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Plasma Aided Process As Alternative to Hard Chromium Electroplating

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Abstract

This paper will present an overview of toxicity of hexavalent chromium as well as effort for its replacement by a wide spectrum of alternative materials and technologies. Cr-based materials such as trivalent electrodeposit will be one of strong candidates for hard chromium by surface modification of its surface hardness. Ni-base alloy deposits has proved its application in specific mold for glass. HVOF has been studied in aircraft and military sector. There are still under way of development for commercially available alternatives. To date, no single coating has been identified as universal process as comparable to conventional hard chromium electroplating.

Keywords : Chromium plating, Hard chromium, Replacement, Alternative coating

1. INTRODUCTION

Electroplated hexavalent chromium coatings have been used in many technical applications for many decades.

Chromium plating has constantly enlarged its field of applications, having today an exceptionally wide range of use in almost every aspect of everyday life and modern technology. As a example, the US consumes approximately 5.3×10^8 kg of chromium each year with about 4.1×10^6 $kg \cdot year^{-1}$ being used for hard chromium plating and about $10^6 kg \cdot year^{-1}$ for decorative chromium plating[1)].

It is worth mentioning that, compared with most other electroplating processes, chromium plating has many unsatisfactory features, like an aggressive electrolyte, a high energy consumption, a slow deposition rate, and a poor efficiency. But despite of disadvantages, it survives as a common coating because of its high hardness, its high service temperature, and its excellent properties when combined with certain other coatings. In this review, the regulations upon hexavalent chromium electroplating is outlined in connexion with environmental issues. The alternatives to hexavalent chromium have been focused in view of materials as well as processes based on plasma and electrochemistry.

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2. TOXICITY OF HEXAVALENT CHROMIUM AND REGULATIONS

Although chromium plating has many advantageous coating properties, its major drawback is that it uses hexavalent chromium, classified as toxic and carcinogenic by the International Agency of Search on the Cancer.

It was reported that there has been an increase in lung cancer of 15%in workers in the chromium plating industry[2]. The hexavalent chromium can also cause irritation of the upper respiratory track, skin irritation, and chronic ulcers[3]

Therefore the Environmental Protection Agency (EPA) ammended the national regulation to control air emission for chromium under the so-called MACT (Maximum Achivable Control Technology) Standards in 1990 and issued the federal Nation Emission Standard for Hazardous Air Pollutants (NESHAP) in 1994[4].

Effluent limitations also exist for hexavalent chromium in electroplating wastewater discharges under the Clean Water Act (CWA). Resulting electroplating wastewater sludges are regulated as listed hazardous wastes under the Resource Conservation and Recovery Act (RCRA).

In addition, worker exposure to hexavalent chromium is regulated by the Occupational Safety and Health Administration (OSHA) through its permissible exposure limits (PELs). The chromium plating process is a low efficiency process which results in vigorous gas evolution at the electrode this can result in hexavalent chromium contaning airborne mist which has been widely recognized as an environmental, safety, and occupational health problem

OHSA air standards currently allow a PEL of 0.1 mg/m^3 in the workplace. However, A study at a PEL of 0.051 mg/m^3 by Johns Hopkins in 1996 has indicated that there is a significantly increased cancer risk at this PEL and therefore there is consideration of reducing the PEL. New PELs of at most 0.005mg/m^3 to as low as 0.0005 mg/m^3 have been discussed and were to have been implemented as law in October, 1999. However, the signing into law of the new PEL has been temporarily delayed while opposing advocacy group contest over the final new PEL value. As PEL of less than 0.01mg/m^3 would significantly increase the cost of plating, there is a general consensus that hexavalant chromium plating will no longer feasible[5].

