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#### ABSTRACT

#### SYNTHESIS AND CHARACTERIZATION OF ATMOSPHERIC PRESSURE CHEMICALLY VAPOR DEPOSITED ALUMINUM

#### by Sipeng Gu

This study investigates the use of atmospheric pressure chemical vapor deposition (APCVD) to produce high quality aluminum coatings for corrosion protection of steel. The coatings were produced through thermal decomposition of tri-isobutyl-aluminum (TIBAL) over the 275 to 300°C temperature range. Under optimal deposition conditions, growth rates as high as 1.2 µm/min were achieved. X-ray photoelectron spectroscopy, auger electron spectroscopy, glow discharge optical emission spectroscopy and nuclear reaction analysis revealed that the coatings consisted essentially of pure aluminum (~99 at.%) with oxygen and carbon present as minor constituents. The coatings were characterized in terms of their morphological, structural, electrical, and mechanical properties, and corrosion performance. The coatings were found to be continuous with a rough surface topography typical of CVD metal deposits. The Al coatings showed x-ray diffraction patterns that were similar to the typical polycrystalline aluminum powder pattern regardless of deposition conditions. Cross-sectional SEM micrographs confirmed that the APCVD process can offer excellent step coverage and throwing power. Corrosion testing revealed that APCVD Al coatings exhibit excellent corrosion resistance. With such correlations, this study offers an environmentally benign alternative to cadmium plating, as well as promises to provide high production throughput, low cost, and coatings with desirable properties and performance.

#### SYNTHESIS AND CHARACTERIZATION OF ATMOSPHERIC PRESSURE CHEMICALLY VAPOR DEPOSITED ALUMINUM

by Sipeng Gu

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Materials Science and Engineering

Interdisciplinary Program in Materials Science and Engineering

August 2008

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To my parents and my wife

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## CHAPTER 1 INTRODUCTION

#### **1.1 Cadmium Coatings**

Cadmium (Cd) coating has been used on high strength steel parts to provide corrosion resistance in a wide range of Department of Defense (DoD) weapon systems. However, cadmium is a hazardous material, to be a carcinogenic, teratogenic, and toxic metal that can be easily leached causing potential contamination of the ground water supply and food chain. Those environmental and health related concerns are further aggravated by the common use of sodium cyanide as part of the plating process and the use of hexavalent chromium-based post-treatments, which pose serious worker safety concerns [1, 2].

Cadmium has been widely accepted as a coating for high strength steel applications due to its excellent adhesion, corrosion resistance, and proper lubricity characteristics. Proposed replacements for cadmium must, therefore, not only match or surpass its current performance, production throughput, maintainability, reparability, and cost, but also guarantee elimination of the current cadmium related waste streams without generating another Environment, Safety and Occupational Health (ESOH)-regulated hazardous waste stream.

#### **1.2** Alternatives to Cadmium Coatings

Several technologies pertinent to coating high strength steels have emerged to address this challenge and these were reviewed by Legg [3]. They include the use of electrodeposited Zn-Ni, Sn-Zn and Zn-Ni-X (X = Cd, P) alloys [4-6], metal-filled polymer composites [7],

novel stainless steel alloys [8], and electrodeposition [9] as well as ion vapor deposition (IVD) of aluminum [10].

#### 1.2.1 Electroplate Zn-Ni and Sn-Zn

The Zn-Ni and Sn-Zn alternatives involve alloy plating, which are more complex and less robust than the deposition of elemental cadmium because the alloy composition, which determines the final coating performance, depends on many bath processing parameters that are difficult to control. Furthermore, because steel parts are exposed to aqueous solutions during plating, hydrogen generated in the part during plating must be removed by either: 1) a post plating baking protocol (typically 24 hours at 375 °F) or 2) mitigated by pre-coatings such as a nickel strike that provide a barrier to the migration of hydrogen into the substrate during plating [6].

#### **1.2.2** Polymer Composites

Another alternative technology to cadmium plating consists of using polymers filled with metal flakes (i.e., Zn or Al). These coatings are deposited by the dip-spin method, in which fastener parts to be coated are loaded in a basket that is dipped into the polymer resin composite, then lifted out and spun at high speed to eject the excess material. The parts are subsequently baked to set the resin. This technology has been tested by TACOM and found to be as good as cadmium plating in the case of fasteners. Although highly cost-effective (~\$.30 per pound of parts), control of the process is crucial in insuring the proper resin viscosity in order to avoid excess coating thickness that clogs fastener threads. Coatings also typically require an elevated temperature cure that makes their use impractical for in-situ repair of sacrificial coatings [7].

#### 1.2.3 Stainless Alloys

The environmental issues associated with cadmium-coated steels can be totally eliminated by using specially designed stainless steel alloys. Stainless steel is defined as an iron-carbon alloy with a minimum of 10.5% chromium content. It has high resistance to oxidation and corrosion because of forming a passivation layer of chromium (III) oxide  $(Cr_2O_3)$  when exposed to air. Aircraft manufacturers have successfully implemented this approach in engines (e.g., F-119 engine used in the F-22), aircraft actuators, and landing gears. Although such an approach works well for the aforementioned applications, stainless steels are generally more costly and in some cases (e.g., 15-5 PH precipitation hardened steel) are inferior in strength to cadmium-coated high strength steel.

Furthermore, stainless steels still cannot be used without a sacrificial coating in situations where painting is required or galvanic corrosion may develop, such as in the case of airframes, where the steel would be in contact with the aluminum skin of the aircraft [8].

#### **1.2.4 Aluminum Coating**

The simplest approach to cadmium replacement appears to be aluminum. It is environmentally friendly, non-toxic, and safe to handle and use by workers. These environmental qualities eliminate some life cycle costs, such as waste collection, storage, and disposal in association with the processing of hazardous materials.

Aluminum is the third most abundant element in the earth's crust and the second most commonly used metal in the world after steel, which has unique properties for its outstanding position on the market: light weight, high strength, good thermal and electrical conductivity, good formability, nontoxic and resistance to corrosion [11, 12].

Atomic Crystal Structure. Atomic number of the element aluminum is 13 and the atoms arrange themselves in the face-centred cubic (FCC) structure as shown in Figure 1.1, a typical crystal structure for highly ductile metals.



Figure 1.1 The face-centered cubic (FCC) crystal structure

**Specific Light Weight.** Aluminum has specific gravity of 2.70 g·cm<sup>-3</sup> at 20 °C. Its mass is only 34% percent of an equal volume of iron (7.87 g·cm<sup>-3</sup>). The lightness of aluminum has made it an attractive material for use in transportation applications, Aircraft, *et al.* 

**Corrosion Resistance.** As a chemically active metal, it is stabile and corrosion resistant due to the presence of an extremely hard and tenacious transparent aluminum oxide  $(A1_2O_3)$  film on the metal surface forming immediately when the metal reacts with the oxygen in air or water. This oxide layer is inert, giving a higher corrosion resistance than any of aluminum alloys, and fairly resistant to most acids but less to strong alkalis.

Aluminum can be safely used in the range of pH 4 to 8.5. Corrosion of aluminum can occur only if the oxide layer is ruptured and cannot be reformed. Acid salt fog, neutral salt fog, and outdoor exposure tests, has demonstrated unequivocally that aluminum coatings provide equal or superior corrosion protection to cadmium-plated steel parts.

**Non-toxicity.** Aluminum and its corrosion products are non-toxic [13]. One statement from the World Health Organization mentioned that there is no evidence to prove the toxicity of aluminum, alumina and other inorganic aluminum salts [12].

Aluminum coatings offer additional advantages. They can be subjected to temperatures as high as 925°F (496°C), while cadmium is limited to 450°F (232°C). They may be exposed to fuels with no adverse effects and can be used in space applications, while cadmium sublimates in a vacuum environment and plates out on neighboring surfaces.

#### 1.3 Conventional Growth Techniques of Aluminum Coating

The advantages of aluminum coatings are widely recognized, and several processes are available. In this section, typical examples of conventional growth techniques are reviewed. Aluminum coatings can be deposited on steel by hot dipping, pack cementation, spraying, ion vapor deposition (IVD), sputtering deposition and chemical vapor deposition (CVD), respectively.

In particular, IVD and CVD methods will be paid more attention since both have been proven to be the most successful techniques for aluminum coating growth.

## **1.3.1 Hot Dipping Aluminum**

Hot dipping deposition is used to increase corrosion and wear resistance. It is based upon atomic diffusion of elements at the interface and a chemical bond between the two metals will be produced. The process is carried out by immersing a pre-treated substrate in a bath of molten aluminum at 1023 k for a specific time to yield both an intermetallic layer of Al<sub>3</sub>Fe and aluminum coating [14]. Hot dipping aluminum coating has two main disadvantages: 1) A brittle iron-aluminum inter-metallic layer forming in hot dipping process, which cases poor impact resistance of the coating, giving a severe drawback in highly corrosive environments. 2) Poor coating thickness control on complex shapes and poor surface smoothness.

#### 1.3.2 Pack Cementation Aluminum

Pack aluminum coatings are widely applied to steels to improve their hot temperature oxidation for gas turbine components [15, 16]. In the pack cementation process, the parts to be coated are packed in metal powers in sealed retorts, which placed in a furnace with well controlled coating temperature (700 - 1100 °C) and a protective atmosphere (Argon or Nitrogen) to prevent their oxidation. A gaseous halide activator aluminum salt will be delivered to the component surface in the aluminizing process, then decomposes to yield aluminum coating and to release the halide activator. During this process, the aluminum and metal atoms diffuse into each other with the deposition and the heat treatment occurring simultaneously.

It should note that the pack cementation method suffers several drawbacks. The coating thickness often varies widely in different substrates due to poor thermal conductivity of the power pack. The coating diffusion may stick the parts together if the parts come into direct contact with each other. Furthermore, this process will waste a large amount of aluminum salt [17].

#### **1.3.3 Thermal Spray Aluminum**

Thermal spray is a continuous, directed, melt-spray process, in which particles of 1 to 50 micron are, at least partially melted, and accelerated to high velocities through either a

combustion flame or a dc or rf arc. The molten droplets successively impinge onto a substrate surface and rapidly yield a film [18, 19].

The porous structure of thermal spray aluminum coatings provide paths for the easy access of the corrode species. It is necessary to conduct pretreatments, such as porosity sealing and pre-heating treatment to increase adherence for preventing steel corrosion [20].

Thermal spray aluminum coatings have some shortcomings including: 1) Producing oxide content in the coating during spraying processes, 2) Generating open pores and crevices within the coating structure, a big problems for the corrosion protection in that the corrosive environment maybe penetrate towards steel substrate. 3) Degrading of coating materials during spraying [20].

#### **1.3.4 Electroplating Aluminum**

The aluminum plating process, known as Alumiplate<sup>®</sup> (produced by alumiPlate, Inc. in Minneapolis, MN), is the only commercially available aluminum electroplate in the U.S., requiring the use of a toluene-based solution. It is achieved by an electric current passing through an electrolyte containing aluminum alkyls and metal fluoride. Pure aluminum serves as the cathode, dissolving in an electrochemical cell and providing a 99.99% pure aluminum coating during plating. The deposition takes place in an enclosed, oxygen-and water-free environment where the parts to be coated are introduced through a load-lock system. No hydrogen is generated and, therefore, no post baking is required to mitigate hydrogen embitterment [9, 21-23].

Although the coatings produced by this process appear to have excellent corrosion resistance properties, several shortcomings are evident, namely: 1) the process uses toxic chemicals and is unlikely to be implemented at DoD depots, logistics centers, or OEM

facilities; 2) the technology is proprietary and controlled by a small business with only one processing site; and 3) the part geometries and sizes that can be coated are limited by the plating bath size [3].

#### **1.3.5 Vacuum Evaporation Aluminum**

Vacuum evaporation, is the first physical vapor deposition process used on an industrial basis for the aluminum metallization [24, 25]. The basic evaporation process involves the transfer of atoms or molecules from a vaporization source to substrate without colliding with residual gas molecules, forming a coating by physical means alone [26]. The energy for volatilization of the source material can be provided by resistance heaters, radio frequency (RF) induction or magnetically focused electron beams.

Aluminum films via vacuum evaporation can be produced with high growth rates over large areas [27]. However, the resultant films provide non-uniform coverage and relatively low adhesion unless glow discharge cleaning is used to remove surface atoms from substrates [28]. Furthermore, it is a line-of-sight process. Although evaporation is very successful in applications in decorative and optical uses [29], it is not used for critical corrosion application because of low adhesion.

#### 1.3.6 Sputter Aluminum

Aluminum sputter deposition, one of principal physical vapor deposition methods, is commonly used in integrate circuit (IC) metallization processes in the semiconductor industry [30]. Radio frequency (RF) or direct current (DC) sputtering involves the transport of a material in a vacuum chamber from a source (target) to a substrate by ionizing inert gas particles in an electric field to impinge the target, where atoms of the source materials will be sputtered off from target surface [31-33]. Figure 1.2 shows a



schematic view of sputtering deposition system and diagram of sputtering process. The vacuum system is not shown, but will be at low pressure in the mTorr or lower ranger.

Figure 1.2 Schematic of sputtering deposition system and sputtering process.

In putter deposition method, film composition will be the same as that of source target. In addition, both adhesion and uniformity of films are excellent. Nevertheless, sputter method is a thickness limited, cost-inefficient, and line-of-sight deposition.

#### 1.3.7 Ion Vapor Deposited (IVD) Aluminum Coating

Currently, Ion vapor-deposited aluminum coatings have been used on a variety of parts including steel and titanium fasteners, electrical connectors, engine mounts and stator vanes, landing gear components, integrally machined wing skins, and a large number of miscellaneous components for corrosion protection [34]. IVD is a relatively new and typical physical vapor deposition (PVD) process that takes place in an evacuated chamber where aluminum is evaporated onto a substrate being simultaneously subjected to bombardment by plasma-ionized argon gas. The major difference of IVD with general PVD is that the substrate during plating is held at a high negative potential (typically -5 kV) with respect to the vapor source [34, 35].

IVD process is applied in a batch mode, where parts to be coated are held at a high negative potential relative to the evaporation source. Positively charged gas ions bombard

substrate surface and perform a final cleaning action. Consequently, aluminum is vaporized and ionized, to be accelerated toward the substrate surface where it plates as a dense, tightly adherent coating.

IVD aluminum coatings are attractive as cadmium alternatives for both barrier and sacrificial protection to the steel substrate in most common environments due to its immunity of the environmental and toxicological problems associated with cadmium. Meanwhile, since the aluminum deposition takes place in vacuum and no hydrogen is generated, a hydrogen embrittlement relief bake is not necessary [10].

Unfortunately, the IVD aluminum process exhibits several limitations as follows: **Columnar Grains.** The IVD growth mechanism results in the formation of columnar grains [36] that provide a conduit for oxygen and corrosive agents to readily diffuse through the grain boundaries and attack the underlying substrate. Although this problem may be minimized by increasing the coating thickness and penning, it can be eliminated by forming, if possible, a randomly oriented grain structure.

**Throughput.** The fact that an evacuated chamber is required to produce the coatings severely limits the throughput and results in a higher cost per coated part as compared to continuously operated atmospheric processes. Furthermore, the IVD process, being partly a line-of-sight deposition technique, often necessitates two coatings per cycle to achieve acceptable coating thickness uniformity. After the application of the first coating, the system is vented, the parts manually rotated, and the deposition process re-started. Thus, both chamber size and processing times limit the utility of IVD.

**Throwing Power.** In addition to throughput and cost considerations, the IVD process has proved to be unable to coat non-line-of-sight components/parts/surfaces. Typical IVD

"throwing power" (or conformal coverage) allows for functional aluminum coatings to be deposited in a cylinder to a depth equivalent to one time its diameter. In view of the fact that a large percentage of parts requiring corrosion protection have inside diameters, blind holes, and complex geometric surfaces, there is a need to resolve this coating conformability issue.

