Alternative tribological coatings to electrodeposited hard chromium

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Abstract

The traditional importance of hard chromium electroplating in surface engineering is recognised and the key features of this well-established technology are summarised. Despite the high hardness, corrosion protection and wear resistance of chromium electrodeposits, a number of alternative coating compositions and application techniques have been developed for specific applications in tribology. Environmental challenges associated with hard chromium electroplating are highlighted and the need to develop and evaluate alternative coatings is stressed. Key examples of the alternative coatings are described, including their method of application, microstructure and tribological performance in controlled service environments. Research needs requiring rapid development are highlighted. A summary is given of the most competitive coatings and those having the potential to match the performance of hard chromium in selected applications are identified.

Keywords: Alloys; Electroless deposition; Electroplating; Engineering coatings; Tribology.

Contents

(Approx. 6,900 words text, 7 tables, 8 figures and 100 refs)

Abbreviations, matrices and phases

BDD	boron doped diamond
CVD	chemical vapour deposition
DLC	diamond like carbon
EHC	electrodeposited hard chromium
HCP	hexagonal-close-packed
HPPMS	high power pulsed magnetron sputtering
HVOF	high velocity oxygen fuel
PVD	physical vapour deposition
REACH	registration, evaluation, authorisation and restriction of chemicals
SEM	scanning electron microscopy
SFE	stacking fault energy
SME	small or medium sized enterprise
SVHC	substances of very high concern
TEM	transmission electron microscopy
Cr_3C_2	chromium carbide
WC	tungsten carbide
Ni-Co	nickel-cobalt alloy
Ni-Cr	nickel-chromium alloy
Ni-P	nickel phosphorus alloy
Co-P	cobalt phosphorus

1. Introduction

Steels containing a minimum of 10.5%wt chromium are corrosion resistant and stainless due to the formation of a passive oxide film. The use of chromium containing surface oxides for metal protection can be traced back some 2000 years; the Terracotta Army pits (a collection of sculptured statues depicting the armies of Qin Shi Huang) at Xi'an, China, which were unearthed in 1974, contained some weapons (such as swords) which were sharp and rust-free due to a dense, 10–15 μm thick chromium dioxide layer on their surfaces [1]. Modern chromium plating began in the 1910s, being pioneered by Sargent. The commercial process of chromium plating, which resulted principally from the work of Fink and Eldridge in 1924, was patented in 1926 as an aqueous bath of chromic and sulphuric acids with a ratio of 100:1 [2]. A century of developments in electroplated chromium has resulted in its extensive use as a decorative and engineering coating [3].

Conventional chromium plating, electrodeposits the metal (at relatively low current efficiency of <20% due to hydrogen evolution) from a chromic acid solution onto the surface of metallic or polymer substrates. Depending on the coating thickness, electroplated chromium deposits can be divided into two categories. Decorative chromium, with a typical thickness below 0.250 nm, serves as a non-tarnishing surface finish, whilst hard chromium, with a thickness of 1 μm to 500 μm, has been widely used in industry for wear and corrosion resistance. In 2003, the world-wide output of the hard chromium plating market was valued at approximately $3 billion (decorative chromium plating was around $16 billion) [4]. In Europe, there are some 1350 SME companies working on chrome plating and the total assets were estimated at €21 billion in 2014 [5].

As a versatile, low cost process, chromium plating has a long pedigree in many engineering applications which is difficult to overcome. Over the last century, electrodeposited hard chromium (EHC) coatings have been widely used in aerospace, oilfield, automotive, construction, mining, and general industry. In aerospace alone, EHC deposits have provided wear resistant coatings as landing gear, gas turbines, hydraulics and other components. However, the main problem with chromium electroplating is that the main bath component, hexavalent chromium Cr(VI), is extremely toxic, carcinogenic and environmentally persistent. The electrode reactions taking place in a hexavalent chromium plating bath and attendant regulations are discussed in the next section.