Another environmental issue that has perhaps received less recognition has been the permissible concentrations of hexavalent chromium in plant discharge water which goes into POTWs (publicly Owned Treatment Works). The EPA Metal Finishing category standards (CFR 40, Part 433) look at total chrome limits without distinguishing hexavalent chromium. The max daily limit for total chrome is 2.77 mg/liter with a monthly average limits of 1.71 mg/liter. The new limits being looked at for the Metal Products and Machinery category legislation were initially set at 0.3 mg/liter max daily limit and 0.2 mg/liter monthly average after Phase 1. These proposed limits are currently under further review in recently started public hearings

3. EFFORTS FOR CHROMIUM REPLACEMENT

There are several governmental programs charged with evaluating various technology alternatives to hexavalent chromium. The programs under the Environmental Technology Initiative dealt with following subjects.

- Use of a nickel-tungsten-boron alloy
- Replacement with physical vapor deposits (Cr-, Ti- and Ti-Al-N)
- Alloy deposition of hard coatings (Ni-W-Si-C and electroless Ni-W)
- Hard chromium via sputtering

The DoD has been organized in a DoD and industry collaboration known as the Hard Chrome Alternatives Team (HCAT) since 1996. HCAT has recently linked up with the DOD's Propulsion Environmental Working Group (PEWG) which brings together the DoD and Gas Turbine Engine (GTE) manufacturers and their suppliers. They perform the project, "Tri-Service Dem/Val of Chromium Electroplating Replacements" under the sponsorship of the DoD Environmental Security Technology Certification Program (ESTCP), the Air Force, Navy and DARPA with a total commitment of $6 million over five-year period.

In this project, HVOF thermal spray coatings are being validated by the HCAT and the Joint Group on Pollution Prevention under a separate ESTCP program as a replacement for EHC for line of sight applications on aircraft components such as landing gear and hydraulic actuators. The current project will parallel that effort with the objective of validating HVOF coating as a cost-effective, superior performance replacement for EHC plating on different types of components used in gas turbine engine.

Recently, International program to replacement to hard chromium plating is planned. This project entitled "Eco-efficient and high performance hard chrome process" ECHCHROME" is proposed within the framework of the Intelligent Manufacturing System (IMS). IMS is an industry-led, international research and development (R&D) Program. The purpose of this project is to study and to develop process allowing to obtain harder, thick coating of chromium and more resisting to the corrosion than the traditional coatings, from a new and non-toxic electrolytic solution. The solution will combine the advantages of the techniques of trivalent chromium plating under complexed shape (American and Japanese technique) and under free reduced shape (European technique).

On one hand the European technique, based on the hexavalent chromium reduction, with the recent results of a Craft project which proved technically satisfactory but hardly possible to apply on an industrial bias ; this research was conducted by France (with ENSM) 를 norther Europe, with the finish research center VTT ; thus their decision to involve other major european partners towards this topic.

On the other hand, the technique worked on in the USA and Asian countries, based on complexed trivalent chromium which proved only appliable on thin decorative chrome plating, but meeting difficulties on thicker industrial layers. Atotech, Musachi (Japan) and Korea Institute of Machinery and Materials (KIMM, Korea) will be leading other regional partners in this project, in order to work alongside and together with the above european partners and swiss as european leader in chromium plating of big technical parts.

4. ALTERNATIVE MATERIALS

Many alternative materials are avaliable that reduce hazards associated with hexavalent chromium while allowing the existing electroplating process to be used. Some alternative materials are chromium deposited from trivalent chromium solutions, and non-chromium metals and alloys. These alternatives, discussed below are common replacements for decorative and hard chromium.

4. 1 Chromium-based alternatives[6)]

The most common transitional alternative for decorative chromium is trivalent chromium. Recent advances have shown that trivalent chromium offers better physical properties, such as corrosion and wear resistance and the same color as hexavalent chromium. However chemicals used in trivalent chromium electodeposition are expensive and like hexavalent chromium electroplating, exhaust fumes must be treated to remove gases formed during electroplating.

4. 2 Non-chromium-based alternatives.