**Chromium Containing.** IVD aluminum as well as other sacrificial coatings relies on hexavalent chromium containing post treatments for the purpose of optimum corrosion protection and paint adhesion. Therefore, although cadmium is eliminated from the coating system life cycle, hexavalent chromium is still present for all alternatives.

#### **1.3.8 Chemical Vapor Deposition Aluminum**

Chemical vapor deposition aluminum is commonly used for various semiconductor applications, which has been studied for its capability of conformal step coverage and selective growth to overcome limitations that physical vapor deposition techniques encounter in electronics industry [37-39]. Now CVD aluminum is also making great inroads in replacing cadmium in corrosion protection of steel compounds [40]. In the following section, a brief review of chemical vapor deposition techniques is given. Meanwhile, a summary of atmosphere pressure chemical vapor deposition method and CVD aluminum, classified by different precursors, is presented.

#### **1.4 Chemical Vapor Deposition**

#### **1.4.1 Introduction to Chemical Vapor Deposition**

Chemical vapor deposition (CVD) is a well-established process in which gas or vapor chemically reacts with a suitably placed substrate to yield a desired solid product. This product can be in the form of a single thin/thick film or even a massive bulk deposited nanostructured and functionally graded coating. CVD process is used in different material fabrication such as insulators and dielectrics, elemental and compound semiconductors, electrical conductors, and superconductors. Depending on the growth conditions, the coating can be a single crystal, polycrystalline, or amorphous structure.



Figure 1.3 A simplistic view of a CVD process [41].

Figure 1.3 schematically depicts CVD process in which precursors in the vapor phase are broken down, resulting in growth of a thin film on a substrate [41]. Deposition variables such as temperature, pressure, input concentrations, gas flow rates, and reactor geometry determine deposition rate and deposit properties.

A typical CVD process is surface-catalyzed reaction, involving heterogeneous gas phase reaction on or near a heated surface and homogeneous gas phase reaction in the gas phase. Chemical reactions that can take place are pyrolysis (thermal decomposition), oxidation, reduction, hydrolysis, nitride and carbide formation, synthesis reactions, disproportionation, and chemical transport. Specially, alkyl decomposition to yield aluminum coatings in this study is a pyrolysis reaction. As a relatively mature conventional technique, CVD has following distinctive advantages [42]:

1) Producing highly dense and pure uniform films with good reproducibility and adhesion at reasonable deposition rates.

2) Being a non-line-of-sight process with excellent "throwing power" to deposit uniformly on complex shape components.

3) Ability to control crystal structure, surface morphology and orientation of CVD products by adjusting CVD process parameters.

4) Relatively low deposition temperature and flexibility of using a wide range of chemical precursors.

However it still has some drawbacks including chemical and safety hazards caused by the use of toxic, corrosive, flammable precursor gas, difficult to deposit multicomponent materials with well controlled stoichiomety.

#### 1.4.2 Commercial CVD Process

CVD processes are classified according to the type of energy supplied to initiate and sustain the reaction:

(1) Thermally activated reactions at various pressure ranges, where heat is generated by resistance heating, RF induction heating, or infrared heating [37, 43, 44].

(2) Plasma promoted reactions, where an RF- /or DC- induced glow discharge is the source for most of energy that initiates and enhances reaction rate [45-48].

(3) Photon-induced reactions, where radiation of a given wavelength triggers and sustains the reaction by direct photolysis or an energy transfer agent (e.g., UV-activated mercury) [49, 50].

(4) Laser-induced reactions, intensively fast and generally applicable processes for depositing a wide range metals and substrates, which requires well-developed gas exhaust and vacuum systems [49, 51].

## 1.4.3 Atmospheric Pressure CVD (APCVD)

Chemical vapor deposition reactions can occur over the full range of pressure. It is classified into two types in terms of working background pressure: low pressure CVD (LPCVD) and atmospheric pressure CVD (APCVD).

Compared to APCVD, the mass transfer rate relative to the heterogeneous surface reaction rate in LPCVD is enhanced by lowering the gas pressure. Improved mass transfer rate of LPCVD offers a possibility to uniformly deposit films in a highly economical close spaced positioning of the wafers in a standup fashion. However, use of LPCVD has limitations for various industrial applications. It is not suitable to use vacuum technology for large scale processes, since high running cost of vacuum equipment is a concern [52]. Using APCVD process is a way to get around these limitations.

Conventional atmospheric pressure CVD (APCVD), as the simplest CVD process, allows a single or multiple reactant gases in the reaction chamber at normal atmospheric pressure. In general, the pressure in the reactor is slightly above atmospheric value due to impedance of the gas flow at the exit part of system. If it is necessary to control pressure like good uniformity, size of exhaust opening may be regulated. Energy is supplied by heating the substrate to the temperature required to initiate and maintain chemical reaction. Deposition temperature, reactant flow rate, and gas composition constitute of three principal variables that determine coating deposition rate. The continuous processing APCVD system is the most suitable for continuous deposition processes such as those employed in the high volume production of coated glasses. Operation at atmospheric pressure allows a high film deposition rate of 600-1000 nm/min. Homogeneous nucleation occurs in the gas phase because of a high collision rate among the gas molecules, and a large amount of particles can be created in the CVD system.

Figure 1.4 shows a schematic drawing of the APCVD tool. It is a modified commercial Epsilon 1 system fabricated by ASM. The system retains temperature flexibility in the range of 450 – 1200 °C with lamp heating which enables relatively rapid temperature changes. High temperature APCVD deposition (900-1100 °C) of Si at atmospheric pressure is widely used in modern C-MOS and bipolar technology [53].



Figure 1.4 Schematic of the single wafer atmospheric pressure CVD tool.

The advantages of APCVD include simplicity of this technique and no requirements of vacuum pumps and associated vacuum monitoring apparatus, compared to PVD. Optimization of CVD process parameters has proven to yield coatings that are adherent, highly dense, chemically pure, and uniform in thickness as well as in composition, resulting in CVD coatings with low intrinsic stress, desirable microstructures

(i.e., randomly oriented versus columnar grains), and a good surface finish. However, the key property that distinguishes CVD from PVD is its superior surface conformability (or surface coverage).

Large values of mean-free path (resulting from use of high vacuum conditions) and high sticking coefficient of the atoms render PVD processes largely "line-of-sight" depositions. In CVD, the mean-free path of molecules and their sticking coefficients are often reduced, indicating "precursor" undergoes a large number of collisions upon entering the reactor before it collides with a surface. Because of these collisions, both the lower sticking coefficients of molecules (compared to the atoms produced in PVD) and the enhanced surface diffusion caused by the heated substrate, yield perfectly conformal surface coverage. In the microelectronics industry, CVD metal coatings (e.g., TiN, W, Cu, Al, etc.) are routinely used to conformally cover submicron-sized vias (< 0.12  $\mu$ m) with severe aspect ratios (hole depth/diameter ratio ~20:1). For high strength steel parts with blind holes having typical diameters of 0.25 inch, this means achieving conformal surface coverage down to depths of 5 inches, or more.

Strengths	Weaknesses	Result
Potential for intergration directly with process	Reduced coating process flexibility	Reduced labour costs, high volumes
High deposition rates	Need to match line	Thick films possible
possible	speeds	at high throughputs
Hard films		Improved processability and application performance
Degree of film structure control possible	Surface roughness	Conductivity, photo-activity and durability imporved
	Volatile precursors needed	Limited range of depositioable materials
Process differentiation	Limited "off-shelf"	Need to develop in-house
Process unierentiation	process availability	technology, and/or licence

**Table 1.1**Strengths and Weaknesses in APCVD

#### 1.4.4 Strengths and Weaknesses of APCVD

Atmospheric pressure CVD achieves unique combinations of high growth rates and large deposition area. It is particularly suited to high volume continuous growth process, especially in glass industry. Furthermore, APCVD system is relatively simple and cost competitive. Table 1.1 shows the strengths and weaknesses in APCVD process [41].

#### **1.4.5 APCVD Aluminum Coating**

Up to date, little work on pure aluminum coating by APCVD process has been reported. Jesse J. Crosby firstly reported that adherent aluminum coatings with low porosity were deposited by thermally decomposing tri-isobutylaluminum (TIBAL) onto different substrates, such as mild steel, copper, magnesium, titanium *et al.* at atmospheric pressure with argon as the carrier gas [54].

However, this process is somewhat far from ready to be used in commercial systems, since the alkyl must be maintained at a sufficient vapor pressure for deposition; the supply lines of precursor from the source to the reactor chamber must also be heated to preserve a vapor state.

James C. Withers studied use of atomic alkyl into fine droplets over a heated substrate by a process called "pyrolytic spray technique" to deposit good aluminum coatings. In this work the key is to provide the precursor in the form of finely-divided particles of liquid, having a particle size of about 500 nm units to 10 microns, against the substrate heated by induction to the decomposition temperature. This process overcomes the limitations to maintain the precursor in a vapor state for commercial applications. It is also reported aluminum coatings were deposited in the temperature range of 498k to 598k [55]. However, porous and severe surface roughness coatings could be produced over

about 6.35  $\mu$ m to 12.7  $\mu$ m thick with a high coating rate (about 12.7  $\mu$ m/minute). Good coatings could be obtained at about 4.3  $\mu$ m/minutes, but the rate was not easily controlled.

Although previous attempts have obtained good aluminum coatings, it has been proven to be difficult to transfer the process from CVD laboratory apparatus to large scale equipment for mass production, as well obtain coating integrity in large CVD reactors [56]. High quality of aluminum coatings with desirable density still is a challenge.

#### 1.5 CVD Aluminum Using Alternate Routes

The candidates for aluminum CVD precursors can be divided into two main categories: aluminum alkyls and alane complexes. In aluminum alkyls aluminum is directly bonded to an organic structure or ligand. While alane complexes consist of alane (AlH<sub>3</sub>) bonded generally to a tertiary amine ligand.

#### 1.5.1 Aluminum Alkyls and Aluminum Alkyl Hydrides

Both aluminum alkyls (triisobutylaluminum (TIBAL), trimethylaluminum (TMA)) and aluminum alkyl hydrides (dimethylaluminum hydride (DMAH)) are liquid phase at room temperature and have relatively low vapor pressures.

**Triisobutylaluminum (TIBAL).** Triisobutylaluminum (TIBAL) is widely used as a catalyst component in Ziegler-Natta type systems in olefin polymerization [57]. TIBAL has been paid great attention among alkyl aluminum compounds as a CVD precursor because of its ability to deposit high-purity aluminum films [58].

Aluminum alkyls are typically clear, colorless liquids at ambient temperature. Triisobuylaluminum (TIBAL), one of aluminum alkyls with high freezing point (0 °C), is
moisture and air sensitive and also pyrophoric. Figure 1.5 shows molecular structure of TIBAL.



Figure 1.5 Molecular structure of TIBAL.

Back to the late 1950's, Ziegler and co-workers first reported that thermal decomposition of the TIBAL could be used to deposit aluminum thin films at about 250 °C [59]. Later on, a lot of effort was spent on investigation of chemical reactions of TIBAL during thermal decomposition [37-39, 60-62].

$$i - (C_4 H_9)_3 \xleftarrow{50-150 \ C} i - (C_4 H_9)_2 AlH + i - C_4 H_8$$
 [a]

$$i - (C_4 H_9)_2 AlH \xrightarrow{\simeq 220^{\circ}C} Al + \frac{3}{2} H_2 + 2i - C_4 H_8$$
 [b]

Reaction takes place at temperature of 50°C to 150°C. When temperature above approximately 50 °C, TIBAL looses one isobutyl ligand to form di-isobutyl aluminum hydride (DIBAH), which is a hydrogen bridged trimer with a substantially lower vapor pressure of about 1.33 Pa at 40 °C compared to that of TIBAL of 13.3 Pa at 20 °C. TIBAL and DIBALH compounds commonly associate into dimmers and trimers, respectively, via electron-deficient bonding. Reaction [a] is reversible, and formation of di-isobutyl aluminum hydride can be suppressed by adding excess isobutylene gas. At about 220 °C,

reaction [b] occurs, in which pure aluminum is deposited by di-isobutyl aluminum hydride thermal decomposition releasing both hydrogen and isobutylene gas [38, 61].

A study on surface chemistry of TIBAL pyrolysis was done in depth during aluminum thin film deposition [37]. Dominant simplified assumption is that TIBAL undergoes a surface reaction to produce a metal film and gaseous byproducts of isobutylene and hydrogen. It is suggested that reaction mechanism involves a  $\beta$ -hydride elimination, a rate determined step [37, 44].

Figure 1.6 shows proposed decomposition pathways during steady state CVD aluminum growth using TIBAL. It is clear that the  $\beta$ -hydride elimination dominates at surface temperatures lower than 227 °C and yields carbon-free aluminum films. If deposition temperature is further raised (above 330 °C), a more highly activated  $\beta$ -methyl elimination leads to carbon incorporation of aluminum films.



**Figure 1.6** Proposed decomposition pathways for isobutene ligands on the surface of aluminum (A) below 227 °C, (B) at higher temperature [37].

J. Y. Tsao, and D. J. Ehrlich investigated mechanism of patterned photonucleation of aluminum thin films from triisobutylaluminum (TIBAL) using laser-assisted CVD (LCVD) technique. This mask-free direct writing of aluminum thin films might be applicable with large nucleation barriers [49]. A very smooth surface aluminum film was deposited on Si (111) using epitaxial growth by gas-temperature-controlled (GTC) CVD method using tri-isobutyl aluminum (TIBAL). The epitaxial aluminum film is likely applicable to hillock-free IC interconnects [63]. However, additional anneal process at 430 °C for 40 minutes was needed to eliminate hillock formation.

**Trimethylaluminum (TMA).** Trimethylaluminum (TMA) was one of the early aluminum precursors[64], but the need to break Al-C bonds and the strong affinity of aluminum typically suggested significant carbon incorporation and correspondingly high resistivity aluminum deposition.

Kato *et al.* reported small roughness aluminum films deposition by a magnetron-plasma CVD system using TMA. But these films were contaminated with carbon of 5.7 at% and possessed relatively high resistivities about 8  $\mu\Omega$ ·cm as deposited and 3.8  $\mu\Omega$ ·cm after annealing at 600 °C [65, 66].

**Dimethylaluminum Hydride (DMAH).** DMAH, as a stable liquid precursor, could be used to produce high purity and conformal aluminum films with low resistivity. It has been reported that smoother aluminum films could be deposited on SiO<sub>2</sub> substrates with DMAH compared to using TIBAL [67]. However, high deposition temperature could be a concern [68-71].

# **1.5.2 Alane Complexes**

Alane complexes, such as dimethylethylamine alane (DMEAA) and trimethylamine alane (TMAA), are monomeric, which have higher vapor pressures than that of aluminum alkyls, offering higher deposition rates. Due to no direct Al-C bonds in their molecular

structures, high purity carbon-free films could be produced. Alane complexes, however, are not as thermally stable as the aluminum alkyls.

**Dimethylethylamine Alane (DMEAA).** DMEAA is one of the promising candidates for CVD aluminum thin film deposition due to its long shelf life and a liquid phase [58], thus providing high and stable vapor pressure [58, 72]. Furthermore, direct Al-C bonds are not present in its molecular structure, which helps to prevent carbon contamination [67].

Deposition of high purity aluminum from DMEAA has been carried out in laser assisted CVD system with selective growth [73]. The resistivity of aluminum films (3.6  $\mu\Omega$ ) was about 1.5 times that of bulk aluminum (2.7  $\mu\Omega$ ).

Ciaodong Li and co-workers investigated microstructure characterization and deposition rate of aluminum thin films as a function of deposition temperature on various substrate surfaces such as TiN, Al, Si, and SiO<sub>2</sub> using DMEAA [74, 75]. There was a maximum deposition rate at around 150°C, whereas the rate became very low when the temperature increased above 250 °C since gas phase reaction became very active. Aluminum oxide particle inclusion was observed at the higher deposition temperature. Meanwhile the aluminum films roughness increased with deposition time.

