Electrodeposited metallic coatings for the surface modification of materials

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Abstract

Recent technological trends in electrodeposited metallic coatings are examined by reviewing the following areas of metal finishing which can be considered to be directly relevant at present:

(i)   Replacements for hexavalent chromium-based coating processes.

(ii)   Electrodeposited composite coatings.

(iii) Compositionally modulated or layered coatings.

The replacement of chromates is an environmentally-driven problem and one which has yet to be achieved, although certain lower toxicity systems are showing promise. Composite coatings have been available commercially since the 1960s and represent a powerful method to enhance surface properties - particularly hardness and wear resistance. Compositionally modulated or layered coatings are at present being examined by researchers as a possible new class of advanced coatings with tangible benefits in terms of performance over their monolithic counterparts.

1 Introduction

Electrodeposition is rightly regarded as a powerful technique for surface coating. At its simplest the technique requires an electrolyte (as the medium in which to stimulate the coating reaction) and an anode/cathode system (the latter forming the surface to be coated) and a DC power supply to provide the electrons to stimulate the coating reaction. It is this simplicity of operation and control that has allowed 'electroplating' to become one of the most widely utilised coating processes, as shown in table 1 [1].

Treatment	Value / £million	% Share
Industrial paint	2000	50
Electroplating	800	20
Surface heat treatment	350	9
Galvanising	250	6
Polymer powder coating	150	4
Phosphating, chromating	100	3
Thermal spraying	100	3
Anodising	70	2
Blasting and peening	70	2
New tecnologies and others	60	2
Total	**3950**	

Table 1: Estimated value and percentage share composition of the UK surface engineering industry. After Gawne and Christie [1]

Electroplating has clearly evolved, maybe somewhat slowly, over the years to form a mature and effective industrial process. It is the purpose of this paper to review some of the more recent developments, these give an indication of the directions in which the technique, itself, is progressing. It is with this in mind that I propose to review the following three areas of development that are presently at the forefront of surface engineering research/development:

(i)   Replacements to hexavalent chromium-based processes.
(ii) Electrodeposited composite coatings.
(iii) Compositionally modulated or layered coatings.

2 Replacement of hexavalent chromium in electrodeposited coatings

In the last twenty years, with the advent and increase in environmental issues, electroplating and other electrochemical-based coating processes have fallen under the 'spotlight' as being, in some cases, environmentally questionable. This has resulted in in-depth research into more acceptable alternative systems and products. One area of interest at present is in the removal of hexavalent-

based chromium coating systems from surface treatment processes. This effects not only decorative and engineering chromium coatings but also many passivation processes/conversion coatings which are applied to bulk and coated surfaces.

2.1 Toxicity of chromium (VI) compounds

It has been known for many years that the hexavalent oxidation state of chromium is toxic. The metallic state (Cr°) is thought to be biologically inert and the trivalent state (CrIII) is thought to be of a lower toxicity and not known to be a carcinogen [2]. The level of toxicity in Cr(VI) compounds is much higher and some of its compounds are carcinogenic. Prolonged exposure of the skin to chromates and other hexavalent chromium compounds can cause rashes, blisters and ulcers [3,4].

2.2 Electrodeposition processes using hexavalent chromium

It is clear that from a process toxicity and effluent control viewpoint both chromium electroplating processes (decorative and hard) and some conversion coating/passivation processes are problematic.

2.2.1 Hard chromium
Hard or engineering chromium has many intrinsic properties which have resulted in its widespread use as a hard abrasion- and wear-resistant finish in the engineering industry. It has a high hardness of 800-1000HV, a low coefficient of friction and good corrosion resistance [5]. Its tensile internal stresses, although sufficient to cause cracking of thick coatings, can be utilised, as the cracks can act as surface reservoirs for lubricant [5]. The drawback with the hard chromium processes is that they are usually based on chromic acid and sulfuric acid and hence contain Cr(VI). A more environmentally acceptable alternative would therefore be timely.

Many alternatives to hexavalent hard chromium have been examined and a good proportion of these have been operated using electrodeposition. One such system which has received repeated examination is the electroplating process based on trivalent chromium-based electrolytes [e.g. 6-10]. The coatings formed from trivalent electrolytes are bright (although a bit darker than those from hexavalent solutions [11]) and have similar wear and corrosion resistance characteristics. Early electrolyte chemistry resulted in a process which would only deposit relatively thin coatings, improvements resulted in thicker coatings, but coupled to very slow process times. However, more recently much more effective (in terms of process times) electrolytes have been reported [e.g. 9,10] an example of which is indicated below:

$$0.80 \text{ M } [Cr(H_2O)_4Cl_2]Cl.2H_2O$$
$$0.50 \text{ M } NH_4Cl$$
$$0.50 \text{ M } NaCl$$

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$$0.15 \text{ M} \quad B(OH)_3$$
$$1.00 \text{ M} \quad \text{Glycine}$$
Small quantities of catalyst XEL

It is claimed that this electrolyte can produce electroplating rates of 300 µm/hr as a high speed process.

