respectively. Failure occurred in the adhesive, and there was little difference between the strength of the two types of coatings tested.

The polarization curves obtained for the Al coatings, Al foil, and AISI 4130 steel coupons are shown in Figure 9. The curves are similar in shape (showing an active-passive transition) but displaced because of the differences in the corrosion potential,  $E_{corr}$ . The APCVD Al and Al foil curves overlap, but the former exhibits a lower "active" corrosion current density (lower propensity for pitting corrosion) and passivates more easily than the Al foil. The latter property could be advantageous in service because the APCVD Al would be leached more slowly, providing protection for the steel substrate for a longer period of time. In summary, the APCVD Al provides sacrificial (galvanic or anodic) protection to the steel. The APCVD Al coating was -200 mV to -300mV more anodic than the steel substrate, depending on whether the measurements were made in open air or the salt solution was saturated with O<sub>2</sub> - a much more corrosive environment.



Figure 9. Anodic Polarization Curves of APCVD Al Coated Steel, Bare AISI 4130 Steel, and Aluminum Foil after Immersion in Salt Solution

Some results from the cyclic immersion corrosion test are shown in Figure 10. Panels and coupons were removed after 2, 10, 20, 30, 50, 60, 110, and 165 cycles and inspected for signs of corrosion attack, especially red rust indicating that the coating was no longer providing protection to the steel substrate. Red rust

appeared on some of the scribed coupons after only 20 cycles, although those with the TCP post-treatment showed some red rust on only one of the three panels. By 110 cycles all the scribed coupons exhibited significant substrate corrosion attack, but the unscribed panels did not show any signs of red rust until 165 cycles. At this time, the TCP post-treatment was providing a significant advantage in terms of corrosion resistance. Note that the pass criterion for this test - for the unscribed panels - was 80 cycles with no sign of red rust



Figure 10. APCVD Al Unscribed Panels and Scribed Coupons after 165 Cycles in the GM 9540P Accelerated Corrosion Test

The kinetic coefficient of friction  $(\mu_k)$  for the Cd control was found to be about 0.4 as deposited and about 0.2 after the brief exposure to salt fog to induce a surface more representative of what might be found in service. The as-deposited APCVD Al exhibited a  $\mu_k$  of about 1.0, and about 0.5 after salt fog exposure. The modified surface on both the Cd and Al coatings exhibited less variability in the measured  $\mu_k$  values, as shown in Figure 11. Torque-tension testing is needed to determine if the frictional properties of the APCVD Al coatings are satisfactory.

The hydrogen embrittlement (HE) testing with AISI 4340 notched round bars revealed that the Al coated bars with no post baking (as applied to Cd-plated coatings) failed due to the hydrogen gas byproduct during the APCVD Al process being absorbed by the substrates. This result implies that post baking is necessary to remove the absorbed hydrogen from the substrate. To address this issue, Al coated bars were subjected to baking at 190°C for 23 hr immediately after deposition. Subsequent HE testing revealed that all these post baked bars withstood 202 hours (pass criterion was 200 hours). This result indicates that all the hydrogen diffused in the substrates had been removed. A hydrogen relief baking is, thus, a necessary and effective way to eliminate hydrogen embrittlement.



Figure 11. Kinetic Coefficient of Friction Values of APCVD Al and Cd Coatings As Deposited and after Mild Corrosion

Table 1 summarizes the results of the HE testing in air with APCVD Al coated AerMet 100 notched round bars and Cd plated notched round bars. When the AerMet 100 specimens are given the hydrogen relief bake they pass this test, as do the plated Cd specimens.