Compared to alkyl precursors, DMEAA slowly degrades during storage and its thermal instability can also be a safety concern [76].

**Trimethylamine Alane (TMAA).** It has been reported that high-purity carbon-free aluminum was deposited from TMAA in low pressure MOCVD systems with high growth rates and low growth temperatures [77], as well as in a photo-thermal laser system without heating the source [78]. Despite TMAA has higher stability compared to other amine alane complexes, aluminum films formed from TMAA is through not only surface but

gas-phase reactions [77]. It is difficult to handle TMAA in terms of maintaining constant surface area as a practical CVD precursor due to its solid phase with relatively high melting point [79].

The formation of aluminum coatings by vapor phase deposition has been studied in laboratories with a considerable number of alkyl aluminum compounds, but the adaptation of these laboratory procedures to commercial processing has proved difficult to be achieved.

#### **1.6 Thesis Overview**

The objective in this study is to investigate using atmospheric pressure chemical vapor (APCVD) deposition to produce high quality aluminum coatings with Triisobutylaluminum (TIBAL) as a precursor for corrosion protection of high strength steels as the replacement of Cd coatings. In addition to offering an environmentally benign alternative to cadmium plating, this strategy provides high production throughput, low cost, and coatings with desirable properties and performance. Furthermore, the process will be amenable for use at DoD depots, OEM and subcontractor facilities, and logistics centers.

In order to achieve this goal, the following work has been done.

1) Utilization of a bench top reactor to deposit coatings and investigated growth as a function of processing parameters to understand the deposition mechanism and its impact on process throughput;

2) Investigation of coating composition as a function of processing parameters to establish the achievable degree of chemical purity;

3) Characterization of coatings in terms of their structural/morphological, electrical, mechanical properties and electrochemical behavior to assemble a comprehensive property database;

4) Corrosion behavior of APCVD aluminum coating on high strength steels as a replacement of Cd coatings.

#### CHAPTER 2

# APCVD EXPERIMENTAL METHODS AND CHARACTERIZATION TECHNIQUES

This chapter describes APCVD reactor system and the operating procedure for sample preparation. It also gives a briefly review of the techniques used to characterize the coating properties.

#### 2.1 Selection of Precursors

Triisobutylaluminum (TIBAL) is well known as a ziegler Natta catalyst in olefin polymerization. It is an inexpensive organometallic compound, pyrophoric but can be simply handled with safety. In this study, both TIBAL and blend TIBAl are used as a precursor for APCVD aluminum deposition.

## 2.1.1 Pure TIBAL

TIBAL currently used in our deposition process has a commercial grade (min. 95.0% purity) with minor impurities of tri-n-butyl aluminum (0.2%), other aluminum alkyl compounds (0.1%), AlH<sub>3</sub> (0.5%), and isobutylene (2.6%). Typically, the overall aluminum content in TIBAL is 13.6 wt.%.

### 2.1.2 Blend TIBAL

Blend TIBAL used in this project is a mixture of pure TIBAL and other aluminum alkyls, which provides higher vapor pressure than neat TIBAL. The attempt of utilizing blend TIBAL is expected to improve coating quality and process control. The process requires the slightly higher deposition temperature than neat TIBAL for equivalent rates of deposition.

## 2.2 Experimental Apparatus

The Schematic APCVD system setup in this study is show in Figure 2.1. This reactor using FUZEBOX® technology is supplied by Akzo Nobel Polymer Chemicals in deer Park, TX, USA.



Figure 2.1 A close view of APCVD system using FUZEBOX® technology.

Reactor is a custom designed 10 L cylindrical Pyrex vessel with internal mixing baffles. Substrates are tumble-mixed by rotating reaction vessel. Rotation rate will be adjusted to 10-50 Hz according to application requirements. Ameritherm induction L Series is used as heat source for deposition process, 20 KW induction systems with

custom-designed copper heating coil. Heating to reaction temperature (250-320 °C) is controlled by monitoring and adjusting voltage from induction power supply.

The gases from both thermal decomposition and residual aluminum alkyl vapor in the reaction zone pass through a glass adapter and a refrigerated cold oil condenser system. Residual aluminum alkyl in the vapor is condensed and collected in a glass receiver. Gases remaining in the condenser then pass through a demister (filtering system) and are trapped before the vent. The collected aluminum alkyl and solvent are disposed or recycled through proper methods. Identification of the chemical species from the current APCVD aluminum process has been established using gas chromatography (GC). In APCVD aluminum process, pure or blend tri-isobutyl aluminum (TIBAL) as a precursor and  $N_2$  as a carrier gas are used.

As mentioned in Chapter 1, the overall chemical reaction involved in the decomposition of tri-isobutyl aluminum (TIBAL) for the deposition of Aluminum coatings is as following:

$$\left[\left(CH_3\right)_2 CH - CH_2\right]_3 Al \rightarrow Al + 3isobutylene + 1.5H_2$$

FUZEBOX Off gas analysis – TIBAL, precursor						
Hydrogen	Mole%	13.0				
Methane	Mole%	0.05				
i-Butane	Mole%	1.0				
Isobutylene	Mole%	82.1				
i-Pentane	Mole%	0.02				
Nitrogen	Mole%	3.6				

**Table 2.1**GC Analysis of APCVD Vented Gas

Identified chemical species in the vent gas are given in Table 2.1. The effluents consist of  $N_2$  (the carrier gas), isobutylene (major decomposition component),  $H_2$  (major decomposition component), i-pentane (trace), methane (trace), and isobutane. Isobutane

is produced during the hydrogenolysis reaction, a side reaction well documented in the literature. Isobutylene and  $H_2$  represent the major by-products of thermal decomposition process. The remaining species are generated from either olefinic impurities in isobutylene used to produce TIBAL or minor side reactions in CVD aluminum process. Thermolysis of these impurities in the Aluminization process generates methane in concentration equivalent to that in the original TIBAL. These hydrocarbon chemical species can be eliminated using a thermal treatment such as flare (ignition) or a chemical scrubber.

## 2.3 Sample Preparation

#### 2.3.1 Substrate Type

Substrates for APCVD aluminum coating are AISI 4130 or 4340 steel including coupons, screw, bolts, rivet, rivet stem tube *et al.*, which are prepared by degreasing and electrochemically cleaning. Equipment has been designed for deposition of aluminum coatings onto the miscellaneous small parts mentioned above.

**Coupon.** Coupon substrates for APCVD aluminum coating are AISI 4130 steel. Substrate roughness is ~160 nm RMS measured using an Atomic Force Microscope (AFM). Structure and morphology, chemical composition, electrical and mechanical properties and corrosion performance of aluminized coupons are evaluated.



**Figure 2.2** Aluminized AISI 4130 coupon $(1^{"}\times 1^{"})$  and aluminized AISI 4130 coupon after chromate conversion finishing  $(1^{"}\times 4^{"})$ .

**Fasteners.** Fasteners with V-grooved outside and stepped inside surface are used to investigate conformal step coverage of aluminum coating by measuring coating thickness. Meanwhile, aluminized rivet stem sample is used to evaluate the coating density.



Figure 2.3 Aluminized fasteners (Bolts, screw and nuts).



Figure 2.4 Aluminized rivets sleeve and rivet stem.

**Tubes.** Aluminum coated steel tubes with 2-inch long and 5/16-inch or 3/16-inch OD are used to evaluate "throwing power". Surface morphology outside and inside is characterized by FE-SEM.



Figure 2.5 Aluminized 5/16" OD and 3/16" OD 4130 steel tubes (2 " in length).

Notch Bars (AISI 4340 steel). Notched round bars are used for hydrogen embrittlement (HE) testing with ASTM F519-05 "standard test method for mechanical hydrogen embrittlement evaluation of plating processes and service environment". Figure 2.6 shows the specimen tested in this study.



Figure 2.6 Aluminized notch bar.

**Carbon Steel Disks.** Aluminized carbon steel disks, as shown in Figure 2.7, are employed to evaluate the relative sliding friction of aluminum coating using Pin-on-Disc technique.



Figure 2.7 Aluminized carbon steel disk (AISI 4340).

## 2.3.2 Pre-treatment Procedure

The general pre-treatment procedure of substrate is following:

1) Oil removal from substrates by rinsing with solvents of heptane and acetone and drying with nitrogen

2) Acid pickling using 12.5 wt.% HCl at 25 °C for 4 minutes followed by rinsing with DI water for 30 seconds

3) Rinsing with  $3\sim5$  wt.% NaOH at  $25^{\circ}$ C for 2 minutes followed by rinsing with DI water for 30 seconds

4) Rinsing with acetone to remove residual water

5) Drying in vacuum to remove residual acetone and water

## 2.4 Deposition Procedure

After general pre-treatment as aforementioned, substrates with clean, oxide-free and textured surface are used for the deposition step.

An entire APCVD aluminum process is given in Figure 2.8. After loading the substrates into the rotary CVD reactor, aluminum coatings are deposited through TIBAL

pyrolysis in an APCVD system with atmospheric pressure (operation pressure is 760 mmHg), deposition temperature of 275 or 300 °C and a nitrogen carrier gas. Temperature is monitored via vapor phase and solid phase thermocouples. Evolved gas generation rate and total volume are monitored by a totalizing gas meter. TIBAL aspiration is initiated when substrate temperature stabilizes within 275-320 °C. TIBAL injection rate is controlled to generate optimum growth rate (0.5 -1.2  $\mu$ m/min) and maintain substantially saturated vapor/liquid conditions. Vapor temperatures are set to be slightly lower than 230 °C during deposition process. Completed reaction is determined by net gas generation volume (vs target) or by time and temperature criteria. Coated substrates are cooled in an inert atmosphere and rinsed to remove excess reactant. Coating thickness is calculated by net weight gain and total surface area and direct measurement.



Figure 2.8 The schematic APCVD aluminum process.

#### 2.5 Characterization of APCVD Aluminum Coatings

APCVD aluminum coated steels were evaluated using a variety of characterization methods with respect to their structural, morphological, compositional, electrical,

mechanical and corrosion properties. Accurate determination of aluminum coatings performance is the key to assess the viability of APCVD process for commercial use and transfer to the defense industrial base.

Prior to characterization, all coated samples were ultrasonically cleaned in acetone followed by methanol, then rinsed with DI water and dried. The cross-section of aluminum coating samples were ground on SiC paper with a final grit size down to 1200 grit, followed by a polishing process with polycrystalline diamond suspension with particle size down to 0.25  $\mu$ m, then washed with DI water and dried.

Structural and morphological properties were characterized by X-ray diffraction (XRD), optical microscopy (OM), DekTak, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The correlation between processing parameters and resultant coating composition was evaluated using a variety of diagnostic techniques including auger electron spectroscopy (AES), X-ray photo electron spectroscopy (XPS), glow discharge optical emission spectrometer (GD-OES), and nuclear reaction analysis (NRA). A four point resistivity probe was used to measure the resistance of coatings. Characterization of mechanical properties was conducted with Nanoindentation test using Hysitron nanoindenter and adhesion test using SEBASTIAN FIVE-A, respectively.

In the following subsection, the techniques used to examine the quality of APCVD aluminum coatings were described.

## 2.5.1 Structure and Morphology

**X-ray Diffraction (XRD).** X-ray diffraction (XRD) was performed using a Philips X'Pert MRD X-ray diffractometer (Bregg-Brentano  $\theta$ : $\theta$ ) with Cu K $\alpha$  radiation operated at 45 kV and 40 mA to investigate crystallographic structure of aluminum coatings.

**Stylus Profilometer (Veeco Dektak IIA).** Dektak IIA, a very high precision measuring instrument capable of measuring minute physical surface variations, has four standard analytical functions: arithmetic average roughness, maximum height, average height and area-under-the curve. It was used to accurately measure vertical features in height of 131 to 5 nm and scan length of 50 to 30 mm on a wide variety of substrate surfaces. Figure 2.9 shows a close view of Dektak IIA machine. Measurements are conducted electromechanically by moving the sample beneath a diamond-tipped stylus.



Figure 2.9 Dektak IIA diagram.

**Scanning Electron Microscopy with EDS System (SEM &EDS).** Surface morphology and conformal coverage (coating thickness) of the aluminum coatings were investigated using a field emission SEM (FE-SEM, LEO 1530 VP, FESEM/ Oxford EDS system) on the surface and cross-sections of coatings. Elemental analysis of coating was conducted using EDX (Oxford INCA Energy 400).

Atomic Force Microscope (AFM). AFM is a high spatial resolution instrument capable of real space electronic and spectroscopic imaging of surface to visualize individual atoms in the Angstrom scale. The stuff (Nanoscope IIIA Multimode scanning probe microscope, Digital Instruments) in contact mode was explored to examine the topography and degree of surface microscopic roughness with a unit of nanometer root mean square (RMS) of APCVD aluminum coatings.

## 2.5.2 Chemical Composition

X-ray Photoelectron Spectroscopy (XPS). In order to evaluate the composition of coatings, XPS (ThermoElectron VG Scientific ThetaProbe) with X-ray source of monochromated Al K $\alpha$  (1486.6 eV) operated at 15 kV and 100 W was used over the analytical area of 400 × 400  $\mu$ m<sup>2</sup>. Survey and profile pass energies were 300 and 100 eV, respectively. the depth profile during XPS measurement was collected using Ar ion etching with a 2 keV beam energy and 2.1  $\mu$ A beam current over the rastered area of 3 × 3 mm<sup>2</sup>. The corresponding etching rate was 1 Å/min (SiO<sub>2</sub>).

Auger Electron Spectroscopy (AES). AES (Perkin-Elmer Physical Electronic Model 660 Scanning Auger Microprobe) operated under the base pressure of  $< 1.0 \times 10^{-9}$  Torr with the primary beam energy and current of 10 keV and 1.0  $\mu$ A was used to determine composition in depth of coatings over three different areas. During AES measurement Ar ion etching for depth profile was performed with 2 keV beam energy and 2.3  $\mu$ A beam current over 2 × 2 mm<sup>2</sup> area. The corresponding etching rate was 15 nm/min.

**Nuclear Reaction Analysis (NRA).** Nuclear reaction analysis technique has been used to determine H in silicon nitride [80]. It can be both sensitive and accurate for quantitative hydrogen analysis. This method makes use of a narrow isolated resonance in the nuclear reaction:

$$^{15}N + H \rightarrow ^{12}C + ^{4}He + \gamma (4.43 \text{ MeV})$$

where  $\gamma$  represents gamma rays whose flux can be calibrated for H concentration.

If coatings are bombarded with a beam of accelerated beam <sup>15</sup>N ions at a precise energy, 6.385 MeV, the number of  $\gamma$  rays measured coming from the sample is proportional to the hydrogen concentration. There is negligible reaction with hydrogen with the beam energy increasing, but as the <sup>15</sup>N ions slow down passing through the film, the beam reached resonance energy at some depth, and the yield of  $\gamma$  rays was proportional to the hydrogen concentration at this depth. Thus, by measuring  $\gamma$ -ray yield versus <sup>15</sup>N energy, a concentration profile of H versus depth was determined.

In this research,  ${}^{1}H({}^{15}N,\alpha\gamma){}^{12}C$  resonance nuclear reaction method was employed to determine the hydrogen incorporation in the aluminum coatings. The sample was loaded in the analysis chamber at room temperature and bombarded by  ${}^{15}N$  ion of ~20 nA. The ion beam energies used for the depth profiles were 7.0 MeV (0.38 µm), 7.3 MeV (0.57 µm), 7.6 MeV (0.76 µm) and 7.9 MeV (0.79 µm). Measurements at 7.0 MeV were repeated to check the stability of each ion beam energy/depth then averaged.

