IAEG® WG2 Technical Exchange Hard Chrome Plating – Chromate Free Alternative Processes in Aerospace Applications

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Version ***1***

Version History

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1 Purpose

The purpose of this document is to provide voluntary supplemental guidance for replacement of chromates in hard chrome plating processes within the aerospace industry. This industry specific guidance document was developed by the International Aerospace Environmental Group, Work Group 2 “Replacement Technologies”, Hard Chrome Plating project.

2 Scope

This document provides a collection of available alternatives and upcoming technologies with recommendations for their application (applicability, performance, EHS), which may not be exhaustive. All described available technologies are already in use in aerospace industry for certain applications.

3 Background

Functional Hard Chrome plating is widely used throughout the Aerospace industry. To produce functional (thick) hard chrome plating (HCP), chromic acid is used in the plating process. Under applicable government regulatory programs, the hexavalent chromate compound (chromium trioxide) used to produce chromic acid is identified as having an adverse effect on human health and the environment. Consequently, EU has announced it will ban the import and use of chromium trioxide after September 2017 unless authorisations for specific use applications have been approved. An authorisation application for the use of chromium trioxide in hard chrome plating has been made by the CTAC consortium. However, any authorisation granted by the EU commission will be time limited and have EHS restrictions.

Hard chrome is electroplated onto steel or other metal alloys and can provide –

- A cost-effective coating that can be easily applied to complex geometry parts
- A hard coating which is resistant to wear from sliding and fretting.
- Environmental, wear and corrosion resistance.

At present, there are a number of alternatives to functional hard chrome plating but no direct 1:1 replacement. Therefore, any replacement of hard chrome involves application analysis and design modifications.

4 Requirements for alternative technologies

4.1 Performance of current hard chrome plating coatings

Important characteristics of hard chrome coatings are listed below:

- High hardness
- Extensive thickness range
- Good adhesion to base metal
- Visual aspect
- Some corrosion resistance
- Ability to be ground or polished to a very smooth finish

- Can be applied in non-line-of-sight applications

For more specific applications, additional requirements are applicable. An example (AMS2460) is given below:

- Appearance - shall be smooth and uniform in appearance
- Thickness: 0.0001 to 0.010 inches (application dependent)
- Hardness: 600 HVN (Vickers) minimum for plating finished to a semi-bright or matte luster or 850 HVN (Vickers) minimum for plating finished to a bright pebbly luster.
- Adhesion: meet requirements per ASTM B 571 (no mandrel), no visible separation at 4x magnification
- Hydrogen Embrittlement: shall not cause hydrogen embrittlement in steel parts 36 HRC and over (ASTM F 519)

4.2 Additional properties to be considered for replacement technologies

During the development of replacement for hard chrome plating it is obvious more requirements are needed to ensure consistency and understanding of possible applications. Possible replacement technologies might differ in their performance so that not every solution can be applied everywhere. The replacements are less versatile to use than the original hard chrome plating. The main considerations for replacements technologies are:

- Wear Resistance
- Friction Properties
- Fretting Behaviour
- Load Resistance
- Corrosion Resistance
- Fatigue Resistance
- Lubricity Properties

Additionally, process specific criteria must be fulfilled and, the coated components must be tested for certain applications separately. For example, tests like: track roller, pin-in-bushing, wear and sealing tests, etc., will be necessary for process qualification.

5 Critical Replacement Technologies

Replacements which are relying on nickel and / or cobalt are seen as critical.

Nickel metal is known as a skin sensitizer and also classified as carcinogenic Cat.2. Inside the European Union (EU) further restrictions like lower exposure levels are expected.

Nickel salts (like e.g. nickel sulphate) used for electrolytic coating processes are classified as carcinogenic and reprotoxic Cat.1.

Cobalt and Cobalt salts are classified in the same way as the nickel salts. Cobalt carbonate, cobalt dichloride (anhydrous), cobalt di(acetate), cobalt dinitrate and cobalt sulphate are already part of the EU REACh candidate list.

These technologies would not provide meaningful reprieve or long term benefit in terms of environment health and safety. However, they might be applied as a short-term solution due to regulatory pressure – to replace hard chrome within the EU due to REACh authorisation.

6 Existing Alternatives

For ease of selection the hardness and some additional properties (e.g. corrosion resistance) of the alternative coatings are given in the following section. These values are provided for illustration purposes only. Exact values will need to be agreed to and confirmed for the given combination of part, coating technology and coating shop.