ASTM F519 Hydrogen Embrittlement Test											
Coating	Substrate Material	Heat Treat (Hydrogen Relief)	Spec. No.	Avg. Notch Tensile Strength (lbf)	Test Environment	Test Load % NTS	Total Hours	Spec. Fail?	Step Load?	Fail during Step Load?	Pass/ Fail
Cd Plated & Baked			74				000	N	NI/A	N1/A	
Cd Control (QQ-P-416, Type I, Class 1)	AerMet 100	375F / 23H	Z-1 Z-2 Z-3 Z-4	10,600	Lab Air	75	200 200 200 200	NO NO NO NO	N/A N/A N/A N/A	N/A N/A N/A N/A	Pass
Cd Control (QQ-P-416, Type I, Class 1)	AerMet 100	375F / 23H	Z-5 Z-6 Z-7 Z-8	10,600	3.5% Salt Soln	45	21.4 12.9 22.7 29.2	Yes Yes Yes Yes	-		Fail
Cd Control (QQ-P-416, Type I, Class 1)	AerMet 100	375F / 23H	Z-9 Z-10 Z-11 Z-12	10,600	Deionized Water	45	200 200 200 58.2	No No No Yes	Yes Yes Yes Req'd	Yes, 66 hr @ 75% No Yes, 24.8 hr @ 75% -	Fail
	(5705) 8 Dala										
APCVD at 300C	ea	15				000		N1/A	N1/A		
Aluminum Coated	AerMet 100	375F / 23H	AD AE AF AG	10,545	Lab Air	75	200 200 200 200	NO NO NO NO	N/A N/A N/A N/A	N/A N/A N/A N/A	Pass
Aluminum Coated	AerMet 100	375F / 23H	AH AI AJ AK	10,545	3.5% Salt Soln	45	22 13 3.8 1.9	Yes Yes Yes Yes	-		Fail
Aluminum Coated	AerMet 100	375F / 23H	AL AM AN AO	10,545	Deionized Water	45	1.7 20.8 20.5 0.1	Yes Yes Yes Yes			Fail

Table 1.	Results of Hydrogen Embrittlement Testing of APCVD Aluminum and
	Cadmium Coatings on AerMet 100

However, when the testing was conducted in a corrosive environment (in this case 3.5% salt solution or deionized water) both the Cd-coated and the APCVD Al-coated specimens failed.

Some constant amplitude, axial fatigue testing results for APCVD Al on AerMet 100 are shown in Figure 12. Bare, smooth round bar specimens were used as a control, and the Cd-plated smooth round bars were used to determine the fatigue debit that the APCVD Al-coated specimens should not exceed.



Figure 12. Fatigue Test Results for AerMet 100 Smooth Round Bars Coated with Cadmium and APCVD Aluminum

The S/N curves out to ~5,000,000 cycles for the bare and the Cd-plated specimens were similar in shape, but displaced by about 20 ksi, indicating a fatigue debit of 10 - 15% resulting from the application of the Cd coating. The curve for the APCVD Al-coated specimen shows a greater drop off in maximum stress as a function of cycles, indicating a greater fatigue debit than that obtained for the Cd-plated specimen. Reasons for this may be associated with (i) softening of the AerMet 100 and reduction in ultimate tensile strength (UTS) during the exposure to temperatures in the range of 275 - 300°C during deposition; (ii) damage to the substrate surface as a result of impingement during rotation of the reaction chamber at the start of the deposition cycle; or (iii) uptake of hydrogen during deposition that weakens the substrate. Further experiments are needed to explore these possibilities, but it is known from some preliminary experiments with notched, round AISI 4340 steel bars that a loss in UTS of 5 - 15% is observed if they are held at temperature for the equivalent time to deposit a 12.5 - 25  $\mu$ m APCVD Al coating. Also, in this fatigue testing the specimens received a

hydrogen relief bake, so that the hydrogen uptake hypothesis does not hold, unless not all the hydrogen was driven from the specimens during baking.

#### **Summary and Conclusions**

As part of a multifaceted development effort to validate the feasibility of using APCVD Al coatings as a replacement for Cd or IVD Al coatings for industrial and military applications, the physical and chemical properties of deposited Al coatings on a range of substrate materials have been investigated. The Al coatings, regardless of deposition conditions (i.e., type of precursor, temperature, time) were found to be polycrystalline (face centered cubic structure) with XRD patterns equivalent to an Al powder reference. The coatings were dense (~2.6 g/cm<sup>3</sup>), rough on a nano-scale, and relatively free of defects. Both step coverage and throwing power (expressed by the ratio of average coating thickness ratio on inside and outside of small tubes) of the APCVD Al coatings were found to be close to 100 %, confirming that this process produces uniform coatings with excellent coverage. As a result, this deposition process can be used for non-line-of sight applications, *as well as* line-of-sight applications, unlike the approved IVD process currently used to deposit Al as an alternative to Cd.

Compositional analysis revealed that the Al coatings prepared with pure TIBA exhibit a lower carbon concentration as the deposition temperature is increased from 275 to 300°C. The carbon concentration of Al coatings produced with blended TIBA was found to be lower than that in coating produced with pure TIBA. However, in both cases, deposits made at 300°C had a relatively low carbon concentration (<1.0 at.%). The NRA results indicated that that hydrogen incorporation in all the coatings was higher at the surface, as expected, and lower in the bulk (<0.5 at.%). This hydrogen could be removed from the coating by a subsequent low temperature heat treatment. Low concentrations of oxygen and nitrogen also were found in the coatings.