**Glow Discharge Optical Emission Spectrometer (GD-OES).** To evaluate thickness and chemical distribution of APCVD aluminum coatings, LECO GDS-750A optical emission spectrometer was employed, which has the unique combination of fast sputtering rate, high depth resolution, excellent sensitivity and multi-element capability for surface and depth profile analysis [81-83]. Due to its ability of be applicable to conductive and semi-conductive materials up to depths of tens of micrometers GD-OES was selected to measure chemical depth profiles across aluminum oxide layers, aluminum coatings and the substrates. GD-OES was more sensitive than other depth profiling techniques like AES, detecting all elements of the periodic table with content above 10 ppm. The principle mechanism for GDS was as follows: positively charged argon (Ar+) ions generated by the electric field of the source are accelerated in a vacuum across the negative potential samples surface. These ions continuously bombard the sample and cause atoms to be ejected toward the anode, then subsequently excited or ionized in the negative glow of the plasma gas mainly by collisions with electrons, emitting energy in the form of characteristic light emission. The light emitted by the sample passes into the spectrometer to photomulitiplier tubes that simultaneously quantify the intensity of the spectral lines (wavelengths) in the emitted light. Each individual element in the sample has its own characteristic spectrum and its own unique wavelength.

### 2.5.3 Density Testing (He pycnometer)

The density determined using Accupyc 1330 (He pycnometer) is called skeletal density (true density). This method utilizes a gas (He) displacement technique to determine sample volume with high accuracy. The density was calculated using the measured sample weight. The measured sample volume excluded interstitial voids in bulk powders and any open pores in the individual particles where gases can access. Internal (closed) porosity was still included in the volume. This test was normally performed at room temperature, could be performed at a temperature in the range of 0 °C to 50 °C as well. Almost all of solid samples as well as some fluid samples could be measured by this technique [84, 85].

The density measurement method using He pycnometer and mercury porosimeter is widely used not only for coated sample, but for bulk samples. Generally, it comprises several steps. After general pre-treatment and aluminum deposition, the weight (Ws+c) and volume (Vs+c) of coated substrates were measured. Substrate weight (Ws) and volume (Vc) were measured after completely digesting aluminum coating from surface.

The density of coating was calculated according to the equation:

$$\rho_c = \frac{W_{s+c} - W_s}{V_{s+c} - V_s}$$

Unlike density measurement by X-ray reflectivity (XRR) that highly requires smooth (mirror-like surface) and thin coating, no particular coating requirements were needed in this method.

For precise measurement of coating density, selected substrate should possess maximal difference in weight and volume before and after aluminum deposition. For instance, cylindrical tube substrate (both-end open) rather than cylindrical bar (identical length and outer diameter) can provide more reliable density information of coating.

The procedure for digesting aluminum from parts is simple:

- 1) Preparing an NaOH solution by dissolving 5 wt.% NaOH in DI water in a hood
- 2) Immersing aluminized substrates into freshly prepared NaOH solution (at room temperature) and waiting until no hydrogen bubbles generated, then waiting another 5-10 minutes. Since produced fumes are very corrosive and will irritate throat, eyes and skin, much more attention needs to be paid

3) Rinsing substrate thoroughly with water and drying in the air.

# **2.5.4 Electrical Properties**

**Electrical Sheet Resistance Measurements.** Resistivity is one of the most important properties revealing uniformity and purity of the deposited aluminum coating. Electrical

sheet resistance measurement was conducted using a four-point (FPP) resistance probe with a mode of FPP-100 from Veeco instrument Inc. in NJIT.

Measurement on an Al coating deposited on a steel substrate is not possible because the interface between the Al coating and the steel substrate provides an electrical (grounding) contact. Samples prepared for electrical resistivity measurements consist of AISI 4130 steel coupons on top of which an insulating silicon nitride layer (1µm thick) is synthesized by plasma enhanced chemical vapor deposition (PECVD). Optimal conditions for this PECVD process were established to be a deposition temperature of 350 °C, RF power of 50 W, flow rates of SiH4 at 280 sccm and NH<sub>3</sub> at 4 sccm, and process pressure of 900 mTorr. APCVD Al coatings are deposited on top of these insulating layers at 300 °C without shielding the substrate. The electrical resistivity measurement is conducted using a four-point probe (Veeco FPP-5000).

**Electrical Contact Resistance (ECR).** Electrical and electronic equipment often require a low electrical resistance on its finished surfaces for uninterrupted contact, grounding, and electromagnetic field shielding purposes.

The test method given in MIL-DTL-81706A evaluates a coating system's ability to provide initial electrical contact resistance after application of post-treatment such as chromate conversion coating, and after exposure to a corrosive environment. In accordance with MIL-DTL-81706A, the samples evaluated in this test included APCVD Al coatings as deposited and post-treated with glass bead burnishing followed by a Cr(VI) conversion coating (Iridite<sup>TM</sup> 14-2). The electrical contact resistance (ECR) measurements were conducted before and after continuous exposure to a neutral salt fog for 168 hours. Operation of the fog chamber for this test is done in accordance with

ASTM B 117 [Standard Practice for Operating Salt Spray (Fog) Apparatus]. The samples were placed into a fog chamber at a 6-degree angle. The coupons were not allowed to contact other surfaces in the chamber, and condensate from a coupon did not contact any other coupons. The salt solution and the fog chamber were prepared as specified in the Test Methodology of the Nonchrome Aluminum Pretreatment Project (NCAP) Joint Test Protocol (JTP). The nozzles were adjusted in the fog chamber so that sprayed salt solution did not directly impinge on the coupon surfaces. After exposure, the coupons were carefully removed and cleaned with running water at a temperature less than 38°C (100°F). The coupons were then air-dried at ambient conditions, and then visually examined for corrosion.

#### **2.6 Performance Testing of APCVD Aluminum Coatings**

#### 2.6.1 Mechanical Testing

The mechanical characterization of the aluminum coatings consists of measurements of hardness, Young's modulus, adhesion, tensile strength and fatigue debit testing.

**Nanoindentation Testing.** Nanoindentation is a depth-sensing indentation testing for characterization of material mechanical properties in the sub-micrometer rage, a few square micrometers or even nanometers. In such a test, a hard tip is pressed into a sample to make such tiny indentations while recording load and displacement with very high accuracy and precision. Then hardness and modulus properties are obtained by analyzing the load displacement data [86].

In this study to estimate the hardness and Young's modulus of aluminum coatings [86, 87], nanoindentation testing was performed using the Hysitron nanoindenter device

equipped with a triangular (Berkovich) pyramid-shaped diamond tip as shown in Figure 2.10. It is a low load nanomechanical test system for measuring the hardness and elastic modulus of thin films and coatings.



Figure 2.10 Hysitron nanoindenter equipment and the associated schematic diagram.

Young's modulus is calculated based on the reduced modulus (Er) from nanoindentation test:

$$\frac{1}{E_{r}} = \left[\frac{\left(1-\nu^{2}\right)}{E}\right]_{Specimen} + \left[\frac{\left(1-\nu^{2}\right)}{E}\right]_{Indenter}$$

where E and v are the Young's modulus and Poisson's ratio, respectively.

Adhesion Testing. Adhesion test (pull test) to evaluate adhesive bond strength between aluminum coating and the steel substrate was carried out using the SEBASTIAN FIVE-A, with the maximal load of 1755 kg/cm<sup>2</sup> and the accuracy of within 1% at 20  $\pm$  4 °C, as shown in Figure 2.11. Figure 2.12 illustrates the overall layout and method of mounting stud on sample. For comparison, similar measurements of thermal oxide film on silicon were conducted as well, which exhibited relatively high adhesion (498.3 kg/cm<sup>2</sup>).

Prior to adhesion test, aluminum coated sample was mounted onto a stud by curing standard high strength epoxy between them on a hotplate at 150 °C for one hour, then cooling down to room temperature. Adhesion test was also confirmed by examining

previously mounted surface area of the sample with FE-SEM/EDX after adhesion measurement.







Figure 2.12 Overall layout and method of mounting stud on sample.

**Tensile Testing.** A tensile test, also known as tension test, is probably the most fundamental type of mechanical test performing on material. By pulling on material, its strength will be evaluated along with how much it will elongate. A complete tensile profile can be obtained by continuing to pull on the material until it breaks. A curve will result showing how it reached to the forces being applied. The point of failure is of much interest and is typically called its ultimate strength strength (UTS).

According to the specification provided by an independent source (Dirats Laboratories, Westfield, MA), the UTS of the notched round bars used for HE testing was 400.7 ksi (mean value of 10 bars) with a minimum of 395.1 and a maximum of 405.2 ksi. Tensile tests were carried out by applying a load to the bars at a constant rate of 1,000 lb per minute until fracture occurred. As per Table 2 in the ASTM F 519-97 test method, the notched fracture strength (NFS) of the specimens under evaluation should exhibit a difference within  $\pm 10$  ksi of the average value measured for the bars [88].

### 2.6.2 Hydrogen Embrittlement (HE) Testing

Hydrogen embrittlement (HE) testing was performed by NAVAIR according to ASTM F519-05 "Standard Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating Processes and Service Environment". Notched round bars used in this test were type 1a.1 (per ASTM F519-05) made of AISI E4340 steel per MIL-S-5000E. The bars were 2.540" long with a notched diameter of 0.1750" (Figure 2.13). They were quenched and tempered per AMS-H-6875A to hardness of 51-53 Rockwell C. According to the specification provide by manufacturer (Dirats laboratories, Westfield, MA), the ultimate tensile strength of the notched round bar is 400.7 ksi (mean value of 10 bars) with min. 395.1 and max. 405.2 ksi.

HE test consisted of applying a load (75 % of the ultimate tensile strength (UTS) of bare notched round bar) to specimens and sustaining the load for 200 hrs. Subsequently, the sustained load was stepped up by 5 % per hour until the specimens were fractured. Substrate qualified with HE test must withstand the 200-hour test period without showing any signs of fracture.



**Figure 2.13** Circular notched round bar (ASTM 519-05 Type 1a.1) with dimension of d=4.445 mm (0.1750"), D=6.350 mm, and L=64.567 mm (2.540").

#### 2.6.3 Sliding Friction Testing

Sliding friction samples consisted of cadmium coated mild steel and APCVD aluminum coated 4340 steel substrates. The steel substrates were initially Rockwell C52 and nominally 1" diameter round flats, 0.5" in thickness.



Figure 2.14 Pin-on-disc tribometer test apparatus.

APCVD aluminum coatings deposited at ~300 °C using a blended TIBA precursor and no post treatment was performed. The cadmium coated samples were mild steel panels, with electroplated cadmium per SAE AMS QQ-P-416, Class II, Type II. The initial friction of each coating was measured using a pin-on-disk technique. The samples were then subjected to ASTM-B117 salt fog chamber for a total duration of 75 hours. The samples were removed from the chamber for observations and friction measurements at intervals of 3, 51, and 75 hours. After each removal from the chamber, the samples were rinsed in deionized water and allowed to dry in ambient conditions for at least two hours before testing. Different wear tracks were used for each test.

The relative sliding friction of each coating was measured using the Pin-on-Disc technique. The system consisted of an Implant Sciences Corp ISC-200 tribometer and a computer interface data acquisition unit, PC-stripchart, which is a computer based chart recorder used to display and store data in real time. The samples were mounted on the top of a rotating platform of the tribometer (in Figure 2.14). A 0.5-inch diameter stainless steel ball (pin) was attached to a precision balanced lever arm that was used to both apply vertical loads to the disc and to read the friction force on the pin. The ball was put in contact with the surface of the sample and a load was applied. To measure friction coefficient of the sample, the applied load used was 10 grams. The sample was then rotated and the total distance the steel ball traveled on the sample was set. In this case, it was rotated 200 revolutions (approx 8 meters). All the friction measurements were conducted in dry condition (without lubrication).

#### **2.6.4 Corrosion Testing**

**Potentiodynamic Polarization Measurement.** Measurement of polarization can provide significant useful information in terms of corrosion mechanisms, corrosion rate and susceptibility of a metal over a wide range of oxidizing conditions in a single test solution.

Polarization methods involve changing the potential of working electrode and monitoring current response as a function of potential. A Flat cell (Princeton Applied Research) was used for both potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) with a three-electrode configuration consisting of a saturated calomel electrode (SCE), a platinum gauze reference and auxiliary electrodes. The specimen exposure area was 1 cm<sup>2</sup>.

To investigate anodic polarization behavior of APCVD aluminum coatings, potentiodynamic polarization experiments were performed in 3.5 wt.% NaCl solution with and without  $O_2$  saturation at room temperature using a Gamry Reference  $600^{TM}$  Potentiostat. Potentiodynamic polarization was measured with a scan rate of 10 mV/min from -0.2 to +1.5 V versus the open circuit potential (OCP) after 1 hr immersion.

**Electrochemical Impedance Spectroscopy (EIS) Measurement.** Electrochemical impedance spectroscopy (EIS) as a function of immersion time (up to 10 days), tests were performed using a Gamry Reference 600 in 3.5 wt.% NaCl saturated with oxygen at room temperature in a frequency range of 0.01 Hz to 100 kHz. The Ac amplitude used was 10 mV at open circuit potential. An electrochemical flat cell (Princeton Applied Research) used in these measurements has a three electrode configuration including working electrode (sample), a saturated calomel electrode (reference electrode), and a platinum gauze (an auxiliary electrode). All electrochemical tests were carried out with an exposure area of 1 cm<sup>2</sup>. IVD aluminum coating, aluminum foils (99.999% purity) and AISI 4130 steel coupons were used as references for comparative purposes. Both Bode magnitude plots and Nyquist plots of the data were obtained as representatives of characteristic corrosion behavior.

**Corrosion Screening Testing.** Corrosion tests based on ASTM B117 Salt Fog including bare and painted aluminum coatings (~20 µm thickness) to evaluate their general corrosion resistance and ability to provide sacrificial (galvanic) protection to the steel substrate materials. Bare Al-coated specimens consist of unscribed and scribed coupons, post-treated both with and without a trivalent chromium conversion coating (TCP) or other post-treatment. Painted Al coatings are painted with a MIL-PRF-23377C primer and a MIL-PRF-85285 topcoat. In addition, a paint adhesion test - based on ASTM D3359 Method A - can be conducted before and after corrosion testing.

Stage	Description	Time, min	Temp., ±3°C
1	Ramp to salt fog test conditions	15	25
2	Salt fog cycle	1	25
3	Dry cycle	15	30
4	Ramp to salt fog test conditions	70	25
5	Salt fog cycle	1	25
6	Dry cycle	15	30
7	Ramp to salt fog test conditions	70	25
8	Salt fog cycle	1	25
9	Dry cycle	15	30
10	Ramp to salt fog test conditions	70	25
11	Salt fog cycle	1	25
12	Dry cycle	15	30
13	Ramp to relative humidity test conditions	15	49
14	Humidity cycle	480	49
15	Ramp to drying test conditions	15	60
16	Dry cycle	480	60
17	Ramp to ambient temperature test conditions	15	25
18	Ambient temperature cycle	480	25

 Table 2.2 GM 9540P Cyclic Corrosion Test Sequence GM

**Cyclic Immersion Corrosion Testing.** Corrosion more representative of in service conditions was measured at the Army Research Laboratory facilities using the GM 9540P Method B 18-stage testing protocol (Table 2.2).

The AISI 4130 steel panels were 25mm wide by 35mm long (scribed) or 50mm long (unscribed) and about 1mm thick. These were coated with APCVD Al for this test. Some received a commercial, trivalent chromium [Cr(III)] CCC post-treatment. The C-ring specimens were coated with AlumiPlate Al, and some of these received a commercial, Cr(VI) CCC post-treatment. An Atotech Model CCT-NC-20 chamber was used to perform the testing. Standard steel mass loss specimens were used to calibrate this chamber. The test solution was 0.9 % NaCl + 0.1 % CaCl<sub>2</sub> + 0.25 % NaHCO<sub>3</sub>. The arbitrary acceptance criterion was 80 cycles with no visible red rust for unscribed specimens and 40 cycles for scribed specimens.