4.2.1 Ni-based alternatives

Alloy coatings containing nickel, tin, and cobalt have received considerable attention as substitutes for hexavalent decorative and hard coating. Ni-based alternatives include pure Ni and Ni alloy ; Ni-P, Ni-B, Ni-Mo, Ni-W, Ni-W-B alloys by both electroplating and electroless plating. As an alternative to hard chromium, several composit coating process, like a Ni-W-SiC, $Ni-Si_3N_4$ and $Ni-CrO_3$, has been developed and evaluated, particularly for aircraft application.

Tin-based alternatives

Sn-Ni and Sn-Co alloy coating has been suggested for decorative coatings. A major advantage of tin-based alloy plating is that it can be obtained by barrel coating because of their good throwing power. Sn-Ni alloy coating, especially those containing 33 to 35% nickel has a good hardness (650 Hv) and corrosion resistance to strong acid.

4.2.2 Cobalt-based alternatives

The color and corrosion resistance of Co-W (20-40%) alloy coatings is similar to that of chromium and their hardness is about 1.5 times softer than the hard chromium deposits. Therefore Co-W alloy coating has been considered for decorative.

4.2.3 Inorganic coatings

Main candidates are WC or WC-Co coatings and coatings containing mixtures of Ni, Cr, Fe, Si and sometimes other elements deposited by high-velocity oxy-fuel (HVOF) spray process. The driver for the commercial and millitary aircraft sectors and the defense industrial base. Cr_3C_2-NiCr, -NiMo by HVOF coating have shown a good performance for high power density desel engine. Another materials-SiO_2 and diamond-like carbon coating-by vacuum coating process also have been proposed as an alternative to chromium.

5. ALTERNATIVES TO DECORATIVE CHROMIUM COATING

Trivalent chromium was developed in about 1975 to substitute for hexavalent decorative chromium. Depend upon the process, trivalent

Table 1. Comparison of decorative chromium baths

Characteristics	Trivalent Chromium	Hexavalent Chromium
Chromium concentration (g/L)	4-25	100-300
pH	3.5-3.9	0
Current interrupt	tolerant	causes "white wash"
Temp (C)	40-50	40-50
Current density (A/ft2)	37-84	95-140
Throwing power	good	poor
Skin contact	similar to nickel	causes acid burn
Deposit structure	microporous	microdiscontinuities

chrome electroytes can produce a metallic white deposit almost identical in appearance to the bluish white hexavalent chromium deposits. The typical characteristics of trivalent chromium bath and hexavalent chromium bath are com pared in table[17].

As the chromium content is lower in a trivalent bath, the sludge are reduced as well. The cost of trivalent chromium plating is generally higher but the cost associated with waste treatment and sludges handling is far less than for hexavalent baths.

Trivalent chromium plating also has another advantages such as relatively high current efficiency, good metal distribution, good coverage around holes, high current density of operating. However, trivalent chromium plating has some difficulties due to the electronic state of Cr (III) affecting its chemical and electrochemical behavior.

- Slow formation of metal complexes on mixing trivalent chromium salts with potential bonding ligands
- Negative potential for the deposition reaction Cr (III) + 3e → Cr.
- The electrodeposition of chromium from solutions containing trivalent chromium has a significantly overpotential.
- Trivalent chromium readily hydrolysis, especially in the region close to the cathode.
- The ease of oxidation of the trivalent chromium species to hexavalent chromium takes place at the anode. Small amount of hexavalent chromium in solution reduce the efficiency of the trivalent chromium process.
- As trivalent chromium bath can be affected with metallic impurities, operating conditions, maintenance of bath is difficult.

At present, about 200 companies in US and Europe and about 60 companies in Japan and Korea apply the trivalent chromium plating for mostly automotive parts, accessaries, and golf shaft.

Alloy coatings containing the tin and tungsten element have been investigated as coating for alternative decorative coating. The color of deposits is very important because decorative coating is final process in manufacturing. However no alternatives has the same bluish-white color of hexavalent chromium. Sn-Co alloy and Co-W alloy coatings have chromium-like color and Sn-Ni alloy is slightly pinky and Ni-W alloy is brownish tone.

