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DEVELOPMENT OF THREE ALTERNATIVES FOR HEXAVALENT CHROMIUM COATINGS

CONTENT

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In recent years, efficient alternatives for hard chrome applications have been sought. An urgent need, as the deposition process for hard chrome uses chromium trioxide, which is toxic and carcinogenic, and therefore subject to heavy regulation. It will be banned in the short term for various applications. Although there are alternatives, they do not necessarily meet the desired specifications or may require major modifications to the production facilities.

An ongoing research project explores three ways for developing alternative coating technologies and materials.

One of the technologies most subject to such regulations is hard chrome plating (hexavalent chrome plating). This surface treatment makes it possible to apply multifunctional coatings at an acceptable cost to products that resist both wear and tear and corrosion and can thus be used in many applications. During the deposition process, however, hexavalent chromium, which is toxic and carcinogenic, is used, leading to a strict regulation within the REACH regulation, which will lead to a ban on the use of this process in the foreseeable future.

The transport and processing sectors, which are very active in the Belgium-France border region, are largely affected by these regulations. As today's alternative treatments do not meet industry's specifications or are not compatible with certain applications, large companies, start their own authorization procedure to continue the use of CrO3 in a save way for several years. By doing this, the companies are winning time to explore the best alternatives before implementing them.

The aim of the Interreg project AltCtrlTrans, in which Sirris participates, is to offer these companies new alternatives to hexavalent chrome plating, which meets their real needs and for which the old treatment lines may (partly) be recovered. Mise au point de technologies et de matériaux de revêtement alternatifs

1 DEVELOPING ALTERNATIVE COATING TECHNOLOGIES AND MATERIALS

AltCtrlTrans investigates three ways for developing alternative coating technologies and materials:

1. development of nickel-boron coatings through an electroless process, free from heavy metals;
2. development of electrochemical technologies, based on baths, based on trivalent chromium with improved properties compared to existing deposits, or other promising formulations;
3. improvement of the deposition method by Plasma Transferred Arc (PTA).

1.1 Nickel-boron coatings – electroless

Electroless nickel deposition is conducted in an electrolyte, similar to nickel electroplating, in which a chemical reducing agent is added, and it does not require any external current source. The nickel ions are reduced by the oxidation of the chemical reducing agent. In electroless nickel deposition, a uniform coating is obtained even on a complex, intricate and recessed substrate, and this is another significant advantage over electroplating. The deposits obtained through electroless nickel deposition vary according to reducing agents used. Electroless nickel-phosphorus deposits are obtained through hypophosphite-reduced baths, electroless nickel-boron deposits are obtained through either amine-borane or borohydride-reduced baths, and pure nickel deposits are obtained through hydrazine-reduced bath.

Among the electroless nickel deposits, the electroless nickel-phosphorus deposits are more popular, however, the interest and the demand for the electroless nickel-boron deposits through borohydride-reduced baths have increased considerably, due to their excellent mechanical properties, outstanding wear resistance, low friction, good lubricity, improved solderability, and conductivity, to name but a few. Furthermore, the electroless nickel-boron deposition has a higher efficiency than the electroless nickel-phosphorus deposition, since the borohydride has a higher reduction efficiency than the hypophosphite. In addition to the reducing agent and the nickel source, the electroless nickel processes contain numerous compounds, such as a complexing agent, stabilizer agent, pH adjuster, buffering agent, surfactant, etc.

The electroless nickel-boron coating process has been known for improving the surface properties of numerous substrates since 1954, when the first electroless nickel-boron deposit was produced, and since 1989, which was the starting date of the mass production of the electroless nickel-boron deposits. Substrates plated by electroless nickel-boron deposition can be stainless steel, carbon steels, iron, aluminium and aluminium alloys, magnesium and magnesium alloys, titanium and titanium alloys, glasses, plastic, ceramic and metallic powder. The reason the electroless nickel-boron deposits attract remarkable attention is due to their outstanding properties that are significantly dependent on the deposit chemistry, particularly the content of boron, varied from the deposition bath. The prominent properties of the electroless nickel-boron deposit are its excellent hardness and outstanding wear resistance, which are close to or superior to the hard chromium coating. In addition, the aforementioned properties can be pointedly enhanced after an appropriate post-treatment, such as a heat treatment. Therefore, the electroless nickel-boron deposits have a noteworthy potential to replace the hard chromium coating. Additionally, the electroless nickel-boron deposits with low friction coefficient, unique cauliflower-like and columnar morphology, which can decrease the contact up to 70% and allow retention of lubricants, and with lubricity action of the boron can meet the standards set by the hard chromium coating. An issue is that the electroless nickel-boron coating process contains a lead-based stabilizer, used as a standard stabilizer for almost 30 years. There is an environmental and health concern linked to the use of lead, the same as the hexavalent chromium.

In the AltCtrlTrans-project, the focus of the research is to produce the electroless nickel-boron deposit in an environmentally-friendly bath that does not contain a lead-based or any toxic compound as a stabilizer.

