Chrome Plating From Cr(III) in Ionic Liquids

An Industrial Perspective

Dr John Archer
Poeton Industries Ltd
21 February 2008

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Traditional Hard Chrome Plating

- Hard chrome is traditionally produced from solutions containing chromium trioxide and sulphuric acid.
- It is used in a variety of applications due to its hardness and wear resistance. In addition, its microcracked structure give it good oil retention properties producing a low friction surface.
- Unlike decorative chrome plating which is limited in thicknesses that can be applied, hard chrome can be applied many hundreds of microns thick, producing a load bearing surface.
- Due to Health, Safety and Environmental pressures, a search for alternatives to hexavalent hard chrome plating has been in progress for many years.
- The search for alternatives also covers other traditional hexavalent chrome processes such as passivates
- Cr(III) salts are not classified as hazardous and are ideal alternatives

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Environmental Issues

- The use of hexavalent chrome in the electroplating industry has long been strictly controlled to minimise its effects on both employees and the environment.
- The classification of chromium trioxide has recently been upgraded from toxic to very toxic. This can have very costly implications for users of this material (COMAH registration).
- Under current legislation, users are obliged to use alternatives to hazardous materials wherever practicably possible. Pressure in this area will increase as REACH legislation comes into force.
- In the Aerospace Industry this has reached the stage where large end users such as Boeing and Airbus have stopped specifying hard chrome on all new aircraft.
- Commercial uses are not as advanced as Aerospace in this area.
- 80%+ of Poeton hard chrome business is for Aerospace

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Current Alternatives to Cr(VI)

- For decorative applications (a thin layer of electroplated chrome on top of electroplated nickel), aqueous solutions based on Cr(III) salts have been commercially available for many years.
- To date, hard chrome deposits produced from aqueous Cr(III) systems have produced thick, hard or microcracked deposits. The combination of all 3 has proved elusive.
- The current preferred option for hard chrome replacement in Aerospace is HVOF (High Velocity Oxy Fuel) sprayed coatings.
- There are some major problems with use of HVOF coatings as hard chrome replacement, amongst which are:
  - Limited geometry parts can be coated.
    - HVOF is a 'line-of-sight' process and, as such, small diameter bores, etc cannot be sprayed.
  - Health and Safety concerns are now being raised about the post spray grinding of such coatings.

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The advantages of using Cr(III)

- Specifications and drawings!
- Due to the nature of the end product, coatings on Aerospace components are strictly controlled by drawings and specifications:
  - Drawings specify the coating and its thickness.
  - Specifications describe the method used for applying the coating and what properties it must have (confirmed by regular deposit testing).
- Drawings are sealed documents and cannot be changed without lengthy, rigorous and very expensive testing of components processed under the proposed changes.

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The advantages of using Cr(III)

- Specifications are easier to amend as only the application method is changed. All that is required is proof that the deposit has exactly the same properties .
- A hard chrome deposit produced from a Cr(III) system would not require changes to drawings, only specifications.
- Design engineers are already familiar with the properties and performance of hard chrome coatings.
- A direct hard chrome replacement using trivalent chemistry is the Holy Grail of many designers in the Aerospace industry.
- However, such a solution has to be affordable.

Industrial Objectives of Cr(III) from Ionic Liquids

- Produce a coating from a trivalent chrome system with identical properties to deposits produced from traditional aqueous hexavalent chrome baths
  - Appearance
  - Hardness
  - Wear resistance
  - Corrosion resistance
  - Microstructure
- A commercially viable process

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Development of Chrome Deposits from Ionic Liquids

- Poeton first became involved in depositing chrome from Ionic Liquids in 2001 as part of a DTI/Link project .
- Participants included Leicester University, Scionix (Genacys) and Smiths Aerospace Activation Systems (end user).
- Coatings produced from an Ionic Liquid containing chrome (III) chloride hexahydrate, choline chloride and an additive.
- Black coatings were produced from the original formulations. Deposits had a similar appearance to ‘Black Chrome’ coatings produced from sulphate free hexavalent aqueous solutions.
- Coating thicknesses were greater than those obtained from aqueous baths
- Deposit did not have sufficient sliding wear performance for end user
- Black Chrome deposits from Ionic Liquids are finding interest from end users who require properties such as heat absorption

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Ionic Black Chrome Piston on Test

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Ionmet Project

- The development of hard chrome from Ionic Liquids has continued under the EC funded Ionmet programme.
- The majority of the further progress has been achieve by Ecole Nationale Supérieure des Mines (ENSM-SE/ARMINES) in Saint –Etienne.
- With a slight modification to the earlier Leicester formulation, a silver, metallic chrome deposit could be produced from an Ionic Liquid based on chrome(III) chloride hexahydrate.
- Poeton have been able to reproduce these deposits using a 5 litre plating tank.
- Using this equipment, Poeton have produced deposits 100µm thick.
- Deposition rates at a current density of $20 A/dm^2$ are 0.7-0.8µm/minute. This is much faster than conventional hard chrome with a plating rate of 0.3-0.4µm/minute at $40 A/dm^2$.