The electrical resistivity of Al coatings deposited using blended TIBA was measured to be  $3.5 \pm 0.1 \mu$ ohm-cm as compared to 2.7  $\mu$ ohm-cm for bulk Al, indicating that contact resistance in service would be satisfactory. Adhesion tests showed that Al coatings deposited using blended TIBA exhibit a similar adhesive strength (684 kg/cm<sup>2</sup>) as those using pure TIBA. Failures occurred in the adhesive and not in the coatings.

Potentiodynamic polarization measurements made after 1 hour of immersion in a 3.5 % NaCl solution revealed that Al coatings (pure TIBA) exhibit a greater tendency to passivate than the Al reference foils, and that the corrosion resistance is comparable to that of pure Al foils used as a reference material. The ability to provide galvanic (sacrificial) protection was confirmed, and the activepassive transition properties indicate that the APCVD Al coatings may not be leached too quickly in service in a corrosive environment. The aggressive GM 9540P alternating immersion test indicated that the APCVD Al coatings had excellent corrosion resistance, especially if given a trivalent chromium conversion treatment (TCP) after deposition.

The hydrogen embrittlement (HE) tests in air revealed that premature failure occurred of Al-coated bars without being given a hydrogen relief bake. However, all the coated bars with such a post treatment passed the HE test criterion, similarly to the results obtained for the heat-treated only (no coating) notched round bars. This result implied that that all the hydrogen diffused in the substrates during deposition had been eliminated through baking. Post baking of Al coatings is, thus, a necessary and effective way to eliminate hydrogen embrittlement. Cd-plated notched round bars tested in a 3.5% salt solution or in deionized water failed during HE testing, as did those with an APCVD Al coating. Consequently, based on these limited tests, the APCVD coatings may be said to exhibit equivalent - but not better - HE performance than the plated Cd coatings that need to be replaced with a more environmentally acceptable material.

Constant amplitude, axial fatigue test data revealed that the APCVD Al coatings produce a greater fatigue debit than comparable Cd-plated coatings on AISI 4340 steel and AerMet 100, even after receiving a hydrogen relief bake. The reason for this behavior is not known at this time, and further testing and analysis are required.

Overall, considering the results from the wide range of properties measured, and comparing them to the alternative coating requirements listed in the introductory section above, there is the possibility that further optimization of the APCVD process could lead to APCVD Al coatings becoming a potential candidate for replacing Cd in a wide range of applications.

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## References

- 1] K. O. Legg, *Proceedings of the 15<sup>th</sup> International Conference on Surface Modification Technologies*, ASM International, Materials Park, OH, pp. 235-244 (2002).
- [2] G. F. Hsu and R. C. Colonel, U.S. Patent # 4,765,871 (1988).
- [3] J. Fischer, B. Fuhr, *Advanced Materials & Processes*, **155** (4), pp. 27-29 (1999).
- [4] D. E. Muehlberger, *Plating & Surface Finishing*, **20**, p. 65 (1978).
- [5] D. P. Monaghan, D. G. Teer, P. A. Logan, K. C. Laing, R. I. Bates, R. D. Arnell, *Surface Coating Technol.*, **60**, pp. 592-596 (1993).
- [6] A. Malazgirt, J. W. Evans, *Metallurgical Transactions B*, **11**, pp. 225-232 (1980).
- [7] R. A. Levy, M. L. Green, P. K. Gallagher, J. Electrochem. Soc., 131 (9), pp. 2,175-2,182 (1984).
- [8] M. L. Green, R. A. Levy, R. G. Nuzzo, E. Coleman, *Thin Solid Films*, 114, pp. 367-377 (1984).
- [9] B. E. Bent, R. G. Nuzzo, L. H. Dubios, J. Am. Chem. Soc., 111, pp. 1,634-1,644 (1989).
- [10] D. A. Mantell, J. Vac. Sci. Technol. A, 9(3), pp. 1,045-1,050 (1991).
- [11] Strategic Environmental R&D Program, Project WP-1405, "Investigation of Chemical Vapor Deposited Aluminum as a Replacement for Cadmium", SERDP Office, Arlington, VA.
- [12] D. L. Deavenport, J. L. Thompson, Jr. N. H. Tran, S. S. Newberg, U.S. Pat. Appl., US 20050064211 A1 (2005).