### **CHAPTER 3**

# **RESULTS AND DISSCUSIONS**

# 3.1 Surface Morphology

Figure 3.1 (a) and (b) illustrate the morphology of the surface of APCVD aluminum coated steel coupon and bolt (thread), respectively. The analyses revealed that the aluminum coatings were dense and the overall surface of the substrates was completely covered with the coating.



Figure 3.1 FE-SEM images of aluminum coatings on a steel coupon (a) and bolt (b).





In addition, Figure 3.2 illustrates the topography of the Aluminum coating, which is relatively rough on a nanoscale ( $R_{RMS}$ =917 nm) compared to the underlying steel substrate surface ( $R_{RMS}$ = 160 nm).

# 3.2 Microstructure of Aluminum Coating

The microstructure of a coating has a significant effect on its performance. For a coating with a certain composition the microstructure can be altered through varying the processing route used.



**Figure 3.3** Visual depiction of cross-sectional aluminum coating for different deposition technologies.

Figure 3.3 visually depicts the relative difference of microstructure of coating structure among APCVD aluminum, IVD aluminum and sputtered aluminum [89]. Sputtered aluminum is a denser coating than IVD and APCVD aluminum and was expected to better performance on corrosion protection. However, both sputtered and IVD aluminum show a columnar structure, while it is clear that APCVD aluminum coatings exhibit a non-columnar structure with a rugged surface ( $\sim 20 \mu m$ ). Pure aluminum coated by APCVD process on high strength steel for corrosion protection, will perform better compared to sputtered and IVD coating.

## 3.3 Coating Structure

The microscopic structure of aluminum coatings on AISI 4130 coupons with APCVD process was inferred from x-ray diffraction measurements. Diffraction pattern of aluminum coatings deposited at 275 and 300 °C suing pure TIBAL and 300 °C using a blended TIBAL was shown in Figure 3.4 along with the aluminum powder diffraction pattern. Aluminum coatings were polycrystalline (face centered cubic structure) regardless of deposition conditions.

	Miller indices (hkl)	FWHM (deg)			
20 (deg)		Pure TIBAL	Pure TIBAL	Blended TIBAL	Al foil
		(275 ℃)	(300 °C)	(300 °C)	
38.47	(111)	0.0960	0.1968	0.2165	0.1030
44.74	(200)	0.1200	0.1574	0.1680	0.1410
65.14	(220)	0.1200	0.1378	0.4320	0.1270
78.23	(311)	0.1200	0.1920	0.3360	0.1040
82.44	(222)	0.0960	0.1440	0.4320	
99.08	(400)	0.1920	0.3840	0.5760	
112.05	(331)	0.2400	0.1680	0.3360	
116.57	(420)	0.1440	0.1920	0.2880	
137.46	(422)	0.2880	0.2400	0.4800	

**Table 3.1**Full Width at Half maximum of All Peaks Measured from XRD Analysison APCVD Aluminum Coated Steel and Aluminum Foil

The full width at half maximum (FWHM) of each peak , shown in Table 3.1, together with that of aluminum foil, indicated that there was slight difference in the value of FWHM between aluminum coatings with different deposition conditions. Meanwhile,

all the coatings exhibit high degree of crystallinity expressed by FWHM compared to that of pure aluminum foil.



Figure 3.4 XRD pattern of APCVD aluminum coatings on steel substrates.

## 3.4 Coating Composition

#### 3.4.1 AES Analyses

Aluminum coatings deposited on steel substrates at 275 and 300 °C using pure TIBA and blended TIBA at 300 °C were analyzed by AES to obtain comprehensive information about composition as a function of depth. As mentioned earlier in the characterization method section, three different areas on APCVD aluminum-coated steel substrates were examined. Coating thicknesses corresponding to each deposition condition were 15.6, 13.1 and 16.9  $\mu$ m, respectively.

Using AES, additional information about impurity elements was gathered for the surface, as well as for the bulk of aluminum coatings. Figure 3.5 shows an elemental AES survey of the surface of APCVD aluminum coating using pure TIBAL at 300 °C,

exhibiting signals of aluminum, oxygen, carbon. The tendency of aluminum to combine readily with oxygen in the environment to form a thin corrosion-resistant film of  $Al_2O_3$ accounted for the presence of the oxygen in the spectrum, whereas the carbon was considered here to be surface contaminants.



Figure 3.5 AES elemental survey of APCVD aluminum coatings at surface.

A second elemental survey taken at a depth of ~200nm exhibited the expected aluminum peaks and low levels of oxygen and carbon, as shown on Figure 3.6.



Figure 3.6 AES elemental survey of APCVD aluminum coating at a depth of ~200nm.

Depth profiles analysis achieved by ion-beam sputtering with Ar reveals in Figure 3.7 the rapid decrease in the oxygen concentration below the surface level and the increase

and subsequent stabilization of the pure aluminum signal with the bulk of the coatings. Atomic concentration of carbon and oxygen as impurities detected in depth was found to be 1.8 and 5.6 at.% respectively, with pure TIBAL at 275 °C; 0.7 and 2.2 at.% with pure TIBAL at 300 °C; 0.2 and 11.0 at.% with blended TIBAL at 300 °C. Aluminum concentration in each deposition conditions was the balance with 92.6, 97.1 and 88.8 at% respectively. Due to the inhomogeneous and rough surface of aluminum coatings, Ar etching used for depth profiling was not able to completely remove the coatings layer by layer, indicating that oxygen concentration detected in the deep region appeared to be attributed mostly to a native aluminum oxide presenting on coating surface.




**Figure 3.7** AES depth profiles of APCVD aluminum coatings produced with different deposition conditions achieved by ion-beam sputtering with Ar.



**Figure 3.8** AES depth profile of carbon impurity present in aluminum coatings produced with different deposition conditions achieved by ion-beam sputtering with Ar.

Figure 3.8 shows depth profile of carbon impurity concentration for each deposition conditions. APCVD aluminum coatings prepared with pure TIBAL exhibited the decrease in carbon concentration with the increase in deposition temperature of 275 to 300 °C. In addition, the value with blended TIBAL was found to be lower than that of aluminum coatings with pure TIBAL. In the case of the APCVD aluminum coatings

deposited at 300 °C using either pure or blended TIBAL, significant low carbon concentrations were noted (< 1.0 at.%).

Furthermore, it has been reported that TIBAL pyrolysis on aluminum (100) at a temperature below 327 °C resulted in carbon-free aluminum deposition [37]. Considering the APCVD aluminum deposition temperature used (275 and 300 °C) it is assumed that the carbon detected in the aluminum coatings mostly originated from carbon contamination, not from the reaction of TIBAL pyrolysis during deposition.

## 3.4.2 XPS Analyses

To evaluate both the composition and element's bonding environment of aluminum coatings, XPS analysis was conducted on aluminized steel substrates with different deposition conditions.

Typical XPS survey spectrums of aluminum coating using pure TIBAL at 300 °C on the surface and at a depth of ~120 nm were shown in Figure 3.9 and Figure 3.10, indicating all peaks for oxygen, carbon, and aluminum consistent with the AES analysis.



Figure 3.9 XPS spectrum of APCVD aluminum coatings at surface.



Figure 3.10 XPS spectrum of APCVD aluminum coating at a depth of ~120 nm.

XPS spectra of Al 1p, O 1s, and C 1s in aluminum coatings were plotted as a function of argon sputter/etching level in Figure 3.11 without correction for binding energy shift due to surface charging. The surface of aluminum coatings was charging slightly because of aluminum oxide film naturally formed. The convention for determining chemical composition in XPS data analysis was to reference the measured peak energy to the well-known energy of C 1s line for elemental carbon, typically having a binding energy of 285 eV. C 1s peak on aluminum coating surface was positioned at 287.4 eV. Therefore, the surface charging caused all peaks shifting up in binding energy by approximately 2.4 eV.

This binding energy shift also was seen in the Al 2p line. The reference XPS data base from NIST gives a range of energies for  $Al_2O_3$  from 74.2 to 74.9 eV. The approximate average of these values (74.5 eV) was used for charge referencing in the Aluminum coatings, as long as there was enough oxygen to ensure an oxide existing. As the sputter etching time increases, Al 2p peak was clearly seen, indicating that coatings were mostly pure aluminum in the bulk region. As for the carbon present in the Aluminum coatings, the binding energy of C 1s with increasing sputter etching was found to approach to 285 eV, implying that the carbon observed in the coatings appeared to exist as elemental carbon and/or as carbide. It could be concluded that aluminum coatings were contaminated with carbon, which was not form TIBAL pyrolysis process. This result was consistent with the AES analysis.

XPS results were gathered on aluminum coatings deposited at 275 and 300 °C with pure TIBAL and at 300 °C with blended TIBAL, revealing that all aluminum coatings exhibited no difference in the composition chemistry regardless of deposition conditions.





**Figure 3.11** XPS Al 2p, O 1s, and C 1s spectra as a function of sputter time for the APCVD aluminum coatings.

## 3.4.3 GD-OES Analyses

To know bulk chemical compositions of APCVD aluminum coatings, LECO glow discharge optical emission spectroscopy with quantitative depth profiling (GD-OES -QDP) was used for quantitative depth characterization. Before analyzed by GD-OES, the samples were cleaned with spectroscopically clean hexane.

The QDP results for the two samples were plotted in Figure 3.12 and Figure 3.13, indicating that the coatings were made for elements C, O, N and Al. The depth at which the Al-Fe analyze curves cross over (50-50 point) represents the thickness of the coatings on top of the substrate. Stable plasma was achieved after a depth of 0.020  $\mu$ m for both samples, below which data should be discarded for any analysis. The QDP analysis shown high pure aluminum coatings were deposited by APCVD methods using blended TIBAL on steel coupons with thickness of 26.93  $\mu$ m at 275 °C and 30.42  $\mu$ m at 300 °C, respectively. Meanwhile, the QDP results illustrated no impurities was presented at the interface between the aluminum coating and the steel, indicating good pre-cleaning of substrates.



Figure 3.12 GD-OES depth profiles of APCVD aluminum coatings at 275 °C.



Figure 3.13 GD-OES depth profiles of APCVD aluminum coatings at 300 °C.

# 3.4.4 NRA Analyses

The hydrogen incorporation in the Aluminum coatings was evaluated by NRA with a <sup>15</sup>N ion beam probing different depths. The concentrations of hydrogen incorporated in the aluminum coatings as a function of coating depth was shown in Figure 3.14.



Figure 3.14 Depth profile of hydrogen present in APCVD aluminum coatings.

The significant drop in H measured between beginning of the first run at 7 MeV and the end of the final run at 7 MeV was observed in the aluminum coatings deposited on the rivet substrates. This effect was much smaller (or absent) in the larger planer sample such as the Aluminum coating deposited on the steel coupon at 300 °C using blended TIBAL, indicating that there was an unstable component of the H in the aluminum coatings deposited on the rivet substrates at 275 and 300 °C using pure TIBAL. Nonetheless, the results revealed that the hydrogen concentration was well below 1% (atomic) in depth of  $0.8 \,\mu\text{m}$ .

#### **3.5** Electrical Properties

15 16

### 3.5.1 Electrical Sheet Resistance

Electrical sheet resistance measurements on aluminum coatings were conducted using a four-point resistance probe (Veeco FPP-5000). Direct measurements of the electrical sheet resistance of aluminum coatings deposited on steel substrates were not possible

because of an electrical contact of the interface between the aluminum coatings and the steel substrates.

Samples were prepared for electrical resistivity measurements with an insulating silicon nitride layers (1 $\mu$ m thickness) between aluminum coatings and steel substrates, which were synthesized by plasma enhanced chemical vapor deposition (PECVD). Optimal conditions for this PECVD process were established to be deposition temperature of 350 °C, RF power of 50 W, flow rates of SiH<sub>4</sub> (280 sccm) and NH<sub>3</sub> (4 sccm) and process pressure of 900 mTorr. APCVD aluminum coatings (~14.7  $\mu$ m thickness) were deposited on top of these insulating layers at 300 °C without shielding the substrates.



Figure 3.15 SEM image of an aluminum coating deposited on  $Si_3N_4$ -coated steel substrate.

Electrical resistivity value of aluminum coating was found to be  $3.5 \pm 0.1$  µohm·cm, close to that of bulk aluminum (2.7 µohm·cm), indicating good electrical conductivity of APCVD aluminum coatings. The morphology of aluminum coatings on silicon-nitride-coated steel substrates was shown in Figure 3.15, revealing no different with that coated on steel substrates.

## **3.5.2 Electrical Contact Resistance**

The ECR test results are shown in Table 3.2. All samples passed the initial electrical contact resistance test criterion by measuring less than 5 milli-ohms per square inch. After the Al deposited coatings (with chromate conversion coatings) were removed from the salt fog chamber, rinsed and dried, they were subjected to electrical contact resistance measurement. The results were a little higher than those measured before salt fog exposure.

Sample	Condition	ECR (milli-ohms/in <sup>2</sup> )					
Sumpre	Condition	Before Salt Fog	Testing	After Salt Fog Testing			
ADOVD AL at 27590	A a damaaita d	1.76	Ave.	1.79	Ave.		
APCVD AF at 275°C	As deposited	1.56	1.66	1.70	1.75		
APCVD Al at 300°C		1.70	Ave.	2.78	Ave.		
	As deposited	1.71	1.71	2.29	2.54		
		1.83		1.80			
		1.78		1.89			
APCVD Al at 310 –	Glass bead burnishe	1.87	Ave.	2.16	Ave. 1.90		
320°C	d and with chromate	1.96	1.84	1.79			
	conversion coating	2.00	7	1.88			
		1.60	1	1.90			

**Table 3.2** Electrical Contact Resistance of APCVD Aluminum Coatings

### **3.6 Mechanical Properties**

### 3.6.1 Young's Modulus and Hardness

Young's modulus and Poisson's ratio of the indenter were 1140 GPa and 0.070, and Poisson's ratio of polycrystalline bulk aluminum is 0.345. Prior to the measurement on the aluminum coatings the calibration was conducted by using the fused quartz with reduced modulus of 70.7 GPa and hardness 10.0 GPa. Afterward the aluminum single

crystal with (100) orientation was used as a reference sample, resulting in hardness of  $836.5 \pm 215.4$  MPa and Young's modulus of  $40.7 \pm 3.6$  GPa.

# 3.6.2 Adhesion Testing

The adhesion (pull-off) test on aluminum coating samples was conducted to obtain information about the adhesive bond strength of the aluminum coatings to the steel substrate. No failure of adhesion was observed by FE-SEM/EDX inspection.

The adhesive strengths of aluminum coating using pure TIBAL and blended TIBAL were  $703 \pm 85 \text{ kg/cm}^2$  and  $684 \pm 30 \text{ kg/cm}^2$ , respectively, indicting no significant difference between the coatings with different precursors. Furthermore, these results were even superior to those measured for thermal oxide on silicon (498.3 kg/cm<sup>2</sup>).

#### **3.7** Tensile Strength Tests

Bare bars without pretreatment were used as control in tensile testing. Aluminum coated bars with and without baking (23 hr at 190.6 °C) were tested to examine tensile strength and hydrogen embrittlement. Meanwhile, the effect of deposition temperature on the weakening of notched round bars was evaluated through tensile testing on the bars treated in the APCVD process chamber only with heat. The temperatures of the heat treatment were 250, 275, and 305 °C with exposure time of 20 minutes that is normal deposition time and 275 °C for 45 minutes to see the effect of elongation of exposure time. The time of 45 minutes represents the time needed to obtain the same coating thickness as that at 300 °C. Additionally, to evaluate the effect of HCl etching in pre-cleaning procedure on the hydrogen embrittlement, bars pre-cleaned only in HCl were tested.

According to the factory specification, the ultimate tensile strength (UTS) of the bars was 400.7 ksi (average of 10 bars) with a minimum value of 395.1 ksi and a maximum one of 405.2 ksi. To confirm this, tensile testing on 4 uncoated bare bars was performed at NAVAIR, resulting in average UTS of 407.3 ksi and a higher standard deviation than the factory value (Table 3.3). Instead of using the factory value, the average UTS value of 407.3 ksi from our measurement was adopted as the reference for this effort.

