

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
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1. REPORT DATE		2. REPORT TYPE Professional Paper		3. DATES COVERED	
4. TITLE AND SUBTITLE  Evaluation of Aluminum-Manganese as a Cadmium Replacement			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)  Michael Kane, Craig Matzdorf, James Green			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Naval Air Warfare Center Aircraft Division 22347 Cedar Point Road, Unit #6 Patuxent River, Maryland 20670-1161			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Naval Air Systems Command 47123 Buse Road Unit IPT Patuxent River, Maryland 20670-1547			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT  Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT  Aluminum-manganese is currently being evaluated as a replacement for cadmium plating. Aluminum-manganese is applied by electroplating in molten salt and as such the process can plate internal diameters, complex geometries, and threaded applications. The salt bath is operated at 190 degrees Celsius and is compounded of aluminum chloride, sodium chloride, potassium chloride, and a small amount of manganese chloride. Aluminum-manganese has potential for use in high strength steel applications where other electroplated cadmium alternatives such as tin-zinc and zinc-nickel have concerns with environmentally assisted cracking. Aluminum-manganese should prove to be much more affordable than ion vapor deposition and physical vapor deposition processes.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)
Unclassified	Unclassified	Unclassified	Unclassified	11	Michael Kane/Craig Matzdorf/James Green (301) 342-0986/9372/2322

Standard Form 298 (Rev. 8-98)  
Prescribed by ANSI Std. Z39-18

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# **Evaluation Aluminum-Manganese as a Cadmium Replacement**

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Note: This work was funded by the Environmental Securities Technology Certification Program and the Aviation Pollution Prevention Technology Program (CNO 45).

## **Abstract**

Aluminum-manganese is currently being evaluated as a replacement for cadmium plating. Aluminum-manganese is applied by electroplating in molten salt and as such the process can plate internal diameters, complex geometries, and threaded applications. The salt bath is operated at 190 degrees Celsius and is composed of aluminum chloride, sodium chloride, potassium chloride, and a small amount of manganese chloride. Aluminum-manganese has potential for use in high strength steel applications where other electroplated cadmium alternatives such as tin-zinc and zinc-nickel are have concerns with environmentally assisted cracking. Aluminum-manganese should prove to be much more affordable than ion vapor deposition and physical vapor deposition processes.

## **Introduction**

Cadmium is a toxic metal and a possible human carcinogen. Compliance with current environmental, safety and health regulations regarding the use of cadmium must be considered over the whole lifecycle. Coating deposition costs of cadmium are only a small portion of the total ownership costs of cadmium coatings. Coating deposition is conducted in a controlled environment with trained personnel, personal protective equipment, and engineering controls. The raw material and equipment costs for cadmium plating in a cyanide bath are minimal. Though increasing, the cost of compliance with environmental, safety, and health regulations concerning the deposition of cadmium are easily and affordable addressed.

Cadmium coatings, regardless of the coating deposition process, are toxic and lead to significant in-service costs. In-service costs of cadmium coatings are attributed to a wide variety of factors. Generation of cadmium containing wastes is unavoidable when cadmium coated parts

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are used in-service, required maintenance procedures yield cadmium containing wastes or cadmium contamination. Cadmium contamination has been observed in rinse waters for equipment containing cadmium coated parts. Cutting or grinding of cadmium coated nuts and bolts that have seized will generate cadmium fume or dust. Stripping of cadmium coatings by mechanical means generates cadmium dusts. Chemical stripping of cadmium coatings generates large amounts of hazardous wastes. Collection, treatment, and disposal of cadmium containing wastes are expensive. Exposure to small amounts of cadmium dust or fume can easily exceed the action levels and personnel exposure limit of cadmium that may result in significant medical and legal costs. Compliance with environmental, safety, and health regulations and the potential legal liabilities for the continued in-service use, removal, and disposal of cadmium coatings are making the continued use of cadmium coatings extremely expensive and unacceptable. These types of costs are difficult if not impossible to quantify and therefore are not taken into account in cost studies. Considering deposition costs alone, it is likely that cadmium alternatives will be more expensive than cadmium plating. However, tremendous cost savings will be realized over the total lifecycle by eliminating the use of cadmium.

