Electrodeposited Alloys as a Alternative for Decorative Hexavalent Chromium

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With increasing environmental and economic pressure on traditional rack decorative chromium plating, a series of nickel and cobalt alloys have begun to see commercial use as alternatives. These alloys will be characterized for both barrel and rack applications with deposit data presented on hardness, appearance, wear resistance, alloy composition and corrosion resistance. In addition, a review of trivalent chromium and Ni/W as a alternative for hexavalent chromium for both a decorative and functional replacement will be presented.

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Introduction

Decorative chromium plating has been used for more than 70 years. The main purpose for the chromium electrodeposit is to provide a tarnish resistant coating. Other properties which chromium gives are abrasion resistance, hardness, and corrosion resistance.

Decorative chromium finishing can be looked at as a combination of two metals each with its own separate function. The undercoat metal is to protect the basis metal from corrosion and to provide the type of finish required (high polish, satin, matte, etc.) while the function of the chromium is to provide a thin covering reproducing the appearance of the undercoat, protecting the latter from tarnish and abrasion. When nickel is used as an undercoat, the covering power of the chromium is also improved.

Over the last 10 years, the environmental regulations for hexavalent chromium have become more stringent for both air and water emission.[1] For these reasons industry is looking for alternatives for hexavalent chromium for both decorative and functional application. This paper will expand on the alternative electrodeposited alloy coatings as a possible alternative for decorative and functional chromium coatings.

Plating Process

Commercially viable decorative hexavalent chromium alternative have been around for more than 20 years.[2] The first alternative processes are based on trivalent chromium chemistry. The trivalent chromium species is not as toxic as the hexavalent chromium species; therefore, industry has, and is using plating processes based on trivalent chromium as a replacement for hexavalent chromium.

Initial deposits of chromium from the trivalent chromium electrolyte were darker than the hexavalent chromium electrodeposits. This made acceptance of the color an issue. Over the last few years, research on trivalent chromium electrodeposits has increased and deposits that resemble hexavalent chromium are being produced. [2,3] Figure 1 shows the color differences of the various generations of trivalent chromium electrodeposits. None of the trivalent chromium electrodeposits possesses the blueness of hexavalent chromium but the newer trivalent chromium come close to matching hexavalent chromium electrodeposits. The older trivalent chromium electrodeposits were yellower and greener than hexavalent chromium deposits.

With proper operation and experimental design optimization, it is possible to obtain deposits that are indistinguishable from hexavalent chromium deposits.[4]

Tin/Nickel Alloys

Nickel and cobalt alloys with tin were first developed more than 45 years ago. They were developed to see whether the hardness and abrasion resistance of tin could be improved by the presence of iron group metals.[5] Most of this work consisted of Sn/Ni alloys. Electrodeposited Sn/Ni alloy is an example of an alloy with properties that are not the average of the properties of its elements. In hardness, tarnish resistance, and resistance to chemical reagents, it far excels both nickel and tin. Table 1 shows solution composition.

Table 1

$NiCl_2 \cdot 6H_2O$	300 g/L
$SnCl_2 \cdot 2H_2O$	50 g/L
NaF	28 g/L
NH_4F	35 g/L

The operating parameters of this solution are quite severe and the electrolyte is very corrosive. Special care is used when operating this electrolyte. Table 2 shows operating parameters for decorative applications for barrel and rack solution. Sn/Ni coatings can be plated thick and there is an ASTM standard for Sn/Ni coatings.[6]

Table 2

Time	2-8 minutes
Current Density	1-30 ASF
pH	<2.5
Cathode Efficiency	100%
Anode	Nickel
Agitation	mechanical-no air

There is another Sn/Ni process that operates at a higher pH than the first Sn/Ni. The higher pH process does not use hydrofluoric acid to adjust pH as the acid process does. This process uses a complexor to chelate the nickel so it does not precipitate as NiF_2. A Pourbaix diagram, Figure 2, of the Sn/Ni process shows as the pH goes above 2.5 NiF_2 will form which has a limited solubility in the acid electrolyte.

The high pH Sn/Ni process offers higher current density range and less corrosive electrolyte than the acid Sn/Ni electrolyte. Also, there is no difference in alloy composition from the high pH Sn/Ni versus the acid Sn/Ni electrolyte.