Sn-Ni coating has a good corrosion resistance and high hardness (about 650 Hv). Meanwhile, Hardness of Sn-Co alloy coating is about 300 to

400 Hv.

As the Sn base alloy has a good coverage and throwing power, barrel plating is available.

Ni-W and Co-W alloy coating have been proposed in the tungsten alloy system.

The electrolytes are acid or alkaline, the content of tungsten is about 5% in the former, and about 20 to 40% in the latter. The coverage and throwing power of tungsten base alloy is better than those of hexavalent chromium though worse than those of tin alloys.

Usually, the corrosion resistance of alternative alloy coatings for decorative chromium have not so good in comparison with chromium plating. When the decoloration or corrosion occurs in decorative coating, the value of goods goes down. Therefore these alternative coatings are need to post treatment - dipping in chromic acid solution, chromate or lacquer coating - to improve the corrosion resistance.

6. ALTERNATIVES TO HARD CHROMIUM COATING

As the alternative coating technologies that can replace hard chromium, Alloy coating and/or composit by both electroplating and electroless plating, vacuum coating, ion implantation and thermal spraying have been proposed.

6. 1 alloy coating[8-11]

Alloy coatings can obtain solid solution in the supersaturated state. The examples of thess cases are alloys coating with nonmetallic elements ; P, B, C and alloy coatings with high melting point elements ; W, Mo, Co. These alloys have much higher hardness than pure metals. As the amount of codeposited elements increase, grain size of alloy coatings becomes finer, eventually alloy coating turns to amorphous structure. Usually, heat treatment make the coated structure coarsen and soften. however these alloy coatings become harden through heat treatment, because of precipitation of intermetallic compounds. Phosphorous and boron based alloy coatings have been deposited by electroless plating in the early year, however electroplating method are preferred recently due to its advantages : high deposition rate, low operating temperature, etc.

In the meanwhile, the alloy coatings containing tungsten and molybdenum which show high hardness under high temperature because of there high melting point elements. Thus these alloy coatings can be applied for mould, especially galss mould and gun barrel and so on.

The corrosion and wear properties of electroless Ni-P coatings are depend on the phosphorous content, which can be varied from 1.0 to 12.0 percent. Conventional medium phosphorous and high phosphorous electroless nickel deposits typically provide an as-plated hardness between 500 and 550 Hv. Heat treatment will increase this hardness to value of 900 to 950 Hv, approximately the hardness of as-plated hard chromium.

The excellent wear characteristics of electroless nickel coatings make them suited for a wide range of applications and problem solving tasks. This is due to their high hardness, good adhesion, excellent lubricity, low coefficient of friction, and uniform coverage capability. The overall wear properties of electroless nickel deposits under the lubricated conditions, can be equal or even superior to hard chromium plating.

The corrosion protection of electroless nickel is generally considered to be superior to that of hard chromium, when compared at equal thickness. The corrosion protective properties are partially attributable to its dense, essentially amorphous structure which can be free from porosity.

In general, greater corrosion resistance is exhibited by coatings with higher phosphorous contents. however, in alkaline solutions good corrosion resistance is exhibited by low P deposits.

Electrodeposition of Ni-P, containing from 5 to 15% phosphorous can be deposited in a wide range of bath component concentrations and electrolysis conditions. Good quality coatings can be obtained from the bath containing phosphorous acid, however can hardly be deposited from the bath containing phosphoric and hypophosphorous acid bath.

As plated, Ni-B alloy is equivalent to chromium in hardness and to Teflon in coefficient of friction. But with heat treatment, Ni-B can achieve hardness results 18% higher than hard chromium. This is done at temperature as low as 400C for 12 hours to as high as 725C for 90 minutes. The temperature tolerance of Ni-B, known today, range from as low as -150C to as high as 1800C.