### **Why Aluminum-Manganese?**

There are several alternative coating compositions applied by various deposition techniques that could be evaluated as cadmium alternatives. Zinc, tin-zinc, and zinc-nickel can be deposited by aqueous plating. Aqueous plating processes are the most affordable coating deposition methods. The current environmental, safety, or health concerns for the use of zinc, tin, and nickel are much less stringent than those of cadmium or cyanide. However, coatings containing zinc will lead to environmentally assisted cracking of high strength steels. Susceptibility to environmentally assisted cracking increases with increases in strength for high strength steels. The higher the strength level the more susceptible a steel is to environmentally assisted cracking. Grade 8 (SAE J429) fasteners will fail due to environmentally assisted cracking when coated with zinc. Grade 8 fasteners have a tensile strength of 150 ksi. Many weapon critical high strength steel parts have strength levels up to 300 ksi in which the use of zinc containing cadmium alternatives will be technical unfeasible.

Aluminum coatings can not be deposited using aqueous plating techniques. Aluminum can be deposited using non-aqueous plating techniques or ion vapor deposition processes. Non-aqueous plating of aluminum is conducted in a toluene based electrolyte containing pyrophoric organometallic aluminides and must be kept dry and free of air. Non-aqueous plating of aluminum poses serious environmental, safety, and health risks. Ion vapor deposition of aluminum is a clean environmentally friendly process. However, ion vapor deposition of aluminum cost significantly more than plating processes due to expensive capital equipment, vacuum system maintenance, and large energy requirements. In addition, ion vapor deposition is limited when it comes to depositing coatings on internal diameters and for bulk quantity processing. Regardless of deposition process, aluminum coatings are environmentally acceptable and would provide for significant in-service cost savings compared to the continued use of cadmium coatings.

Aluminum-manganese coatings are deposited via a molten salt electroplating process. Typical of plating processes aluminum-manganese can be deposited on internal diameters, threads and other complex shapes as well as barrel plated for coating bulk quantities of fasteners. Plating of aluminum-manganese does not have the environmental, safety, and health risks associated with non-aqueous plating of aluminum. Aluminum-manganese plating can affordably deposit coatings to a wider variety of applications than is possible with ion vapor deposited aluminum. Aluminum-manganese alleviates some of the concerns regarding environmentally assisted cracking found with zinc based coatings. Aluminum-manganese plating has potential to be an affordable alternative for cadmium plating that can be utilized for high strength steel applications as well as processing of bulk quantities.

Aluminum-manganese plating is not commercially available in the metal finishing industry. This paper will discuss some of the practical aspects that are being addressed in order to transition aluminum-manganese to industry and Department of Defense facilities. Environmental, safety, and health issues of aluminum-manganese deposits, plating process, and salt bath neutralization and disposal are discussed. Chemical bath make-up costs for a 1000-gallon tank are provided to put aluminum-manganese in perspective compared to other coating technologies.

## **Environmental, Safety, and Health Benefits of Aluminum-Manganese**

Aluminum - 13 weight percent manganese coating electroplated from a molten salt bath has potential to be an affordable replacement for cadmium over the whole lifecycle of a weapon system. Manganese-based 3000 series aluminum alloys are used in the manufacturing of soda cans. Aluminum Alloy 3003 has 0.5-1.5 weight percent manganese and is used in the manufacturing of cookware. With a manganese content of 13 weight percent, an aluminum-manganese deposit has higher concentration of manganese than most 3000 series alloys, though it is likely that aluminum-manganese coatings will provide for toxicity characteristics similar to 3000 series aluminum alloys. Aluminum-manganese will provide for a significant environmental, safety, and health, improvement over the continued use of cadmium.