Alloy composition of the Sn/Ni is remarkably stable over a wide current density range. The reason being that Sn/Ni is deposited as an intermetalic compound rather than an alloy. Table 3 shows alloy composition over a wide current density range. From this observation, the alloy composition did not vary significantly over these current densities.

Table 3

Current Density	%Sn	%Ni
5 ASF	69.8	30.2
10 ASF	70.3	29.7
20 ASF	70.2	29.8
30 ASF	70.5	29.5
40 ASF	70.3	29.7

Besides uniform alloy composition over a wide current density range Sn/Ni has exceptional covering power (ability to plate in low current density areas) compared with most acid electrolytes. The only other electrolytes which posses as good of covering power are cyanide copper or stannate tin electrolyte.

Hardness of the Sn/Ni, 650 HK_{100}, is between that of bright nickel, 450-550 HK_{100}, and chromium, 900 HK_{100}. This hardness is especially important for barrel plating large parts. With small parts, the force with which the parts tumble against each other is small and other types of alloy coatings can and are used to plate this type of part. When the parts get large the force against each other is considerable, soft coating will scratch. The Sn/Ni is hard enough not to scratch but other tin-based alloys are not and will be discussed later in this paper.

The corrosion resistance of Sn/Ni is not as good as one would expect given its chemical resistance. Tin/Nickel is cathodic to steel but anodic to nickel, like all the alloys that will be discussed in this paper, and the corrosion protection is based on nickel thickness. See Figure 3 for a comparison of Tafel plots of the various alloys. All the alternative coatings need to be passivated in a hot dilute chromic acid solution for optimum corrosion protection. Table 4 shows the open circuit potential of the various alloys and their corrosion current.

Table 4

Alloy	E(0) V	I corr
Sn/Ni	-0.364	1.11 µA/cm^2
Sn/Co	-0.49	16.2 µA/cm^2
Ni/W	-0.505	1.82 µA/cm^2
TriCr	-0.293	68 nA/cm^2

Thin nickel deposits, less than 7 microns will be porous and corrosion is accelerated due to porosity of the nickel. Thicker nickel coatings will give better corrosion protection and duplex nickel coatings will give even better corrosion protection.

Color is a significant factor for decorative application. None of the alternatives quite match hexavalent chromium blue-white hue but the new trivalent chromium and the acid Sn/Co are the closest. The Sn/Ni has a slight red hue compared with all the alternatives.

Tin/Cobalt Alloys

There are two kinds of electrolytes for plating Sn/Co alloys, acid and alkaline. The acid electrolyte is similar to the low pH Sn/Ni process. The basic composition for the acid Sn/Co process is listed below in Table 5.[8]

Table 5

$CoCl_2•6H_2O$	375 g/L
SnCl	45 g/L
NH_4HF_2	82.5 g/L
NH_4Cl	37.5 g/L
pH	<3

The operating parameters are similar to the acid Sn/Ni process except insoluble anodes are used and the anode is usually graphite. Composition of the alloy is higher in tin than the Sn/Ni process. Alloy composition is 80/20 Sn/Co that is Sn_2Co whereas the Sn/Ni is 70/30 and the molecular formula is SnNi.

This difference in molecular formula has a significant difference in physical properties. The hardness of the Sn/Co is between 300-400 HK_{100} ; this is significantly softer than chromium and Sn/Ni. This softness limits the usefulness of this coating. With a soft deposit and with barrel plating parts there is a tendency for the parts to have a scratched topcoat.

Covering and throwing power are similar to the Sn/Ni process and one positive aspect of the Sn/Co process is the color of the coating. Figure 4 shows all the alloys. Acid Sn/Co has almost the equivalent amount of blue as the hexavalent chromium but has a slightly higher amount of red compared to hexavalent chromium.

Alkaline Sn/Co has similar properties to the acid Sn/Co except color. The alkaline Sn/Co color is similar to that of trivalent chromium also seen in Figure 4. Alkaline Sn/Co is more yellow than the trivalent chromium electrodeposits.

Table 6 shows the alloy composition of the alkaline Sn/Co.