The key o the Ni-B coating performance is the nodules which result of a columnar growth structure. They reduce surface-to-surface contact, by as much as 70%, between parts and thus reduce friction.

Futhermore, Ni-B coating is 23% harder than Ni-P, and hydrogen embrittlement is substantially reduced because the process is accomplished in an alkaline solution, not acidic. This coating has been succeefully applied in jet engines, glass manufacturing, foundary moulds, gears and cams.

It is well known that Ni-Mo (20%) alloy coating exihibit both high corrosion resistance in hydrochloric acid and sulfuric acid media and high microhardness (500-600Hv). Molybdenum, among other metal, has one of the lowest friction coefficient. Nontheless, Ni-Mo alloy has not found wide application, apparently because of low bath stability.

Ni-W alloys can be hard chromium replacement coatings. Ni-W (about 40%) alloys have a chromium-like wear resistance, especially outstanding performance in Falex and Taber wear tests, good corrosion resistance to string oxidizing acids, excellent lubricity.

Table 2 shows the corrosion rates of Ni-Mo and Ni-W alloys in sulfuric acid. In sulfuric acid immersion corrosion tests, it was shown that the corrosion resistance of the Ni-Mo coatings increased with increasing molybedum content up to 27% molybdenum, but then decreased slightly when the content was increased to 33%. Similarly, the corrosion resistance of the Ni-W coating increased with increasing tungsten content of 27%.

Table 2. Corrosion rates of Ni-Mo and Ni-W alloys in sulfuric acid

Coatings	Corrosion rate ($mg/cm^2/min$)
95Ni-5Mo	82
83Ni-27Mo	4
67Ni-33Mo	6-11
90Ni-10W	70
80Ni-20W	2
77Ni-23W	4
83Ni-27W (pulse plated)	0

The hardness and wear properties on Ni-W, Ni-Mo alloy coatings can be modified with minor additions, such as B, P.

Interest in Ni-W-P alloy coating results from their high hardness which is unaffected by temperature up to 600C, high wear resistance and good corrosion resistance. However, it is impossible to obtain sound coatings of required thickness from the normal bath, because of very low current efficiency. Therefore the thick and hard coatings can be obtained with high current efficiency only from the bath containing both tungstate and hypophosphite additions.

Another electroplated ternary alloy coating is Ni-W-B. Composition of this alloy was 65% Ni, 31% W and 1% boron. The hardness of as-plated amorphous Ni-W-B alloy is low (about 600Hv), but is over 900Hv after annealing for one hour at 400C. Moreover, boron increases the hardness of ternary alloys as compared to binary Ni-W case. General corrosion on the Ni-W-B coatings was about three to four times less in acetic, phosphoric and hydrochloric acids, but an order of magnitude less in the highly oxidizing nitric and fluoboric acids than that on hard chromium.

The hardness and wear properties on Ni-W, Ni-Mo alloy coatings also can be modified by occluding fine particles, which are either hard or lubricant particles. These platings are called composit coating. The hardness of deposits depend on the kinds of matrix coatings and kind, size and amount of particles. If the hard particles are selected, hardness increases with the amount of codeposition. SiC, Al_2O_3, Si_3N_4, SiO_2, BN and diamond have been studied as a hard particles. Composite coatings are improved in corrosion resistance, for example, Corrosion resistance of a Ni-W-SiC exhibits 100 times that of chromium in 15% hydrochloric acid solution. The applications of composit plating with hard particles are engine cylinder, piston ring, aircraft, FRP mould and valve and so on.

When lubricant particles are codeposited in the coatings, hardness of coatings are decrease. However, friction coefficient of coatings is decrease by occluded particles, and wear amount is markedly decreased.

It is reported that the friction coefficient of composite coatings containing 10 vol.% Teflon is 10% of chromium's. The particles for lubricating composit coating include PTFE, fluorized graphite, MoS2, and examples of applications are sliding parts, gear, mould etc.