Manganese has detrimental health effects if ingested or inhaled in toxic quantities. Manganese will be present in the deposit, salt bath, and rinse waters. Manganese in the aluminum-manganese deposit is in the form of an  $Al_6Mn$  intermetallic compound and is not likely to be ingested or inhaled. Manganese or manganese chloride additions will be made to the molten salt bath. Use of pellets will minimize exposure during manganese additions. Manganese hydroxide will be present in rinse waters in small amounts.

Manganese in all of these forms should not provide for significant environmental, safety, and health concerns. First, it is unlikely that manganese will be inhaled and ingested in any of these forms with proper handling procedures and personnel protective equipment. Second, if an individual is exposed to small amounts of manganese there should be no adverse effects as the Estimated Safe and Adequate Dietary Intakes for manganese are 2.0-5.0 milligrams per day as listed by the American Society for Nutritional Science at <http://www.faseb.org/asns/NIMANG.html>. Of course grinding just about any material without proper engineering controls or personnel protective equipment will expose individuals above the permissible exposure limit of 15 ppm for inert dust. The ceiling permissible exposure limit for manganese is 5 ppm.

## **Process Parameters and Issues**

Electroplating of aluminum-manganese is conducted in a molten salt bath with a nominal weight percent composition of: 79% aluminum chloride, 10% sodium chloride, 10% potassium

chloride, and 1% manganese chloride. The bath is operated at 190 degrees Celsius (374 degrees Fahrenheit). The bath temperature will not adversely effect high strength steels and stainless steels that are typical post-baked for hydrogen embrittlement relief at the same temperature. Due to alloy temperature limitations molten salt plating of some non-ferrous alloys is not recommended with this system.

Clean dry parts are media blasted then plated in the salt bath. Teflon tape is used as a maskant. Direct current plating from 10 to 30 amps per square foot with forced convection produces a deposit of good quality at a fixed temperature. The manganese content in the deposit is primarily controlled by the manganese content in the salt bath. Approximate plating rates are on the order of 1 mil per hour. Residual salt deposits are best removed by rinsing in hot water, with a triple rinse recommended. Depending upon local regulations rinse water could be discharged to public waste water treatment facilities. High strength steels are embrittled by the decomposition of aluminum chloride and formation hydrogen chloride during rinsing. As a result post baking for hydrogen embrittlement relief is required for aluminum-manganese plated steels. Aluminum-manganese coatings are removed using a caustic solution. Residual manganese products may remain and can be removed by light scrubbing with an abrasive pad.

Salt bath equipment may be fabricated from electroless nickel plated steels or stainless steels, or Inconel alloys. Even though the salt bath is operated at temperatures significantly below other typical molten salt heat treating processes, the use of stainless steel without electroless nickel will lead to chloride cracking of the tank material.

Sublimation of the molten salt bath is the key operational issue concerning the environment, safety, and health. At operational temperatures, the high vapor pressure of aluminum chloride generates vapors that react with moisture in the air producing hydrogen chloride fumes. Proper equipment design and engineering controls address fuming issues. A 10-gallon tank was constructed and operated in a fume hood. The tank was rectangular in shape (18" width x 12" depth x 12" height). The surface area of the molten salt in the 10-gallon tank was 1.5 square feet. At operational temperatures, fuming of the molten salt bath was minimal when covered. When uncovered the tank generated a large volume of white fumes that did not exceed the capacity of the fume hood. The fume hood was certified with a minimum air flow rate of 80-100 cubic feet per minute per square foot (cfm/ft<sup>2</sup>) of open face area. Dregar tubes were used to

analyze for hydrogen chloride around the tank. The tank was heated to operational temperatures and the cover was removed before testing for hydrogen chloride. Outside the hood no amount of hydrogen chloride was detected. Inside the hood on all sides of the tank below the top of the tank, the hydrogen chloride level was 1.5 ppm or less. No visible fuming was observed on the sides of the tank. Above the tank and along the top of the fume hood internal to the fume hood white visible fumes were present. In the area where fuming was observed the hydrogen chloride concentration exceeded 10 ppm. The permissible exposure limit for hydrogen chloride is 5 ppm. Fuming of an open molten salt bath was easily addressed using a properly sized conventional fume hood.