Other electroplated alternatives to hard chromium exist, nickel-tungsten boron and nickel-tungsten-phosphorus being two alloy possibilities [11]. Both systems seem to have their drawbacks in terms of process problems, but certainly the former alloy is undergoing pilot-scale evaluations in the USA [12].

2.2.2 Decorative chromium

As with hard or engineering chromium, decorative versions of the metallic coating are also electrodeposited from a chromic acid-based electrolyte. Trivalent baths are available and produce visually acceptable coatings. Colour differences when compared to the hexavalent chromium do exist, although this should not be taken as a reason to exclude trivalent finishes [13]. Other problems do exist including possible lower corrosion resistance [13], clearly further refining of the process/product is required. Other possible electrodeposited alternatives to hexavalent decorative chromium include bright acid zinc with a suitable blue passivation and lacquer [13] and tin-cobalt alloy [14]. Clearly no alternative, to date, has proved to be a complete replacement.

2.2.3 Chromate passivation treatments

Hexavalent chromium-based passivation treatments have been used as the promoters of passive films (conversion coatings) on a variety of metals surfaces for many years. Their efficacy is unquestionable, the films providing both barrier protection and a degree of 'self-repair' due to the occurrence of Cr(VI) in the coating. However, the toxicity of the process solutions and to some degree of the coatings themselves has lead to the search for low toxicity alternatives. A range of potential replacement systems have been reported, the most effective often being specific to a particular metal. Molybdate-based treatments have been examined on zinc and zinc alloys [e.g. 15,16] and tinplate [17]. They have been found to be generally successful in particular corrosive environments, although certainly could not be regarded as a wholesale replacement for chromates. For aluminium and aluminium alloy surfaces, cerium-based treatments [e.g. 18,19] have proved very successful and permanganate-based treatments [20] are also reported as being effective. Other low toxicity alternatives exist e.g. tungstates, zirconium compounds, cobalt complexes as well as trivalent chromium-based treatments [21] and have been applied to a broad range of metal surfaces with varying levels of success. An overall, single, replacement for chromate conversion coatings is still to be found.

3. Electrodeposited composite coatings

Initial investigations into the production of composite coatings commenced in the late 1950s, with patented processes appearing in the early 1960s [22]. This type of coating can probably be most easily defined as an electrochemically or chemically deposited system containing (usually) a particulate species which has been co-deposited during the coating process. Table 2 illustrates some of the more common composite coating system classifications.

Application	Particles
Corrosion resistance - bright nickel overlaid with thin Cr	$BaSO_4$
Wear resistance - strongly influenced by wear properties of hard co-deposited material	Al_2O_3, TiC, WC, SiC, CrC_3
Dry lubricant coatings - soft particles with a low shear strength dispersed in the metal matrix provide good antifriction properties	MoS_2, graphite, $BaSO_4$, PTFE in electroless nickel
Heat-treatable metals/alloys - particles are co-deposited and then the composite is heat treated	Cr with Ni, B with Ni, and Cr, Al, and Y with Co
Nuclear coatings - composites for possible use in fuel elements or as reactor materials	UO_2 and Pu with Ni, B with Ni
Mechanical properties - improved strength at room and elevated temperatures	Al_2O_3 in gold, Al_2O_3 and TiO_2 in nickel

Table 2: Electrodeposited composite coatings categorised into six classes. After Dini [23]

3.1 Particulate additions

The particulate inclusions can enhance the mechanical properties of the matrix material such as wear resistance, hardness and lubricity. The particulate phase can be co-deposited by two main mechanisms. The first method is by physical dispersion in the electroplating bath and subsequent entrapment in the growing electrodeposit. Clearly, forms of agitation of the electroplating solution are important, as they dictate the efficiency of incorporation. Table 3 lists some of the more common agitation methods.

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Agitation Method	References
Plate Pumper	Keoward et al
	Celis and Roos 1977
Solution Pumping	Kariapper and Foster
Vibrational agitation	Celis and Roos 1978
	White and Foster 1978
	Johal et al
	Kalantary et al
Rotating disc electrode	Roos, Celis et al
	Kyoto Review
Rotating cylinder electrode	Bazzard and Boden
	Masuko and Mushiake
Magnetic rotary stirring	Sadowska-Mazur et al
	Johal et al
Rotary barreling	Foster et al 1965

Table 3: Agitation methods used in composite electroplating. After Johal et al
[24]

The second method is by increasing the zeta potential of the particles to a high
positive value by the addition of suitable cationic substances [22], this then
aids the electrophoretic migration of such particles to the coating surface
where they are entrapped in the growing deposit.