6. 2 vacuum coating[12-15]

Vacuum coatings have been investigated intensively as a replacement for hard chromium in certain applications. Among these are sputtered and cathode arc deposited chromium (Cr), chromium nitride (CrN) and carbide (CrC), titanium-aluminium nitride (TiAlN), diamond-like carbon (DLC), silicon carbide (SiC) and various multilayers.

If CrN coating is compared to conventional hard chromium, it is evidenct from the available results that CrN is at least twice as hard, has very low porosity, better adhesion to all substrate materials, offers precise from reproduction without edge rounding, does not need any additional thermal treatment and finally, gives better corrosion protection at much lower thickness (3-5 um instead of 12-20 micron). Some wear tests for piston rings showed that CrN and

Cr_2N reduce wear to about 1/10 compared to electroplated Cr.

CrN PVD coating seems to be very close to an optimum choice in possible alternatives to hard chromium. In 1997, mass production of CrN coatings has been tried to replace chromium coating for rotating cores of switches in automotive starter. The results were positive. Traditionally, such cores with ground surface are electroplated with 9 micron nickel plus 2 micron hard chromium. The protective coating must be wear and corrosion resistant. However, CrN coating as a replacement is 3-5um of CrN with a 0.5 um of Cr intermediate layer were deposited by arc ion plating.

Diamond-like carbon coatings have found use in such widely ranging application as air-bearing and roller-bearings surface, microtools, magnetic media heads, barcode scanner windows and eyeglass lenses.

Coatings of one to five microns in thicknesses were to have hardness of 2000-5000 Hv, Surface friction behavior was similar to that of hard chromium. DLC coatings also have been reported to be inert with respect to chemical resistance.

6. 3 thermal spraying[16,17]

Among the techniques showing promise in the metal spray arena, is the HVOF methode. The main candidates are WC or WC-Co coatings and coatings containing mixtures of Ni, Cr, Fe, Si. Typically, WC coating is five tiomes more wear resiistanct than hard chromium plating as measured by a stabdard dry abrasive wear test. The Department of Defense of USA has established a program to qualify HVOF thermal spray coatings as viable alternatives to hard chromium plating in aircraft maintenance and manufacturing operations. In fatigue testing, hard chromium plating causes a significant loss of properties whereas there is virtually no effect associated with HVOF deposition of WC/Co and Co-Mo-Cr alloy (Tribaloy 400) coatings. In salt fog corrosion testing, the HVOF coatings did not perform as well as the hard chromium on 4340 steel, 7075 aluminum alloys and PH13-8 stainless steel, but an under-coating for the hard chromium.

Table 3 is summary of salt fog test results of some coatings applied by the HVOF Technique. This results were obtained after 72 hours exposure unless otherwise stated.

Table 3. Average value of the protection rating

Coating	Substrate	Rating No. (face)	Rating No. (edge)	Ave. wear co-efficients,K	H (GPa)	E (GPa)	D (um)
T400	7075 Al	9.0	3.0	13.3			
WC-Co		10	2.0	6.7			
Hard Chromium		10	10	9.3			
T400	4340 Steel	1.6	1.0	15.6	5.7	130	2.8
WC-Co		3.4	3.2	5.7	12.8	272	1.8
Hard Chromium		3.2	2.0	9.9	10.1	201	2.1
T400	PH13-8 SS	8.6	6.8	18.1			
WC-Co		10	10	6.4			
Hard Chromium		10	-	9.7			

7. SUMMARY

The coating materials and technologies for present alternatives to hexavalent chromium plating were described in this document.

There are a number of commercially viable alternatives that can be used for production. In general, their performances will at least equal, and often surpass, that of hexavalent chromium coating, which would warrant making changes on technical merit alone.

However, no one process can be considered yet as a universal replacement for electrodeposited chromium when wear resistance, corrosion resistance, complexity of the process and cost are considered.

Although no single replacement for electroplated chromium exists that can match its unique mechanical properties, several alternative technologies are avaliable for use in specific applications.

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