Lot AU Uncoated Bars tensile test pull at 1000 lbs/minute										
Number	Percentage	rcentage ksi Mean (ksi) Tensile Strength (Factory) ksi Differ								
AU4225	103.3%	413.9								
AU4245	103.3%	413.9	407.3	400.7	6.6					
AU4354	96.7%	387.4	407.5	400.7						
AU4492	103.3%	413.9								

 Table 3.3
 Tensile Strength of Uncoated Bare Notched Round Bars

Sample pretreatments used in these tests are briefly described in Table 3.4. As a control experiment, bare bars without pretreatment were used in tensile test. Aluminum coated bars with and without baking (23 hr at 190.6 °C) were tested to examine tensile strength and hydrogen embrittlement. The effect of deposition temperature on the weakening of notched round bars were evaluated through tensile test of heating treated bars. The temperature in heat treatment was at 250, 275, and 305 °C with exposure time of 20 minutes. Another heat treatment at 275 °C and of 45 minutes was conducted to examine the effect of extending exposure time on tensile strength of the samples. Additionally, bars pre-cleaned with HCl solution were tested to evaluate the effect of HCl etching in pre-cleaning procedure on the hydrogen embrittlement.

Amou	int		
Tensile	HE	Description of samples	Sample pretreatment*
test	test		
	0	Uncoated bare bars without	NLa
4	0	pretreatment or aluminum coating	100
		Aluminum coated bars (22.1 $\mu\mu$ )	
4	4	with deposition temperature	RO/S+HCl+dil NaOH
4	4	of 310 ~ 320 °C;	+2X Acet+Vac Dry
		no baking performed	
		Aluminum coated bars (17.3 $\mu$ m)	
4	4	with deposition temperature	RO/S+HCl+dil NaOH
4		of 295 ~ 305°C;	+2X Acet+Vac Dry
		baked (23 hr-190 °C)	
4	0	Heat only treated bars	RO/S (No HCl)+dil NaOH
4	U	at 250 °C for 20 minutes	+2X Acet+Vac Dry
	0	Heat only treated bars	RO/S (No HCl)+dil NaOH
4	0	at 275 °C for 20 minutes	+2X Acet+Vac Dry
	0	Heat only treated bars	RO/S (No HCl)+dil NaOH
4	0	at 275 °C for 45 minutes	+2X Acet+Vac Dry
	2	Heat only treated bars	RO/S (No HCl)+dil NaOH
4	3	at 305 °C for 20 minutes	+2X Acet+Vac Dry
		Pretreatment only bars	DO/SHUCH HINGU
2	2	including 12 wt.% HCl	KO/S+HCI+dil NaOH
_		cleaning only for 4 minutes	+2X Acet+Vac Dry

**Table 3.4** Tensile and Hydrogen Embrittlement Samples

#### \* Sample pretreatment

RO/S: Removing oil with solvents, rinsing with Heptane and Acetone, drying with nitrogen blowing HCl: acid etching in 12.5 wt.% HCl solution at room temperature for 4 minutes, rinsing with water Dil NaOH: rinsing with diluted NaOH (3~5 wt.%) solution at room temperature for 2 minutes 2X Acet: Rinsing with nonaqueous acetone by two times to remove water at room temperature Vac Dry: Drying in vacuum

The results of tensile testing of aluminum coated bars with or without baking at 190.6 °C for 23 hrs was given in Table 3.5 indicating that the tensile strength of the aluminum coated bars after baking was slightly greater than that of without baking. Regardless of baking, the coated bars underwent a loss of  $4.6 \sim 15.3$  % from the ultimate tensile strength of the bare bars. The weakening of these bars appeared to be attributed to the deposition temperature (~300 °C) of the process. Therefore, the effect of deposition temperature on the weakening of notched round bars was evaluated through tensile testing

on heat treated bars only (no deposition). The temperatures used for the heat treatment were 250, 275, and 305 °C and the heat treating time was 20 minutes to simulate deposition time.

**Table 3.5** Results of Ttensile Testing of APCVD Aluminum Coated Notched RoundBars Before and After Baking at 375 °F (190.6 °C) for 23 Hrs

Lot AU CVD Aluminum Coated Bars without baking tensile test pull at 1000 lbs/minute									
NumberPercentag eksilMean (ksi)Tensile Strength (uncoated bars) ksi									
AU4212	90.4%	362.3							
AU4007	82.5%	380.6	2.0.4	407.2	16.0				
AU4046	89.7%	359.3	360.4	407.3	-46.9				
AU4011	84.7%	339.2							

Lot AU CVD Aluminum coated Bars with baking (23 hr-375 °F) Pull only Tensile Test									
Number	Percentag	VSI	Mean	Tensile Strength (uncoated	Differenc				
Number	e	L DI	(ksi)	bars) ksi	e				
AU4057	95.4%	382.3							
AU4265	93.5%	374.5	272 2	407.2	24.1				
AU4365	92.3%	369.7	575.2	407.3	-34.1				
AU4292	91.4%	366.3							

Heat treatment was also conducted on a sample at 275 °C for 45 minutes to evaluate the effect of heat treating time. The results given in Table 3.6 revealed that the loss in tensile strength is highly dependent on temperature while no significant difference in tensile strength was seen with exposure time at a given temperature.

The effect of the pre-cleaning procedure including HCl etching on tensile strength was evaluated through tensile testing. As shown in Table 3.7, the results indicated no effect.

Lot AU Heat Only Bars Pull only Tensile Test, 250°C with exposure of 20 Minutes									
Number	Percentage	1:	Mean	Tensile Strength (uncoated	Differenc				
Number		KSI	(ksi)	bars) ksi	e				
AU4148	95.5%	382.6							
AU4379	94.0%	376.5	2025	407.2	22.0				
AU4475	4475 95.9% 38		383.3	407.3	-23.0				
AU4217	97.4%	390.5							

 Table 3.6
 Results of Tensile Testing of Notched Round Bars Treated with Heat Only

Lot AU Heat Only Bars Pull only Tensile Test, 275°C with exposure of 20 Minutes								
Number	Demoente de	kci	Mean	an Tensile Strength (uncoated				
Inumber	reicentage	K31	(ksi)	bars) ksi	e			
AU4251	91.9%	368.3						
AU4332	94.3%	377.8						
AU4022	93.2%	373.6	373.2	407.3	-34.1			
AU4049								
*	NA	NA						
*Note round bar AU4049 was tested but a software error occurred during testing giving a false result which								
is not listed	in the data							

Lot AU Heat Only Bars Pull only Tensile Test, 275°C with exposure of 45 Minutes									
Number Percentage KSI			Mean	Tensile Strength (uncoated	Differenc				
INUITIOCI	rereentage	IX51	(KSI)	bars) KSI	e				
AU4066	94.1%	377.2							
AU4138	90.4%	367.2	2742	407.2	22.1				
AU4013	94.4%	378.2	574.2	407.3	-33.1				
AU4262	93.4%	374.3							

Lot AU Heat Only Bars Pull only Tensile Test, 305°C with exposure of 20 Minutes									
Number Demonstrate VSI		VSI	Mean	Tensile Strength (uncoated	Differenc				
Number	reiceinage	K 51	(KSI)	bars) KSI	e				
AU4142	91.4%	366.1							
AU4099	91.0%	364.8	265 4	407.2	-41.9				
AU4374	90.4%	362.3	303.4	407.3					
AU4226	91.9%	368.2							

Table 3.7	Results of Tensile	Testing of Notched	Round Bars	Treated with	HCl Cleaning
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Lot AU Clean Only Bars 4 min 12 % HCl Pull only tensile test								
Number	Number Environment Result							
AU4437	Air	Passed fractured at 103.6%						
AU4458	Air	Passed fractured at 103.7%						

As mentioned in the previous subsection, hydrogen embrittlement (HE) testing was performed on aluminum coated bars with and without baking. Tests were also conducted on heat-treated bars and pre-cleaned bars (without aluminum coatings) in air. Aluminum coated bars without post baking experienced a premature failure of HE due to hydrogen gas that evolved as one of the byproducts during the APCVD Aluminum process and was absorbed by the substrates, implying that post baking was necessary to relieve the absorbed hydrogen from the substrate. To address this issue, aluminum coated bars were subjected to the baking at 190.6 °C for 23 hrs immediately after deposition.

				Avg. Notched Tensile Strength		% Notched Tensile					Process
Coating	Steel	Heat Treat	Spec. No	(lbf)	Environment	Strength	Total Hours	Spec. Fail?	Step Load?	Step Load Fail?	Embrittling?
			D-1				. 31	Yes	•	· •	
			D-2				30.9	Yes	-	-	
ALCVD			D-3				31	Yes	-	-	
275 °C	4340	190C/23hr	D-4	9,054	3.5% Salt Soln	45	31	Yes	-	-	Yes
			D-9				48.4	Yes	Req'd	•	
			D-10				200	No	Yes	Yes, 85%, 30 min	
AI CVD			D-11				200	No	Yes	Yes, 85%, 32 min	
275 °C	4340	190C/23hr	D-12	9,054	Lab Air	75	200	No	Yes	Yes, 90%, 0 min	Yes
			C-5				0.3	Yes	-	•	
			C-6				0.5	Yes	-	•	
ALCVD			C-7				2.8	Yes	-	•	
275 °C	4340	None	C-8	8,805	Lab Air	75	1.7	Yes	-	-	Yes
			B-5				200	No	N/A	N/A	
			B-6				200	No	N/A	N/A	
AI CVD			B-7				200	No	N/A	N/A	
300 °C	4340	190C/23hr	B-8	8,744	Lab Air	75	200	No	N/A	N/A	No

**Table 3.8** Results of Preliminary Hydrogen Embrittlement Testing

The results of the preliminary HE testing shows in Table 3.8 reviewing that the specimen coated with APCVD aluminum at 300 °C after a hydrogen relief bake, passed the test's criterion in air as expected. In contrast, the APCVD Al deposited at 275 °C and tested in air failed this test, even though most specimens that had received the

hydrogen relief bake did last for 200 hr without cracking. Specimens coated at 275 °C and exposed to a salt solution also failed, even after receiving the post heat treatment.

## 3.9 Sliding Friction Testing

The mean coefficient of friction measurements at a distance of 6 meters were plotted as a function of ASTM B117 exposure for each sample described and compared (see Figure 3.16).



**Figure 3.16** Mean coefficient of friction of cadmium and APCVD aluminum coated steel substrates as a function of ASTM B117 exposure time (Not sealed, unlubricated).



**Figure 3.17** Two samples tested following 75 hours in ASTM-B117 salt fog: a) cadmium coated steel, b) APCVD aluminum coated steel.

Figure 3.17 illustrated (a) cadmium coated steel and (b) APCVD aluminum coated steel tested following 75 hours in ASTM-B117 salt fog. As expected, the cadmium has a lower coefficient of friction, and maintains a low coefficient of friction even after significant exposure to corrosive conditions. The aluminum coated samples also showed an initial reduction in the measured coefficient after a few hours of exposure, but these returned to the initial levels after the 75 hours of exposure.

### CHAPTER 4

#### **STEP COVERAGE AND THROWING POWER**

Chemical vapor deposition is the only conformal growth method, offering surface chemistry controlled conformality and good coating thickness distribution on substrates with complex geometry [90]. Conformal step coverage is defined that the horizontal as well as vertical surface of substrates is coated to the same thickness [91]. Figure 4.1 shows schematic illustration of film coverage of stepped substrate. Meanwhile, the ability to coat oblique or hidden surfaces is called "throwing power" (TP) [92]. Both step coverage and throwing power are very important parameters related to uniformity of film thickness on non-planar substrates, such as steps, holes, and trenches.

The uniformity of APCVD aluminum coating thickness on different non-planar substrates is discussed thoroughly by step coverage and throwing power, respectively in Section 4.1 and 4.2.

### 4.1 Step Coverage

Conformity of step coverage is an important factor in a variety of coating technologies. In fabrication process of integrated circuits, inadequate step coverage can lead to minute cracks in the metallization, a major source of failure in device reliability testing [93]. In gas separation systems, conformal coatings will reduce pore sizes in a highly controlled way [94, 95]. Furthermore, these coatings can also improve catalyst efficiency through enlarged surface area [96, 97].

A lot of effort is being spent on numerical and theoretical studies of conformal step coverage of CVD coatings. However, there are few papers on APCVD process. K. fujino and coworkers simulated the APCVD experimental profile of the TEOS/O<sub>3</sub> thin films (<1  $\mu$ m) using an analytical gas diffusion model [98]. Unfortunately, systematic study on thick metal coatings (~10  $\mu$ m or more) via APCVD process has not been reported.



**Figure 4.1** Schematic illustration of film coverage of stepped substrate: (A) uniform coverage; (B) poor sidewall coverage; (C) lack of coverage-discontinuous film [91].

## 4.1.1 Coupon and Bolt Specimens

To evaluate step coverage, the cross-sections of aluminum coating on the steel coupon and bolt specimens were investigated. Conformal coverage of aluminum coatings was observed from typical cross-sectional optical micrographs of aluminum coating deposited on bolts, as seen in Figure 4.2 (a) and (b).



Figure 4.2 Optical micrographs of conformal aluminum coating on bolts.

Furthermore, FE-SEM analysis revealed that uniform aluminum coatings were deposited on bolt and coupon substrates with thickness of ~16  $\mu$ m (Figure 4.3 (a)) and ~20  $\mu$ m (Figure 4.3(b)), respectively. Meanwhile, this uniform thickness was also confirmed by EDX mapping analysis [Figure 4.3(c) and (d)].





### 4.1.2 Hollow Rivet Sleeve Specimen

To further evaluate step coverage, one type of hollow rivet sleeve (plain steel) was used to deposit APCVD aluminum coating using a blended TIBA at 300 °C. Figure 4.4 shows the cross section schematic diagram of a hollow rivet sleeve with a step present inside.

After aluminum deposition, the specimen was cross-sectioned lengthwise followed by mounting and polishing procedures. The coating thickness at each point (shown in Figure 4.5) in outside and inside of the aluminum coated substrate was measured by FE-SEM. The P4 and P4-1 represent the points of inside substrate where step coverage was measured.



**Figure 4.4** Cross-sectional schematic diagram of hollow rivet sleeve used for step coverage measurement.



**Figure 4.5** Schematic diagram of coating thickness measurement points on aluminum-coated hollow rivet sleeve.

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Figure 4.6 illustrates cross-sectional FE-SEM images of aluminum coating at the steps. Step coverage of aluminum coating was found to be close to 1.0, indicating excellent conformal step coverage by APCVD process.

Except step coverage, the uniformity of coating thickness was examined outside and inside of the aluminum coated hollow rivet sleeve along its length, in the following section, called "throwing power". The average thickness measured inside and outside was  $15.10 \pm 1.44$  and  $15.29 \pm 1.90 \mu m$ , respectively. Therefore, an average ratio of them was ~0.99, a representative of great throwing power (specific point measurement results shown in Table 4.1).



Figure 4.6 FE-SEM Images of step coverage of APCVD aluminum coating.

Table 4.1 Coating Thickness of Outside and Inside of Coated Hollow Rivet Sleeve

Points	P1	P2	P3	P4*	P5	<b>P6</b>	<b>P7</b>	<i>P8</i>
Outside	17.21	16.49	17.95	NA	16.20	14.48	13.79	14.37
Inside	16.08	15.87	13.41	13.24	15.23	15.05	17.18	14.48
Ratio**	0.93	0.96	0.75	NA	0.94	1.04	1.25	1.01
Points	P1-1	P2-1	P3-1	P4-1*	P5-1	P6-1	P7-1	<b>P8-1</b>
Outside	18.25	12.41	14.18	NA	16.61	15.21	12.16	14.76
Inside	18.49	15.11	14.12	13.56	14.53	14.74	13.76	13.30
Ratio*	1.01	1.22	1.00	NA	0.87	0.97	1.13	0.90

\*: Coating thickness (um) at P4 is for step coverage measurement

\*\*: Ratio of inside to outside coating thickness

### 4.1.3 Special Trenches (Crevice)

Rivet stems with a special trench (crevice) were also employed to evaluate the step coverage (shown in Figure 4.7). These substrates were aluminized by APCVD process at 300 °C using blended TIBAL as precursor.