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Chrome Deposit from Ionic Liquid

Deposit produced by ENSM-SE/ARMINES

Deposit produced by Poeton

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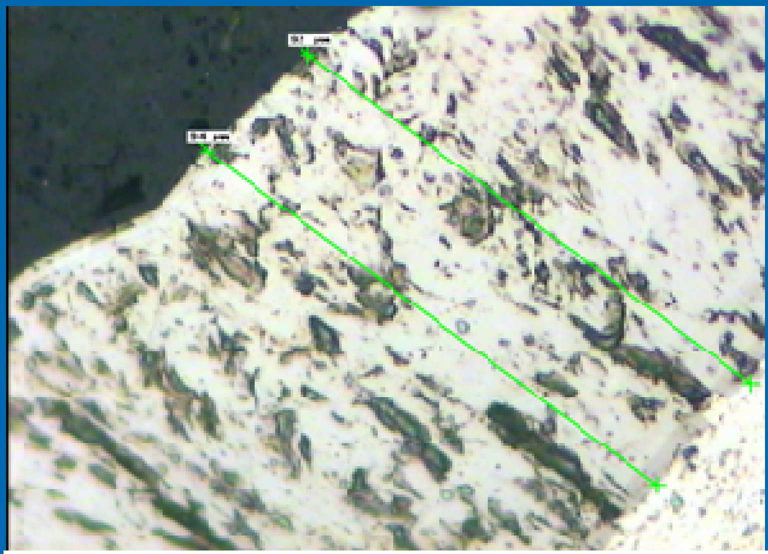
Pilot Equipment and Deposit Cross Section

5 Litre Plating Cell



500X Magnification

Microsection of 95µm thick metallic chrome deposit produced from Ionic Liquid

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Deposit Hardness

- The Aerospace specification for the microhardness of hard chrome deposits is a minimum of 750Hv.
- Conventional as plated hard chrome is in the range 800-1000Hv.
- The hardness of chrome deposited from an Ionic Liquid by Poeton is 800Hv.
- This is at the bottom end of the traditional chrome hardness range, but within Aerospace specifications.
- A post treatment process is being developed to increase deposit hardness to between 1200Hv to 1450Hv

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Coating Adhesion

- In addition to the physical properties of the coating, it also has to exhibit good adhesion to a range of substrates.
- As the plating solution is not an aqueous system, conventional pretreatment methods have to be modified to prevent water build up in the ionic liquid.
- Methods have been established by both ENSM-SE/ARMINES and Poeton for mild steel substrates. Adhesion has been confirmed by file test, grinding and ball indentation testing.

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Areas of Development to Produce a Commercial Deposit

- To make the production of hard chrome deposits from trivalent chrome Ionic Liquids a commercial reality, work is continuing on its development under the Ionmet project:
  - Development of plating protocols for a range of substrate materials.
  - Deposit characterisation
    - Microstructure
    - Wear resistance
    - Corrosion resistance
  - Long term operation of Chrome (III) Ionic Liquid
    - Variation of properties with bath life
    - Maintenance of Ionic Liquid
    - Risk assessment/REACH/Health and Safety Issues
  - Construction of pilot plating tank as first step in scale up of process.

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Conclusions

- A direct replacement for hard chrome produced from a chrome (III) system has been sought for many years.
- Aerospace design engineers see this as their preferred solution to the chrome (VI) problem as they understand its properties and it has none of the downsides exhibited by existing replacements.
- At the moment, hard chrome deposits from aqueous Chrome (III) systems are not available.
- Hard, thick, metallic chrome coatings have been produced from a Chrome (III) Ionic Liquid system which show promising results.
- Work is continuing to turn this technology from a laboratory beaker scale operation into a fully industrial process.
- For further information visit the Ionmet website at www.ionmet.org

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