6.1 No Coating

For new design of parts, through material selection, the material pair can be chosen to eliminate the need for coatings for the specific application. It has been shown that for certain applications e.g. latch combinations of stainless steel/stainless steel and stainless steel/aluminium, a no-coating optionmight be suitable in conjunction with dry film lubricants.

6.2 Electrodeposited Coating

In electrodeposition (or electroplating), electrical current is used to reduce metal cations in solution so that they form a coating on an electrode which is the part to be coated. Due to the need of a homogeneous electrical field in the setup there are limitations to the shape of the part to be coated. The surface to be coated also needs to be conductive as it acts as an electrode.

Coating types:

- Cobalt - Hardness: 400 HV maximum
- Cobalt Phosphorus (e.g. AMS2428) - Hardness: >510 HV, corrosion resistance: >200h SST
- Cobalt Phosphorus with particulate – Hardness > 550 HV/ >850 HV after heat treatment
- Nickel – Hardness >300HV

6.3 Electroless (Nickel) Plating

Electroless plating is a non-galvanic deposition method. In this process several reactions occur simultaneous without external electrical power in an aqueous solution. These reactions lead to the deposition of material onto the substrate. Depending on the bath composition, electroless plating can also be applied to non-conductive surfaces. This process is particularly suitable for complex part geometries due to its uniform deposition thickness. Currently only nickel alloys are in use as potential chrome plate alternates.

Coating types:

- Electroless Nickel (Phosphorus) Coating (e.g. AMS 2404 (AMS-C-26074)) - Hardness: 450 - 550HV, up to 1000 HV with heat treatment. With high phosphorous content (≥10%) it gives good corrosion and chemical resistance.
- Electroless Nickel Phosphorus with PTFE (e.g. AMS 2454) - Hardness: > 300 HK25; low friction
- Electroless Nickel Boron (e.g. AMS2399, AMS2433 Type 1 or 2) - Hardness: >650 HV as-plated; >1000 HV after post treatment

6.4 Thermal Spray

Thermal spray metallic coatings are produced by projecting metal powder heated to its semi-molten state, onto the surface to be coated using a stream of gas or plasma. These coatings consist of a several stacks of metal splats, resulting from spraying multiple passes. Each pass lays a coating layer of ~20µm by piling up of splats on the substrate surface. Some level of porosity can exist between these splats. The morphology and properties of the coating is directly linked to the process type.

In addition to metal, deposition of ceramic materials or cermets is also possible using thermal spray. Examples of ceramic coating that may be applied by thermal spray include aluminium oxide, aluminosilicate and zirconia-based ceramics. A "cermet" is a blend of metal-oxide ceramic (cer) and metal (met) materials binders (e.g. Aluminium Oxide – Nickel Aluminium).

High velocity oxygen fuel (HVOF) spraying uses a mixture of gaseous or liquid fuel (e.g. hydrogen, methane, propane, kerosene) and oxygen which is fed into a combustion chamber, where they are ignited and combusted continuously. The resulting plasma (jet) reaches a velocity above 1000 m/s. Metallic powder is injected into the plasma. The stream of hot gas, including the powder, is propelled towards the surface to be coated. The ceramic and metal binders partially melt in the plasma stream are deposited upon the substrate. The resulting coating has low porosity and high bond strength.

There are some limitations with the thermal spray process: The substrate needs to be cooled during thermal spraying or needs to withstand the relative high temperatures that could occur during thermal spraying. Being a line-of-sight process, thermal spray cannot coat internal surfaces of parts (such as tubes) with small internal diameters (< 75 mm) and might also be not be suitable for complex geometries. Post treatment (grinding) might be needed.

Lower temperatures are only possible with specific thermal spray processes (such as cold or kinetic spraying) and coating materials.

Coating types:

- CuAlFe (Copper Aluminium Iron) - Hardness: >150 HV
- Molybdenum - Hardness: >400 HV
- WC (Tungsten Carbide) - Hardness: 800 – 1200 HV; Corrosion Protection: < 750h SST (ISO9227)
- CoCrMo (Cobalt Chrome Molybdenum) - Hardness: 400 HV; No direct contact with Aluminium alloys or non-corrosion resistant steel recommended to avoid galvanic corrosion
- CuNiIn (Copper Nickel Indium) - Hardness: 120 HV; No direct contact with Aluminium alloys or non-corrosion resistant steel recommended to avoid galvanic corrosion
- WC-Co-Cr (Tungsten Carbide Cobalt Chromium) and WC-Co (Tungsten Carbide Cobalt) (e.g. AMS7882, AMS7881, AMS2448) - Hardness: 850 HV; No direct contact with Aluminium alloys or non-corrosion resistant steel recommended to avoid galvanic corrosion.