3.2 Industrial applications of composite coatings

  Composite coatings have found significant niche uses in industry. Ni/SiC
coatings have been used where wear problems are encountered - often at
elevated temperatures e.g the cylinder walls of internal combustion engines.
Ni/PTFE is used where surface lubrication is important [25]. More recently
copper as been co-deposited with sub-micron particles of phenolic resin to
facilitate adhesion on printed circuit boards - previous methodology had
involved the application of a rough composition-critical copper oxide layer
[22]. Zn/SiO_2 composite layers have been developed to improve the adhesion
of organic coatings to electrogalvanised steel and hence to improve corrosion
resistance of the overall coated system. Finally, micro-capsules of liquid
lubricants have been co-deposited with metals to form a self-lubricating
surface [26]. As wear occurs at the metal surface the liquid lubricant is
released from the capsules and helps to provide lubrication.

4 Compositionally modulated or layered coatings

The concept of layered or modulated coatings is not a new phenomenon in
coating technology. Several 'traditional' multilayered systems have been
evident in surface engineering for many years [27]:

(i) Organic/metal coating systems e.g. painted galvanised steel.

(ii) Metal/metal coating systems e.g. electroplated chromium on a nicke underlayer ('chrome' plate).

(iii) Diffused coatings on a metallic substrate e.g. flow melted tinplate.

More recently investigators have examined coating systems with a large number of very thin individual layers (mostly electrodeposited) on metallic substrates. Figure 1 illustrates an idealised system, where A and B are repetitive layers of different composition. A and B can be different single metals or alloys, or different compositions of the same alloy system.
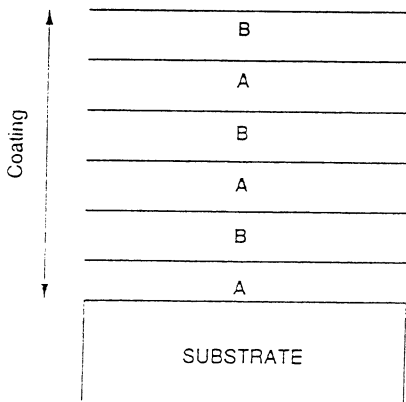

Figure 1: Schematic of a layered or compositionally modulated coating system

Early investigations have been concerned with the Cu/Ni multilayer system. Theoretical forecasts made by Koehler [28] of improved mechanical properties of such coatings have been essentially confirmed by experiment [e.g. 29,30].

4.1 Coating techniques

Electrodeposition of multilayered systems by electrodeposition can be basically achieved by two processing routes:

(i) Dual bath technique - here the substrate to be coated is transferred sequentially between two electroplating baths which are used to build up the two distinct compositions required for repetitive layering. A rinse stage(s) are required between the baths to minimise cross contamination.

(ii) Single bath technique - this differs from the above in that only one electroplating bath is utilised. The compositional variation is achieved by altering electrodeposition process parameters on a periodic basis. In this way electroplating current and/or electrolyte agitation can be varied. Electrolyte composition can also be adjusted to suit the process. For example with the

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Cu/Ni system copper is the more noble of the two metals dissolved in the electrolyte. Therefore if the copper concentration is kept very small, at low overpotentials or current, a copper layer can be electrodeposited, whilst at high overpotentials or currents with high agitation, nickel-rich layers may be electrodeposited.

The concept of compositionally modulated coatings has been extended to some more industrially significant alloy systems [e.g. Zn/Ni 31,32]. Here coatings were primarily electrodeposited for the corrosion protection of steel substrates. Layered coatings were electrodeposited comprising of alternating alloy layers of different composition and also structures of single metal layers deposited to produce a modulated structure.

Coating Type	Hours to Red Rust
Zn/Ni (4 layers)	223
Ni/Zn (4 layers)	336
Zn-11% Ni	313
Zn/Zn-Ni (4 layers)	329
Zn-Ni/Zn (4layers)	552
Ni/Zn-Ni (4 layers)	328
Zn-Ni/Ni (4layers)	208

Table 4: Neutral salt spray corrosion performance for the Zn/Ni layered system, overall coating thicknesses 8μm After Chawa et al [32]

Table 4 shows some pertinent data from some of these investigations. Where layered deposits are listed, the first metal in the couple is the one directly next to the substrate. Conversely the second metal is the one at the surface of the layered coating. Several trends were apparent from these investigations. It was clear that the multilayered coatings with certain orientations and components could produce corrosion resistances (in terms of time to red rust in a neutral salt spray environment) in excess of single momolithic coatings of a similar overall thickness. The most effective orientation was to have zinc as the upper layer and the nickel-rich coating on the bottom of the layer (next to the substrate) and repeat this orientation in the layered structure.

It is clear from these initial experiments that layered zinc alloy based coatings show promise as more effective replacements to monolithic coating structures.

5 Summary and conclusions

In this paper I have tried to highlight what I consider to be three emerging and important areas of electrodeposited coating technology. Like many industries surface engineering is responding to environmental pressures (replacement for hexavalent chromium-based treatments) as well as reacting to more technology

driven stimuli as progress made in composite coating technology and the initial investigations carried out in layered coating technology illustrate.

It must be recognised that there are many other facets of electroplating technology that could have been included in this review. Certainly the technique of pulsed electrodeposition is one of them. However, the restrictions of space did not allow further areas to be explored.

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