The stability of the bath can be controlled through the optimization in the concentration of the compounds in the bath. However, the most important compounds are stabilizer agent, complexing agent, and reducing agent, order of importance concerning the bath stability. To remove lead in the electroless nickel-boron coating process, a unique study was done by researchers of the Metallurgy lab at the University of Mons. The electroless nickel-boron deposit (ENB) was produced in a stabilizer-free bath. Besides, the bath stability was succeeded through the optimization in the concentration of the complexing agent. However, the plating rate and the quality of the deposit obtained through the stabilizer-free bath did not meet the requirements. Further development in the stabilizer-free bath has been accelerated during the AltCtrlTrans project.

The results of the deposits from the stabilizer-free bath are compared with results of the deposits (ENB-Pb) from the lead stabilized bath. Those results are shown below. It is clear that there is a noticeable improvement in the electroless nickel-boron coating process in the stabilizer-free bath. However, the new deposits developed within the AltCtrlTrans project have properties close or superior to the ENB-Pb deposits from the lead stabilized bath. For instance, the corrosion resistance of the new deposit is better than the one of the conventional deposit that is from the lead-stabilized bath. While the corroded area of the conventional electroless nickel-boron deposit is 20%, there was no corrosion with the new deposit.

Properties	Before AltCtrlTrans	Ongoing work AltCtrlTrans	ENB-Pb (reference)
Plating rate (µm/h)	10	14	22
Surface (Vickers) hardness (hv_{50})	713	933	896
Cross-section (Knoop) hardness (hk_{30})	704	886	892
Hardness (Nanoindentation) (GPa)		≈ 12	≈ 12
Elastic Modulus (GPa)		210	190
Critical load (N)	20	22.7	24
Friction coefficient	0.48	0.47	0.45

1.2 Electrochemical coatings

Electrodeposition is a method that uses electric current to reduce metallic ions from an electrolyte to metals which form a metallic coating on a substrate. This technique is widely used in industry for technical and decorative applications. Electrolysis can be controlled by regulation of either current or voltage.

The first challenge for electrolytic deposition is to obtain coatings from water-based solutions with the chemical composition required. For that, cyclic voltammetry will be carried out to understand the electrodeposition mechanism. This study will be performed in unitary system and binary system. The composition of the bath will be optimized, particularly the ratio of the metallic source to the complexing agents. In the electroplating process, the thickness of the coating layer is significantly affected by the plating solution, plating current and time, and also the distance between the workpiece and anode. This work mainly focuses on the factors that significantly affect the thickness and the distribution of the solution plating on the cathode surface. The factors selected included plating temperature, distance between cathode and anode, plating current, agitation and the chemical composition.

The development of new metallic materials which are amorphous alloys are investigated in the project. This metallic glass state combines a low arrangement of atoms with high homogeneity of their distribution. The lack of structurally ordered regions and the absence of grain boundaries usually lead to better wear and corrosion resistance, higher toughness compared to typical polycrystalline alloys. Special cases in amorphous alloys are materials containing significant amounts of either W or Mo. A case-study in this project is the development of binary alloys with the addition of W (FeW, NiW) in the coating, which improves the corrosion resistance behaviour by structure amorphization.

The second approach is the multilayer nickel-chromium plating. It could be a solution to the chromium deposit from trivalent solutions, which reveal some defects in the form of a micro-cracks network. By depositing a low Cr-NiCr alloy layer between two high Cr-NiCr layers a multilayer structure is obtained with great hardness and due to the ductile low-Cr layer the internal stress is reduced. This would also result in a less brittle coating and consequently better corrosion properties.

1.3 Plasma transferred arc coatings (PTA)

Plasma transferred arc (PTA) coating is an automated welding process, compatible with current industrial installations. It is composed of a robotic arm allowing rapid, reliable and repeatable manufacturing. The object supported by this arm is in motion below the fixed plasma torch. The filler metal in powder form is melted by the plasma and deposited on the part to be coated. This process is applicable for deposits of alloy: cobalt base, nickel base, chromium base, iron base and tungsten-carbide mixtures. The materials to be recharged are generally low-alloy steels, alloy steels, stainless steels and copper alloys. The part is coated with a thickness of 1.5 to 4.5 mm in a single pass or more with several passes. The deposit created has optimal characteristics: metallurgical bond between the deposit and the substrate, limited thermally affected zone (Z.A.T), high quality of the deposit (homogeneity, absence of porosity and a low dilution rate). The recharging materials are designed to withstand severe impact while withstanding temperatures between 800 and 900 ˚C. They also exhibit exceptional hardness and toughness and are generally very resistant to corrosion. Thus, the PTA allows the coating of a large number of tools. It is used in the fields of shipbuilding, rail and automotive industries, nuclear industry, glass and mould manufacturing, and plastics industry.

Current research within CRITT-MDTS (Centre Régional d'Innovation et de Transfert de Technologie – Matériaux, Dépôts et Traitements de surface) focuses on the deposition of pure chromium powder. Indeed, there is currently no pure chromium deposit. This powder, produced by grinding, has an angular shape. Deposits are more difficult to implement. However, smooth and molten deposits were obtained and are being characterized.

This article was prepared in collaboration with the research partners of the AltCtrlTrans-project. Further information on this Interreg project can be found on the project page.

1.4 Sources

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