**Figure 4.7** FE-SEM images of top view of aluminized trench and aluminum morphology on the side wall.

Figure 4.8 shows typical SEM photographs of aluminum coating on rivet stems,



indicating an average grain size of  $\sim 4 \mu m$  and a quite uniform size distribution.

**Figure 4.8** FE-SEM photographs of APCVD aluminum coating on stems at low and high magnification.

Figure 4.9 illustrates cross-sectional FE-SEM images of aluminum coating. The results show good conformal step coverage by APCVD process with blend TIBAL.

In general, aspect ratio is defined as the ratio of the structure (trench or via) height to the trench width at the entrance. In this case, the trench width used for aspect ratio was measured at the position of trench with the narrowest aperture diameter.



**Figure 4.9** SEM cross-sectional micrographs of APCVD aluminum coating on stems with trench structure.

The conformality of step coverage was evaluated quantitatively by the ratio of aluminum coating thickness on the different position of the sidewall and bottom in the trench (position 1-5 in Figure 4.10) to that on the top surface (position 0 in Figure 4.10).

Shown in Figure 4.11 are step coverage ratios of aluminum coating with different aspect ratio trenches as a function of trench height. Here, two nearly rectangular trenches were used: one with 450  $\mu$ m in depth by 80  $\mu$ m in width (nominal aspect ratio 5.5), the other with 800  $\mu$ m in depth by 60  $\mu$ m width (nominal aspect ratio 13.3).



Figure 4.10 Illustration of trench cross-section with aluminum coating.



**Figure 4.11** Step coverage ratio of APCVD aluminum coating on trenches with aspect ratio of 5.5 and 13.3.

The trench with the smaller aspect ratio (5.5) possesses better step coverage. Although increased aspect ratio leads to decreased step coverage conformity of the coatings, smallest step coverage ratio was higher than 55% in the trench with aspect ratio of 13.3. This indicated the narrow trenches did not significantly block aluminum deposition into inside structure, even with much thicker coating growth (>8  $\mu$ m) when blend TIBAL was used in APCVD process.

### 4.2 Throwing Power (TP)

High throwing power enables metal coatings onto substrates with complex three-dimensional configurations such as internal and external tubing, gear teeth, and fasteners. Many methods have been proposed to measure the throwing power in electroplating process [99, 100]. W. Stowell and coworkers investigated throwing power of nickel-chromium alloy thin films obtained by magnetron sputtering method. Both the throwing power and shadowing effect were determined for specific geometries of coatings

deposited with different coating process parameters, such as sputtering pressure, target-to-substrate distance and substrate bias.

To date, study on throwing power of APCVD coatings onto irregular surfaces has not been discussed in depth. In this work, AISI 4130 tubes with different inner diameters (ID) were utilized as substrates to evaluate the throwing power of aluminum coatings. The ratios of aluminum coating thickness inside to outside were determined by crosses-sectional SEM photographs.

## 4.2.1 Experimental

AISI 4130 tube has a length of ~50.8 mm. For comparison, two types of AISI 4130 cylindrical tubes were used which possess ID of 3.0 (OD, 4.8mm) and 6.0 mm (OD, 8.0 mm), respectively. Aluminum coatings on tubes were deposited by APCVD aluminum process at 300  $^{\circ}$ C using pure TIBAL and blended TIBAL as precursors for a contrast purpose. As mentioned in Chapter 2, the blend TIBAL is a mixture of two different aluminum alkyls that provide higher vapor pressure than neat TIBAL. Meanwhile, the deposition temperature is slightly higher than neat TIBAL for equivalent deposition rate.



Figure 4.12 Schematic diagram of cross-sectional tube.

After deposition, Aluminum coated tubes were cross-sectioned lengthwise and transversally as shown in Figure 4.12, where R and P represent transversal and lengthwise

cross sections, respectively. The sectioned specimens were then mounted using epoxy followed by mechanical polishing using diamond suspension with particle size down to 3  $\mu$ m.

The cross-sectional SEM photographs of aluminum coated tubes with different IDs using different TIBAL concentrations were collected. At the same time, coating thickness was measured using LEO SEM image manage control tool, and then, the ratios of inside to outside coating thickness were calculated to express the throwing power.

### 4.2.2 Structure

XRD analysis was carried out on the Aluminum coatings on AISI 4130 steel coupons using pure and blended TIBAL as precursors at 300 °C, as shown in Figure 4.13. All aluminum coatings obtained with various deposition conditions were found to be polycrystalline (face centered cubic structure) with (111) preferred orientation, as demonstrated by their x-ray diffraction patterns equivalent to that of the aluminum powder reference.



Figure 4.13 XRD patterns of aluminum coatings deposited at 275 and 300 °C.

The full width at half maximum (FWHM) of each peak revealed a slight difference in the value of FWHM depending on different deposition condition, as shown in Table 4.2.

		FWHM (deg)					
2 θ (deg)	Miller indices (hkl)	Pure TIBA (300 °C)	Blended TIBA (300 °C)				
38.47	(111)	0.1968	0.2165				
44.74	(200)	0.1574	0.1680				
65.14	(220)	0.1378	0.4320				
78.23	(311)	0.1920	0.3360				
82.44	(222)	0.1440	0.4320				
99.08	(400)	0.3840	0.5760				
112.05	(331)	0.1680	0.3360				
116.57	(420)	0.1920	0.2880				
137.46	(422)	0.2400	0.4800				

**Table 4.2**Full Width at Half maximum (FWHM) of Peaks Measured from XRDAnalysis of APCVD Aluminum Coated Steels

# 4.2.3 Cross-sectional Aluminum Coated Tube

Figure 4.14 illustrated a typical cross sectional SEM image of Aluminum coated tube (ID, 6.0 mm), showing a desirable throwing power of aluminum coatings.





### 4.2.4 Throwing Power Evaluation

The aluminum thickness distribution was determined by measuring inside and outside coating thickness of tubes. The ratios of thicknesses at inside to outside with the same position in the tubes were tabulated for the evaluation of throwing power. Typical thickness and ratio data was shown in the following tables. The closer the ratio to 1.0, the better the coating distribution was, indicating higher throwing power.

Thickness Distribution of aluminum coatings using neat TIBAL. Table 4.3 and Table

4.4 presented aluminum coating thicknesses obtained using neat TIBAL as precursor.

Measurement was carried out at each point (shown in Figure 4.12) of outside and inside of the tubes with ID of 6.0 and 3.0 mm, respectively.

For the tube with an ID of 6.0 mm, the average thickness of aluminum coating inside and outside was 14.19  $\mu$ m and 14.57  $\mu$ m providing a ratio of 0.85 - 1.25.

**Table 4.3** Coating Thickness of Outside and Inside of Aluminized 4130 Steel Alloy Tubes (ID, 6.0 mm) (μm)

	R1	P1&1-1	P2&2-2	P3&3-3	R2	P4&4-4	P5&5-5	P6&6-6	R3
Outside	12.29	16.3	11.69	17.55	14.81	13.8	15.29	15.56	13.81
Inside	15.07	14.63	12.64	14.84	13.46	14.22	14.01	14.45	14.36
Ratio*	1.25	0.90	1.11	0.85	0.93	1.04	0.92	0.93	1.07
SD.	0.29	0.15	0.23	0.11	0.16	0.08	0.03	0.01	0.24

\*: Ratio of inside to outside coating thickness

For the tube with an ID of 3.0 mm, the average thickness of Aluminum coating inside and outside was 7.89  $\mu$ m and 14.84  $\mu$ m, respectively (in Table 4.4), providing a ratio of 0.37 - 0.80.

	R1	P1&1-1	P2&2-2	P3&3-3	R2	P4&4-4	P5&5-5	P6&6-6	R3
Outside	12.97	10.65	16.15	16.77	15.17	19.27	16.06	13.35	13.18
Inside	10.02	8.36	6.01	6.45	6.63	8.14	6.99	8.00	10.37
Ratio*	0.79	0.80	0.37	0.38	0.46	0.44	0.44	0.60	0.80
SD.	0.17	0.11	0.01	0.08	0.11	0.17	0.10	0.01	0.10

**Table 4.4** Coating Thickness of Outside and Inside of Aluminized 4130 Steel Alloy Tubes (ID, 3.0 mm) (μm)

\*: Ratio of inside to outside coating thickness

## Thickness Distribution of Aluminum Coatings Using Blended TIBAL. Table 4.5 and

Table 4.6 presented the coating thicknesses measured at each point (Figure 4.12) of outside and inside of the tubes with inner diameter of 3.0 and 6.0 mm, respectively.

**Table 4.5** Coating Thickness of Outside and Inside of Aluminized 4130 Steel Alloy Tubes (ID, 6.0 mm) (μm)

	R1	P1&1-1	P2&2-2	P3&3-3	R2	P4&4-4	P5&5-5	P6&6-6	R3
Outside	12.83	12.58	17.16	14.16	13.59	17.91	15.47	15.58	14.60
Inside	13.39	12.49	14.46	12.88	13.61	15.14	14.57	14.31	12.64
Ratio*	1.04	1.00	0.84	0.91	1.00	0.85	0.94	0.92	0.87
SD.	0.06	0.10	0.06	0.07	0.08	0.05	0.25	0.01	0.10

\*: Ratio of inside to outside coating thickness

For the tube with ID of 6.0 mm, the average thickness of aluminum coating inside

and outside was 13.72  $\mu$ m and 14.88  $\mu$ m, respectively, providing a ratio of 0.84 - 1.04.

For the tube with ID of 3.0 mm, the average thickness of aluminum coating inside

and outside was 9.71 µm and 13.73 µm, respectively, providing a ratio of 0.59 - 0.86.

**Table 4.6** Coating Thickness of Outside and Inside of Aluminized 4130 Steel Alloy Tubes (ID, 3.0 mm) (μm)

	<b>R</b> 1	P1&1-1	P2&2-2	P3&3-3	R2	P4&4-4	P5&5-5	P6&6-6	R3
Outside	15.11	11.21	14.00	14.36	12.15	15.47	13.06	14.90	13.30
Inside	10.91	9.52±0.67	9.28	9.58	9.35	8.86	8.89	9.64	11.36
Ratio	0.77	0.86	0.67	0.67	0.78	0.59	0.71	0.65	0.86
SD.	0.21	0.14	0.08	0.03	0.14	0.13	0.21	0.07	0.10

No\*: Ratio of inside to outside coating thickness

The ratios of aluminum coatings deposited on the tubes with an ID of 6.0 mm was  $0.93 \pm 0.07$  for blended TIBAL and  $1.00 \pm 0.13$  for pure TIBAL, indicating no significant difference in throwing power between pure and blended TIBAL precursors. However, in the case of tubes with the ID of 3.0 mm, aluminum thickness ratio ( $0.73 \pm 0.09$ ) with blended TIBAL as the precursor was found to be larger than that ( $0.56 \pm 0.19$ ) with pure TIBAL as the precursor.

Table 4.7         Aluminum Thickness Distrib	oution in Different Tubes
----------------------------------------------	---------------------------

ID	Precursor	Length	Length Coating Thickness		Coating Thickness	Ratio
		(mm)	Inside	Outside	by weight	
6.0 mm	Blend TIBAL	56.01	13.72	14.88	12.64	$0.93 \pm 0.07$
3.0 mm		50.72	9.71	10.16	10.16	$0.73 \pm 0.09$
6.0 mm	Neat TIBAL	51.59	14.19	14.57	12.15	$1.00 \pm 0.13$
3.0 mm		50.60	7.89	14.84	10.15	$0.56 \pm 0.19$

Note: the unit of thickness is  $\mu m$ 



**Figure 4.15** Ratio of inside to outside aluminum coating thickness onto AISI 4130 tubes along tube length.

In both tubes with the ID of 3.0 and 6.0 mm, aluminum coatings deposited using blended precursor showed less variation in throwing power along tube length than those using pure TIBAL (shown in Table 4.7 and Figure 4.15).

In brief, with the same deposition parameters, aluminum coatings onto tubes with larger ID showed higher throwing power. Different precursors (neat or blend) have no obvious effect on throwing power for the tube sample with the ID of 6.0 mm. APCVD process using blended precursor with higher vapor pressure has better throwing power of aluminum coatings for these tubes with the ID of 3.0 mm.

### **CHAPTER 5**

### **ELECTROCHEMICAL TESTS**

Advanced processing techniques including CVD method can produce pure and reliable aluminum coating as a replacement of cadmium coating for the corrosion protection of high strength steel. It is of great importance to investigate corrosion performance of aluminum coating on high strength steel, thus to better understand its electrochemical behavior.

An important aspect of aluminum is that it is thermodynamically unstable in its natural state. Aluminum quickly reverts back to its stable form which is an aluminum oxide. This protective oxide barrier bonds to the surface of aluminum and restricts the ability of uniform corrosion to occur. In soft waters aluminum is cathodic with respect to steel; however, in seawater or some fresh waters containing chloride ions or sulfate ions, aluminum may become anodic to steel, and aluminum coatings should therefore corrode sacrificially and provide cathodic protection to steel.

The aluminum oxide barrier is not stable under all conditions. The conditions for the stability of the oxide film are expressed by a pourbaix diagram, which can provide useful information about the corrosion behavior of metals. Figure 5.1 shows the E-pH diagram of aluminum, illustrating the behavior of aluminum at given potentials and pH levels. As shown in the diagram, the oxide barrier protects aluminum in a pH range of about 4 to 8.5. At a pH above and below the passivation range, aluminum corrodes in aqueous solutions because its oxides are soluble.

Even in the passive region of the Pourbaix Diagram, Corrosion of aluminum is caused by the electrochemical reaction between aluminum and an aqueous phase according to a complex electrochemical process when the protective oxide barrier fails at a discrete site. Along with the discontinuities, an aggressive species, usually chloride ions which are readily abundant in marine environments will break down the barrier.



Figure 5.1 The pourbaxi diagram of aluminum.

### 5.1 Potentiodynamic Polarization Measurement

Aluminum coatings were deposited onto AISI 4130 steel coupons at 300 °C using pure TIBAL. Aluminum foils (99.99 % in purity) and AISI 4130 steel coupons were used as references. These reference specimens were mechanically polished using SiC with grit sizes down to 600  $\mu$ m followed by a polycrystalline diamond suspension with particle sizes down to 3.0  $\mu$ m.

Prior to potentiodynamic polarization measurements, all specimens were cleaned ultrasonically in acetone and ethanol.

The polarization curves of the aluminum coatings, aluminum foils and AISI 4130 steel coupons were obtained after 1 hour immersion in 3.5 wt% NaCl solutions open to air and purged with O<sub>2</sub>, shown in Figure 5.2 and Figure 5.3.



**Figure 5.2** Anodic polarization curves of APCVD aluminum coating, aluminum foil, and AISI 4130 steel substrate after 1 hr immersion in 3.5 wt.% NaCl solutions open to air.



**Figure 5.3** Anodic polarization curves of APCVD aluminum coating, aluminum foil, and AISI 4130 steel after 1 hr immersion in 3.5 wt.% NaCl solutions with O<sub>2</sub> saturation.

The significant increase in corrosion current density of the AISI 4130 steel was observed when immersed in the  $O_2$  saturated solution, while the aluminum foil experienced little effect of dissolved  $O_2$  on the corrosion current density. As expected, the steel substrate showed much greater corrosion potential and current density over those of aluminum coatings, indicating that aluminum provides good sacrificial corrosion protection for the steel substrate when the two metals are in galvanic coupling. The corrosion resistance and potential of aluminum coatings in the both corrosive environments were found to be comparable to that of the aluminum foils. It is worth indicating from this data that the aluminum coatings exhibit an easier tendency to be passivated than the aluminum reference foils.