Simple engineering controls such as a canopy hood should be capable of handling fuming from production scale equipment that is not directly exposed to the atmosphere. Figure 1 exhibits a molten salt plating equipment design that is not directly exposed to the atmosphere. The work, anodes, filters and stirrers would be fixed to a cover for the tank and will be referred to as the "fixture". The fixture would be lowered into the upper chamber while the inner lid remains in place. The inner lid would be removed and the fixture would be lowered into the molten salt bath. Once the coating has been deposited the fixture would be raised and allowed to drain and cool for several minutes. The inner lid would then be replaced and the fixture would be removed and immediately rinsed. Fumes will be generated as the fixture is immersed in the rinse tank and as such the rinse tank should have adequate ventilation. Care should be taken in the design of a molten salt plating line so that in the event of a spill water will not come into contact with molten salt.

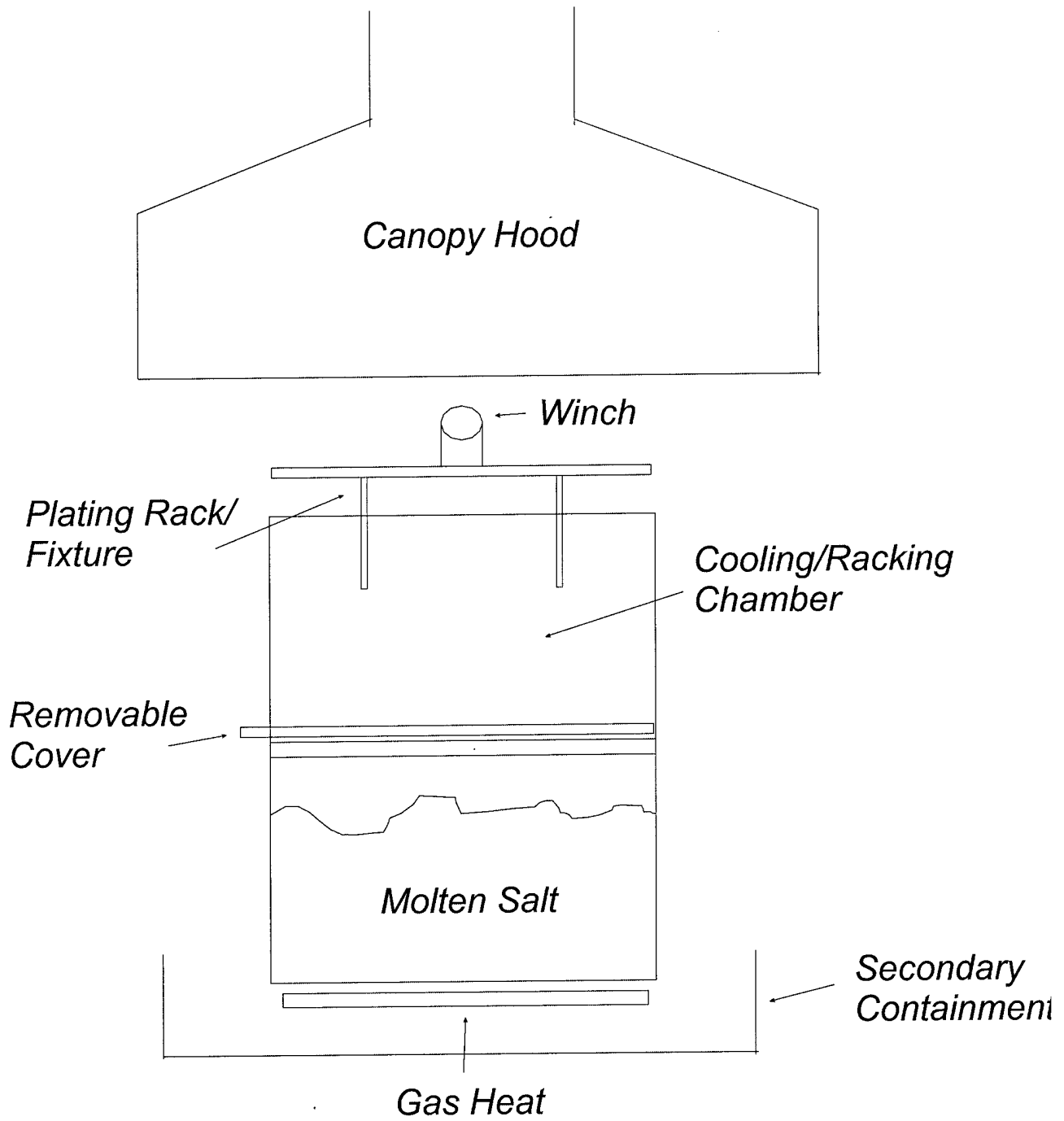


Figure 1. Molten salt plating equipment that reduces fuming of the salt bath.

## Salt Bath Costs

The salt bath is composed of standard industrial chemicals that are readily available and affordable. A cost estimate for makeup of a 1000-gallon salt bath follows. The mass of the salt bath was calculated using the specific gravity of 1.31 for aluminum chloride at 200 degrees Celsius. The approximate mass of a 1000-gallon salt bath is 4960 kg. Table 1 lists the chemical, weight percent, mass, price per pound, total cost of each chemical and total cost for the chemical makeup of the bath. Chemical costs were obtained from industrial suppliers in October 1999 and are subject to change. The cost of manganese chloride was scaled up from catalog prices for the purchase of small quantities. The cost of manganese chloride should be significantly reduced once an industrial supplier is found. If not, manganese could be added to the salt bath by other means. Manganese pellets could be added directly to the salt bath or a manganese anode could be used to electrochemically charge the salt bath. The chemical make-up costs for a 1000-gallon salt bath is less than 20,000 dollars.