Table 6

CD(asf)	%Sn	%Co.
40	80	20
30	72	28
20	70	30
10	65	35
5	65	35

The alkaline Sn/Co composition varies more than the acid Sn/Co and acid Sn/Ni over the same current density range. This process is more suitable for barrel application for this reason and the metal concentration is significantly lower in this process than the acid process. Table 7 lists solution chemistry.

Table 7

Additive	Concentration
$CoSO_4 \bullet 7H_2O$	3-5 g/L
$SnSO_4$	2-4 g/L
Complexor	10-20 g/L
Conductivity Salt	20-30 g/L
Wetter	0-0.2%
pH	6.5-8.5

With low metal concentration, the dragout from the barrel is less than with the high metal concentration electrolytes. This makes the alkaline Sn/Co less demanding on the waste treatment system since the tin-based alloys are not amenable to reclaiming. Tin hydrolyzes to the +4 valance, which is detrimental to all the plating processes discussed so far.

Nickel/Tungsten Alloys.

There are currently two types of Ni/W alloys. One is 65% Nickel and 35% Tungsten and the other is 64.5% Nickel, 35% Tungsten and Boron is <0.5%. Both processes are similar in chemistry. This paper will deal with Ni/W only.

Ni/W alloy electrodeposition
has been around for more than 40 years. There are two types of chemistry: acid and alkaline.[9] The acid type electrolytes only produced alloys with low tungsten levels (5-10%) whereas the alkaline type process gives tungsten levels between 20-65%.

The key requirements for formulation of an alkaline tungsten alloy electrolyte, besides the salts of the metal, are ammonium salts, excess ammonium hydroxide and a complexing agent for the iron group metal. Because these processes were operated hot (greater than 70°C) with the pH about 9, significant amounts of ammonia had to be added to maintain the pH. This is probably why these processes did not gain commercial acceptance.

Over the last few years, research on Ni/W has modified the earlier version by lowering the temperature and pH but still keep the tungsten in the 30-40% range. Table 8 lists the basic chemical composition.

Table 8

Additive	Concentration
$Na_2WO_4 \bullet 2H_2O$	10-75 g/L
$NiSO_4 \bullet 6H_2O$	4-25 g/L
Organic Complexor	30-80 g/L
NH_4	10-20 g/L
Brightener	0-0.4%
Wetter	0-0.3%
pH	6-7.5

The metal concentration of the Ni/W alloy is less than the Sn/Ni and acid Sn/Co process but more than the alkaline Sn/Co process.

The NI/W process can be run for both decorative and functional coatings.

Functional aspect will be discussed later. For decorative use, the Ni/W possesses properties that make it an ideal replacement except for one property. Ni/W possesses high hardness (650±50 HK_{100}) and good corrosion protection, but the color is yellow when compared to the other alloy alternative (Figure 4). In addition, the throwing power of Ni/W is less than the other alloys but better than chromium. Alloy composition of the Ni/W varies moderately versus current density. Table 9 lists the results.

Table 9

CD (ASF)	%Ni	%W
40	85	15
30	66	34
20	71	29
10	63	37
5	60	40

The operating parameters of the Ni/W in rack application are as follows.

Time	1-4 minutes
CD (ASF)	5-50
Temperature	120-140°F
Cathode Efficiency	25-35%
Anodes	Stainless Steel

The corrosion properties of Ni/W are similar to the other alloys evaluated. Figure 3 shows Tafel plots of the various alloys: from this data, it is shown that all the alloys are nobler than Fe but are sacrificial to Ni. In decorative applications the substrate is usually, Ni plated and you do not obtain the corrosion protection of chromium unless you passivate the alloys in a hot dilute chromic acid solution.

Summary of Decorative Alternative.

An assortment of various coatings, both alloys and single metal are available as alternatives for hexavalent chromium.
Each process possesses it own unique property and should be evaluated in the environment for which it is replacing hexavalent chromium.

Functional Alternative for Hexavalent Chromium.

Functional Trivalent Chromium

There are many coatings being touted, as alternatives for functional hexavalent chromium. Most of these processes are dry, non-plating processes. This paper will discus two alternatives: both are electrodeposited coatings as alternatives for hexavalent chromium.