6.5 Chemical Vapor Deposition (CVD)

Chemical vapor deposition or CVD is a generic name for a group of processes that involve depositing a solid material from a gaseous phase in a controlled atmosphere chamber.

Temperature of the substrate may reach temperatures above 500°C during processing.

Coating types:

- Diamond-Like Carbon Coating - Hardness: 500 – 3500 HV, does not provide corrosion protection
- WC (Tungsten Carbide) - Hardness: 800 – 1200 HV; Corrosion Protection: < 750h SST (ISO9227)

6.6 Physical Vapor Deposition (PVD)

Physical Vapor Deposition (PVD) can be broadly defined as a family of processes in which the deposition species is created in a vacuum, transported to a component and deposited on the surface to grow a thin film coating. The PVD processes of most interest for wear resistant coatings utilize a source which produces metal ions that are attracted and accelerated to the components by applying a bias voltage.

Three types of ion source are commercially used.

1. Evaporative ion plating utilizes an electron beam to evaporate ions from a crucible.

2. Sputtering ion plating bombards a solid surface with a flux of energetic particles to eject atomic species (ions) which may be used as a source for deposition.

3. Cathodic Arc ion plating utilizes ions which have been evaporated via a cathodic arc.

Sputtering and arc evaporation sources are the most flexible with respect to ion species. Both can deposit non-metals as well as metals and metal alloys. Electron beam sources are limited to pure metals. In order to produce optimum coating adhesion, deposits are generally applied at part temperatures in excess of 300 °C.

Parts to be coated need to withstand vacuum. Surfaces to be coated may be limited due to part geometry. Line-of-sight coating applications work best. For example, coating of internal surfaces, like tubes, is difficult/impossible. The quantity of parts that can be effectively coated at one time will be limited according to chamber size and area to be coated.

Coating types:

- CrN (Chromium Nitride) - Hardness: >1800 HV, offers limited corrosion protection
- TiN (Titanium Nitride) (e.g. AMS2444) - Hardness: >2000 HV, does not provide corrosion protection
- WC C: H (Tungsten Carbide Carbon) - Hardness: 1000-1500 HV, offers low coefficient of friction but does not provide corrosion protection
- DLC (Diamond-Like Carbon) Coating - Hardness: 500 – 3500 HV, does not provide corrosion protection

7 Upcoming Technologies

Currently efforts focus on improveming the already existing and applied technologies (vapor deposition and thermal spray) targeting the elimination of their specific drawbacks. This is a logical step considering the conclusion from the analysis of existing technologies – there is no one to one solution for hard chrome plating. Companies now try to enable wider application of their technologies (overcome dimensional, geometric and temperature limitations, improve corrosion resistance). Unfortunately, some of these improved technologies still rely on nickel and cobalt which could be a problem with respect to upcoming concerns on those metals and their salts.

A potential future one-to-one replacement could be the electrolytic deposition of Hard Chrome from Cr (III) solution. It is possible to create hard and dense chromium layers with sufficient adhesion which could be an alternative to deposits from chromium (VI). However, the macro cracks in deposits made from Cr (III) are a major concern in terms of sealing and machinability. Current solutions are not yet mature and most of them still rely on a Nickel under layer for the above-mentioned problems. Leakage through the macro cracks is possible, which could lead to corrosion and loss of fluids in hydraulic and pneumatic sealing applications.

These macro cracks need to be eliminated or greatly reduced before the Cr (III) plating process can be considered by aerospace companies.

8 Conclusion

Taking into account all technologies reviewed in this project the most important conclusion is that there is no one-to-one replacement for current hard chrome coatings. For each specific application, a suitable replacement has to be evaluated based on its specific merits.

For the choice of alternative coating, one has to consider not only the performance of the coating but also the different application technologies. The alternate processes have limitations for geometry (line of sight, size) and also for temperature resistance (some processes require high temperatures).

Not all replacement technologies offer a substantial improvement in terms of health and safety concerns. Some technologies contain nickel or cobalt or in some cases, utilize their salts. These substances are also known or suspected to be carcinogenic.

For some technologies, there is no commercial specification available. This is also complicating the wider introduction of these alternatives due to missing performance and quality standards.

A future one-to-one replacement could be hard chrome from Cr (III) solution, however its maturity level is still considered to be too low.