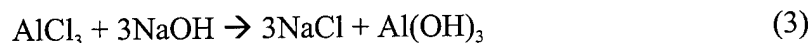
Molten salt plating of aluminum-manganese will cost more than typical aqueous plating processes. Capital equipment costs have yet to be established but should not be exorbitant due to the simple nature of the equipment. Plating of aluminum-manganese will alleviate the concerns of environmentally assisted cracking of high strength steels associated with zinc containing alloys. In addition, aluminum-manganese plating will provide functionality that is not possible with ion vapor deposition of aluminum.

Chemical	Weight Percent	Mass (Kg)	Price (\$/Kg)	Cost (\$)
Aluminum Chloride	79	3968	3.35	13,293
Sodium Chloride	10	496	1.42	704
Potassium Chloride	10	496	6.63	3288
Manganese Chloride	1	49.6	50*	2500*
Total Costs				19,785

Table 1. Chemical make-up costs of a 1000-gallon (4960 Kg) salt bath. \*The price is based on the purchase of small quantities of reagent grade chemicals. Industrial prices will be significantly reduced.

## Salt Bath Neutralization

Neutralization and disposal of the molten salt bath is simple and affordable. The following example will outline the neutralization of the molten salt bath. For simplicity in this example the molten salt bath is assumed to be 100 percent aluminum chloride rather than the nominal bath composition of 79 weight percent. Equation 1 shows the reaction of aluminum chloride with water. For every mole of aluminum chloride, three moles of hydrogen chloride are produced. Equation 2 shows the neutralization of hydrogen chloride with sodium hydroxide. One mole of sodium hydroxide is required to neutralize one mole of hydrogen chloride. Combining Equations 1 and 2 and dropping out intermediary steps yields Equation 3 the neutralization of aluminum chloride with sodium hydroxide. The reaction shown in Equation 3 can be conducted safely in an aqueous solution by limiting the exothermic reaction rate with a controlled addition of molten salt to aqueous solution. Depending upon the rate of addition of molten salt bath to aqueous solution cooling or an excess of water may need to be applied.