The easiest replacement, one would think, is using a trivalent chromium electrolyte to replace the hexavalent chromium. Both deposit, essentially, chromium. The other advantage from the trivalent chromium electrolyte is the reduction from the +3 state versus the +6 state for hexavalent chromium. In addition, trivalent chromium is not a suspected carcinogen like hexavalent chromium. The problem with the trivalent chromium process is that it was designed for decorative application (thicknesses less than 0.6 microns). When plating thick coatings, coherent deposits were not obtained.

To understand the chemistry and how the chemistry affects the operating parameters an experimental design experiment was carried out to evaluate the main variables and their interactions. The main variables evaluated are pH, Compound A, and current density. A modified Box-

Behnken experimental design plan was used. The main factor evaluated was efficiency. Decorative trivalent chromium has efficiency between 12-15%, which correlates to 24-30% efficiency to a hexavalent chromium electrolyte. Figure 5 shows the effect of pH and Compound A on efficiency. As the pH rises, so does the efficiency; as compound A is lowered, the efficiency is increased. Figure 6 shows the effect of current density and Compound A on efficiency. From this work, the efficiency does not change significantly with current density only with Compound A concentration.

Efficiency could increase almost three times higher than the decorative trivalent chromium process if Compound A and pH were lowered. In addition, the soundness of the deposit increased (Figure 7).

Trivalent chromium electrodeposits from this electrolyte contain carbon, which alters the structure of the deposit. Hexavalent chromium electrodeposits are usually body center cubic whereas the trivalent chromium electrodeposits are amorphous. Figure 8 shows an x-ray diffraction pattern of the trivalent chromium electrodeposit.

Hardness of the deposit is 950±50 HK_{100} but can be increased to greater than 1400 HK_{100} with heat treatment to form chromium carbide.

The wear of trivalent chromium is slightly worse than hexavalent chromium. In Taber wear testing the trivalent coating without brightener has an average wear loss of 15 mg per 10000 cycles with a 1000-gram load and a CS-10 wheel, whereas hexavalent chromium has a wear loss of 10 mg for the same cycle. The trivalent chromium wear loss can be improved by the addition of a brightener that makes the deposit less nodular, Figure 9 and 10 show the surface of the trivalent chromium deposit with and without brightener respectively. The wear of this coating by the Taber wear abraser is 12 mg per 10,000 cycles with a 1000-gram load and CS-10 wheels.

Functional Nickel/Tungsten

There are currently two types of Ni/W processes. One process is 65% nickel and 35% tungsten and the other process has similar composition but incorporates SiC in the Ni/W electrodeposit for better wear resistance. The hardness of these electrodeposited coatings are in the range of 650±50 HK_{100} and can be increased to greater than 1000 HK_{100} with heat treatment at 400°C for one hour.[10]

The wear of Ni/W is not as good as that of hexavalent chromium as measured by Taber abrasion tester. Ni/W had a weight loss of 100 mg/10000 cycles with 1000-gram load and using CS-10 wheel. This is 10x more than hexavalent chromium. Ni/W/SiC had only twice as much weight loss as hexavalent chromium and was slightly better when heat-treated. In addition, the problem with putting SiC in the Ni/W matrix is in certain application like hydraulic rods. The seals on the rods fail due to the wear of the SiC on the rubber seals.

The corrosion resistance of Ni/W coating is excellent. This material is resistant to most acids and bases. The structure of this coating is amorphous (Figure 11) similar to the trivalent chromium electrodeposit. However, the problem with the deposition of an amorphous coating is the ability to replicate the surface. A slight defect in the surface, pit, burr, etc., is magnified through the coating. Therefor special care is needed to produce defect free deposits.

Summary of Functional Alternatives.

The trivalent chromium produces deposits with hardness similar to that of hexavalent chromium but can be increased to greater hardness with heat treatment. The corrosion resistance of trivalent chromium is not as good as hexavalent chromium due to defects is the substrate. With good substrate preparation, the corrosion resistance is as good as hexavalent chromium.

Ni/W offers unique properties different from chromium, which might have some application where chromium is not satisfactory, like a high temperature environment. The only problem with Ni/W is it does not possess the high wear resistance of chromium. Like any alternative the material should be tested in the environment in which it will be, operating to make sure the material performs satisfactory.

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