### 5.2 Electrochemical Impedance Spectroscopy (EIS) Measurement

## 5.2.1 APCVD and IVD Coatings for EIS Measurement

APCVD coatings must exhibit equal or better performance than the only currently approved general replacement for cadmium coatings. Boeing-St. Louis arranged for test panels to be coated with ~25  $\mu$ m of IVD aluminum coating. Because these coatings traditionally receive a glass bead peening (or burnishing) after deposition to close surface pores and pin-holes, and a Cr(VI)-containing chemical conversion coating (CCC) to provide better corrosion resistance and paint adhesion, all of the specimens were subjected to these post-treatments.

The protective CCCs on aluminum and aluminum alloys were produced using Iridite 14-2 based on MIL-DTL-81706 B, both Calss 1A and Class 3, offering excellent corrosion resistance of aluminum coatings. However, iridite 14-2 contains hazardous ingredients and friendly replacement technologies are desired.

Both APCVD and IVD aluminum surfaces were glass bead peened manually at 40 psi using number 10 glass beads to reduce porosity before CCC process was applied. SEM photomicrographs of the surfaces are shown in Figure 5.4, which might indicate APCVD aluminum coating is a little harder than IVD aluminum coating because there are fewer small "dimples" left by the glass beads. However, the average surface roughness
$(R_a)$  of the IVD Al coating was  $1.98 \pm 0.18 \mu m$ , and that of the APCVD Al coating was  $3.68 \pm 0.75 \mu m$ , indicating that the APCVD Al coating might be softer than the IVD Al coating. The hardness of these coatings was not determined in order to resolve these differences. The higher magnification photomicrographs in Figure 5.4 were chosen specifically to shown that a few pin-holes may be found in both types of coating.



Figure 5.4 SEM images of APCVD Al and IVD Al coatings.

XRD analysis also was carried out on Al coatings deposited at 300 °C and IVD Al coatings, both with post-treatments comprised of glass bead burnishing followed by a Cr(VI)-containing chemical conversion coating. The results are shown in Figure 5.5 indicating that the post-treatments have no effect on coating structure. However, the APCVD Al coating showed a higher degree of crystallinity than the IVD Al coatings, as indicated by the smaller full width at half maximum (FWHM) values shown in Table 5.1.



Figure 5.5 XRD patterns of APCVD Al and IVD Al coatings with post-treatments.

**Table 5.1** Full Width at Half maximum of All Peaks Measured From XRD Analysis onIVD and APCVD Aluminum Coatings

2θ (deg)	Miller indices (hkl)	FWHM (deg)	
		IVD AI	APCVD AI
38.47	(111)	0.2952	0.0720
44.74	(200)	0.2558	0.0720
65.14	(220)	0.1181	0.0960
78.23	(311)	0.1574	0.0960
82.44	(222)	0.2362	0.0960
99.08	(400)	0.4723	0.0960
112.05	(331)	0.4723	0.1200
116.57	(420)	0.3936	0.1200
137.46	(422)	0.7680	0.1680

## **5.2.2 Corrosion Potential Measurement**

Corrosion potential measurements were conducted by Gamry Reference 600 system using a saturated calomel electrode (SCE) as the reference electrode. Those potential values were collected taking 20 minutes just before each EIS measurement. Up to a maximum of 216 hours potential measurement was conducted at several time intervals before each set of EIS measurements. All solutions were 3.5 wt% NaCl prepared using deionized water.



Figure 5.6 Corrosion potential as a function of immersion time in 5.0 wt% NaCl.

Figure 5.6 shows the change of corrosion potential as a function of immersion time for AISI 4130 steel coupon, aluminum foil and APCVD aluminum coating on steel coupon. Steady values of the corrosion potential were obtained after 48 hours of immersion except aluminum foil sample. AISI 4130 steel coupon achieved a corrosion potential slightly higher than the corrosion potential of the APCVD aluminum coatings with different coating thickness. While aluminum foil achieved the lowest corrosion potential after 12 hours of immersion. A shift of the corrosion potential of aluminum coated AISI 4130 steel coupon in the negative was indicative of the presence of a protective effect on the aluminum coatings. It was not significant different of corrosion potential value with different aluminum coating thickness.

Figure 5.7 shows that the corrosion potential value of APCVD aluminum was as same as IVD sample after 192 hours immersion in 3.5 wt% NaCl solutions with saturated oxygen.



Figure 5.7 Corrosion potential as a function of immersion time in 3.5 wt% NaCl.



Figure 5.8 SEM images of APCVD Al and IVD Al coatings after EIS measurements.

The surface morphology of the APCVD and IVD Al coatings was investigated with a SEM after the EIS measurements, and the surface SEM images obtained are shown in Figure 5.8. Enlargement of open pores that were present originally in the coatings was observed due to the galvanic action between the aluminum coatings and the steel substrate. However, no red rust was observed during the immersion time. Overall, these results indicated that both the APCVD and IVD Al coatings provide excellent sacrificial protection for steel substrates.

### **5.2.3 Electrochemical Impedance Measurements**

The low frequency impedance,  $Z_{lf}$ , determined from data at 0.05 Hz, has been proposed as the optimal EIS parameter to evaluate the corrosion performance of coatings [101]. In the low frequency range (< 0.1 Hz), the magnitude of the impedance appears almost constant. The impedance at this frequency includes the response of the coating as well as part of the response of the oxide and/or corrosion product in the pores at the metal interface. Although the  $Z_{lf}$  values do not give information about how the coating degraded, they could correlate to coating performance.



Figure 5.9  $Z_{lf}$  as a function of immersion time in 3.5 wt% NaCl.

The low-frequency impedance  $Z_{lf}$  as a function of immersion time is shown in Figure 5.9. AISI 4130 had the lowest  $Z_{lf}$ . All aluminum coatings on steel coupon exhibited large decreases in  $Z_{lf}$  compared with that of aluminum foil, indicting the coatings have defect. By 96 hours, the 20.2-µm coating had the highest zlf in 18.9 µm and 16.1 µm coating. The time behavior of  $Z_{lf}$  including APCVD and IVD aluminum coatings was shown in Figure 5.10. By 192 hours, APCVD aluminum coating had a value the same as IVD aluminum coating, similar to that of corrosion potential changing with immersion time in Figure 5.7.



**Figure 5.10**  $Z_{\rm lf}$  as a function of immersion time for AISI 4130, aluminum foil, IVD aluminum and APCVD aluminum coatings.

#### 5.3 Corrosion Screening Tests

Four APCVD Aluminum coated coupons were used for the bare corrosion testing: one as deposited, one as deposited scribed, one as deposited post treated with TCP (A trivalent chromium conversion coating), and one as deposited with TCP Scribed; Note, TCP 5 minute immersion with 50 % dilution. These coupons were then subjected to ASTM B117 Salt Fog testing.

Figure 5.11 illustrates the APCVD Aluminum coated coupons 17 days after exposure in salt fog and shows the formation of a white corrosion product with no red rust. The white corrosion product is caused by corrosion of the Aluminum coatings due to galvanic action. Red rust was observed only after a 27 day-exposure. Post treatment with TCP did not improve corrosion resistance of APCVD Aluminum coated coupons indicating that it has no effect. For painted corrosion testing, two APCVD Aluminum coated coupons were painted with Mil-PRF-23377C primer and Mil-PRF-85285 topcoat. A two-week cure time was allowed for the paint prior to ASTM B117 salt fog testing. Figure 5.12 illustrates the APCVD Aluminum coated coupons with paint 17 days after exposure in salt fog. Neither blistering of the paint nor red rust formation was observed in 17 days of exposure.



Figure 5.11 APCVD aluminum coated coupons after 17 days in ASTM B117 salt fog.



**Figure 5.12** APCVD aluminum coated coupons after 17 days in ASTM B117 salt fog, scribed and un-scribed, respectively.

In addition to the painting corrosion testing, a paint adhesion test based on ASTM D3359 Method A was performed on four APCVD Aluminum coated coupons after a

two-week cure time of paint. DI water was used for wet test coupons. Figure 5.13 illustrate APCVD Aluminum coated coupons with paint in painting adhesion testing. ASTM D3359 calls for a rating system of 0-5 where 5 is the best and 0 is a complete removal of the paint. The ratings for these coupons is 5, indicating that the aluminum coatings exhibit excellent paint adhesion.



Figure 5.13 APCVD Aluminum coatings after paint adhesion testing.

# 5.4 Cyclic Corrosion Measurements

Cyclic exposure testing was performed on unscribed and scribed APCVD aluminum coated mild steel coupons at the Army Research Laboratory Facilities using the GM 9540P Method B 18-stage testing protocol. The unscribed coupons were tested both with and without a commercial trivalent chromium chemical conversion coating. The acceptance criteria were no visible red rust after 80 cycles for unscribed coatings, and 40 cycles for scribed coatings. Here visible red rust means corrosion of the underlying steel substrates.

The panels were removed after 2, 10, 20, 30, 50, 60, 110 and 165 cycles for scanning on a flat bed scanner to provide an electronic record of the appearance of each. In each scan, the top five panels had received the Cr(III) post treatment to the APCVD

aluminum coating, while the bottom panels had no post treatment. The test was halted after 165 cycles, well beyond the acceptance criterion value mentioned above.



Figure 5.14 APCVD Al coated panels after 2 cycles in GM 9540P test.



Figure 5.15 APCVD Al coated panels after 10 Cycles in GM 9540P test.

Note, after only two cycles (Figure 5.14) the beneficial effect of the post treatment can already be seen. The APCVD aluminum coated panels without the Cr(III) treatment exhibited more corrosion and mottling on their surfaces. In comparison, similar mottling appeared on the lower half of the post-treated panels after 10 cycles (Figure 5.15).

Red rust appeared visible on some of the scribed panels after 20 cycles, although the post-treated panels only showed red rust on one panel. However, this did not seem to progressively corrode much until after 50-60 cycles of testing, as shown in Figure 5.16.



Figure 5.16 APCVD Al coated panels after 60 cycles in GM 9540P test.



Figure 5.17 APCVD Al coated panels after 165 cycles in GM 9540P test.

By 110 cycles all the scribed panels had significant substrate corrosion, but the unscribed panels did not show red rust until 165 cycles, as shown in Figure 5.17. At 165 cycles it is still apparent that the post treatment is adding significant corrosion protection.

# CHAPTER 6

## CONCLUSION

In this study, the use of atmospheric pressure, chemical vapor deposition (APCVD) to produce high quality aluminum coatings for the corrosion protection of high-strength steels has been investigated. Both pure and blended TIBAL were used as precursors for formation of the pure aluminum coatings on high strength steel specimens. As part of a commercial development effort to produce atmospheric pressure chemically vapor deposited (APCVD) aluminum, FUZEBOX® technology has been utilized in the aluminization process through thermally induced decomposition. Optimization of the APCVD process by depositing aluminum on high strength steel yielded the best deposition conditions of temperature at 300 °C using blend TIBAL.

The morphological, structural, compositional, and step coverage properties of the APCVD aluminum coating were evaluated using a variety of characterization methods. Meanwhile, Performance testing, such as corrosion, tensile strength, electrical conductivity, hydrogen embrittlement, and lubricity tests were performed on the APCVD Al coatings.

The results of APCVD aluminum coating using TIBAL as precursors are summarized as follows:

Morphological analysis by SEM, AFM and DekTak revealed that aluminum coatings are dense with a rough surface (RMS, 917 nm). Aluminum coatings, regardless of deposition conditions, are polycrystalline (face centered cubic structure).

Compositional analysis using AES, XPS and GD-OES showed that aluminum coatings are oxidized on the surface and pure (99%) within the bulk coatings. The

composition profiles are similar when coatings are prepared with pure or blended TIBAL at 275 or 300 °C. NRA results indicated that that hydrogen incorporation in all the coatings was well below 1 at.%.

The analysis of cross-sectional aluminum coatings deposited using TIBAL as precursors revealed that aluminum coatings exhibited excellent conformal coverage and throwing power with uniform thickness distribution (~20  $\mu$ m) on complex shapes, and inside and outside surface of cylindrical steel tubes.

Electrical resistivity was measured to be  $3.5 \pm 0.1 \ \mu\Omega$ ·cm, compared to  $2.7 \ \mu\Omega$ ·cm of bulk aluminum, indicating aluminum coatings have good electrical conductivity. All aluminum coatings passed the electrical contact resistance test criterion by measuring less than 5 milli-ohms per square inch before and after salt fog exposure.

Nano-indentation measurements on aluminum coatings yielded average hardness and Young's Modulus values of 551 MPa and 36 GPa, respectively. Pull-off adhesion tests on aluminum coatings showed that aluminum coatings deposited using blended TIBAL exhibited as good adhesive strength (684 kg/cm<sup>2</sup>) as those using pure TIBAL (703 kg/cm<sup>2</sup>).

The average density of the Al coating was calculated to be  $2.60\pm0.04$  g/cm<sup>3</sup>. This value is a little lower than that for bulk aluminum (2.7 g/cm<sup>3</sup>) and may indicate some closed pores were present in the coatings.

Potentiodynamic polarization measurements made after one hour of immersion in a 3.5 % NaCl solution revealed that aluminum coatings exhibited an easier tendency to be passivated than the aluminum reference foils, and that the corrosion resistance was comparable to that of pure aluminum foils.

The galvanic corrosion of the APCVD aluminum coatings on high-strength steel substrates has been investigated using EIS and SEM, indicating that a decrease in protection can occur over time if open porosity or coating defects are present, and the adjacent aluminum dissolves too rapidly. Similarly to IVD Al coatings, if fully dense coatings cannot be obtained, post-treatments may be necessary, such as glass bead burnishing and/or the application of a chromium-free chemical conversion coating.

Salt fog exposure corrosion testing on aluminum coated panels depositing at 300 °C using a pure TIBAL precursor showed that red rust on the coatings was not observed until the 27th day of exposure. The pass criterion for this test is 21 days before red rust is visible; therefore, this APCVD Al coating can meet the Type I, Class 1 specification for electroplated Cd coatings. The use of a non-optimized Cr(III) CCC on the scribed panels did not provide any additional benefit in the tests that were performed. In contrast, similar coatings that were painted - using a conventional MIL-SPEC primer and top coat cured for 14 days - did not show any signs of red rust after 27 days.

The results of the tensile strength tests revealed that regardless of a post baking (23hr, 190.6  $^{\circ}$ C), aluminum coated AISI 4340 steel specimens experienced a loss of 4.6 - 15.3% in the notch fracture strength compared to bare specimens. The lower strength of these bars appears to be attributable to the temperature (~300  $^{\circ}$ C) of the APCVD deposition process. This was confirmed by the study of the relationship between tensile strength and temperature, which indicated that the loss in tensile strength was highly dependent on temperature, while no significant difference in tensile strength was seen with exposure time at a given temperature.

The hydrogen embrittlement tests revealed that premature failure was observed in aluminum coated AISI 4340 steel specimens with no post baking. However, all the coated specimens that received a post baking withstood at least 200 hrs in the HE test (conducted in air or a salt solution) and passed. This implies that all the hydrogen that diffused into the substrates was expelled during baking at 190.6 °C for 23hrs. Post baking of APCVD aluminum coatings is a necessary and effective way to eliminate hydrogen embrittlement.

The lubricity testing results showed, as expected, a higher coefficient of friction than cadmium and maintained a high coefficient of friction even after significant exposure to corrosive conditions. The aluminum coated samples also showed an initial reduction in the measured coefficient after a few hours of exposure, but these returned to the initial levels after the 75 hrs of exposure. It is well known that aluminum coatings such as IVD Aluminum have higher coefficients of friction than cadmium. However, this reinforces the need to wisely choose sealers (such as Trivalent Cr) and lubricants for use with any aluminum coating.

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