A one liter quantity of aluminum chloride liquid at 200 degrees Celsius with a specific gravity of 1.31 and a gram molecular weight of 133.34 converts to 9.82 moles (1.31 Kg). For every 9.82 moles of aluminum chloride 29.5 moles of hydrogen chloride would be produced requiring 29.5 (1.18 Kg) moles of sodium hydroxide to neutralize. This quantity of aluminum chloride can be neutralized with 4.92 liters of 6M sodium hydroxide solution. The neutralization process using an approximate volume ratio of 5:1 of 6M sodium hydroxide solution to aluminum chloride will result in 5.4M sodium chloride solution with insoluble aluminum hydroxides/oxides. The solubility of sodium chloride in salt water is 6.1 moles per liter so that for this example all of the sodium chloride will be in solution. Of course the volume and concentration of sodium hydroxide solution can be adjusted to suit specific process needs.

An operational molten salt bath has a nominal weight percent composition of: 79% aluminum chloride, 10% sodium chloride, 10% potassium chloride, and 1% manganese chloride. The sodium hydroxide concentration could be reduced to account for the 21% reduction in

aluminum chloride from the previous example. The neutralized salt bath will contain sodium chloride, aluminum hydroxides, potassium chloride, and manganese hydroxides. Disposal of a 5.4 M salt solution that is pH neutral should be practical and affordable. If disposal regulations warrant the insoluble aluminum hydroxides and manganese hydroxides can be filtered or separated from the salt solution before disposal.

### **Corrosion Performance**

Aluminum-manganese coatings were deposited on 4130 Steel. Processing parameters and bath chemistries were varied to provide deposits of varying thickness, morphologies, and manganese content. Aluminum-manganese deposits approximately 0.5 mils thick with a nodular structure at roughly 13% manganese performed the best. With the use of a chromate post treatment aluminum-manganese plated panels performed well in an ASTM B117 neutral salt fog. Scribed panels lasted 1000 hours in the salt fog chamber with no visible signs of red rust. Panels with no scribe exceeded 3000 hours in the salt fog chamber with no visible signs of red rust. Thicker, 1.0 mil aluminum-manganese coatings will provide improved corrosion performance. Cadmium and all of the other potential cadmium alternatives rely on the use of a chromate post treatment for adequate corrosion performance on steels. A Trivalent Chromium Post-treatment (TCP) is being developed as an alternative to chromate post-treatment for aluminum-manganese. Aluminum-manganese post treated with trivalent chromium post-treatment would provide for an entirely non-toxic replacement for cadmium.

### **Ongoing Work**

Demonstration efforts for the transition of aluminum-manganese salt bath plating to Department of Defense facilities are on going. Technical and practical issues regarding scale-up and implementation of aluminum-manganese molten salt bath plating are being addressed. Process parameters for optimized coating composition, deposition rates, coating thickness, coating adhesion, and appearance continue to be refined. Quality control procedures for salt bath maintenance and coating deposition are also being developed. Functional performance of the aluminum-manganese deposit will continue to be evaluated for sacrificial corrosion performance,

torque-tension relationships, fatigue performance, paint adhesion, hydrogen embrittlement, and environmentally assisted cracking.

Design, construction, and installation of a 100-gallon molten salt plating system is the major milestone for the upcoming year. The 100-gallon system will have the capability for both rack and barrel plating. The 100-gallon system will be able to provide production representative aluminum-manganese deposits. Successful operation of the 100-gallon system and corresponding aluminum-manganese coating performance will validate aluminum-manganese plating process as a viable replacement for cadmium plating.