2. Electroplating Chromium from Chromic Acid Baths

Chromium plating utilises an electrolytic cell consisting of two electrodes and a conventional chromic acid bath (160 g dm^{-3} CrO$_3$ + 2.5 g dm^{-3} H$_2$SO$_4$) with an external source of direct current with a typical current density of 100 A dm^{-2} at 45°C [6]. As sulphuric acid acts as a catalyst and CrO$_3$ is highly soluble in water, there is an equilibrium balance between dichromic acid H$_2$Cr$_2$O$_7$ and chromic acid H$_2$CrO$_4$. Chromium in the +6 oxidation state, i.e., anionic Cr(VI) can reduce to metallic chromium at the cathode surface:

$$Cr_2O_7{}^{2-} + 14H^+ + 12e^- = 2Cr + 7H_2O \qquad (1)$$

A fine mist of Cr(VI) in chromic acid can be generated above the bath by the substantial volume of hydrogen gas released during the plating, as indicated in Figure 1 [7]. Mist generation is exacerbated by the notoriously low efficiency of chromium plating (<20%), most of the current being used to evolve hydrogen at the cathode as a secondary reaction.

$$2H^+ + 2e^- = H_2 \qquad (2)$$

Traditionally, the inert anodes have been lead or a lead alloys, which coat with a chromium-containing lead dioxide (PbO_2) film. In some cases, platinised titanium has been used as a corrosion resistant, long-life electrode. The main anode reaction is oxygen evolution:

$$2H_2O - 4e^- = O_2 + 4H^+ \tag{3}$$

Hydrogen-oxygen gas mixtures always exist above chromium electroplating baths and adequate ventilation is essential to avoid any risk of explosive atmospheres. Cr(VI) has been identified as one of the 17 chemicals posing a great risk to humans. The inhalation of hexavalent chromium species from a chrome plating bath may cause liver and kidney damage/failure, burns and anaemia. Environmental release of Cr(VI) must be carefully minimised as it may result in groundwater and soil contamination which can persist for many years. As a consequence, hard chromium plating is facing strict regulations. In the USA, the permissible exposure for Cr(VI) compounds in workplace air was reduced from the previous 52 $\mu g\ m^{-3}$ to 5 $\mu g\ m^{-3}$ in 2006 by the Occupational Safety and Health Administration [8]. In the automobile industry, the complete elimination of hexavalent chromium plating came into force on the 1st July 2007 [4]. In the European Union, EHC replacement came into existence on 2007 and the use of chromium trioxide without authorization was no longer permitted after 21 September 2017 according to the 'registration, evaluation, authorisation and restriction of chemicals' (REACH) [9]. Despite the demonstration of many processes to minimise mist formation and recycle used electroplating baths, e.g., using electrodialysis [10], environmental pressures have resulted in worldwide cessation of most hexavalent Cr electroplating.

The hardness of EHC can reach values between 800 and 1200 HV. Such a high value is attributed to atomic hydrogen (as a by-product) being adsorbed on the chromium surface [11]. Such high hardness, combined with the stable passivation layer of chromium oxide instantly formed on the top surface, provides good tribological, anti-adhesive and anti-fretting behaviour [12]. Cracks occur when the internal tensile stress exceeds the tensile strength of chromium [13]. Microcracking can be desirable in hard chrome as such deposits have a released stress, facilitating improved adhesion to the substrate. Four variants were classified as micro-cracked chromium, micro-porous chromium, porous chromium and crack free chromium. The cracked / porous chromium may be up to ~150 μm thick as hard chrome, whereas the crack free chromium can only be produced with a thickness up to 2.5 μm for decorative finish [14]. The former has a Vickers hardness of 800-1000 MPa, while the latter has a significant reduction on Vickers hardness between 425-700 MPa [15]. Micro-porous chromium is involved the use of inert suspended particles which locally inhibit the nucleation. Porous chromium has a coarser distribution of pores and ground / polished mechanically or immersed in an etching solution. The porosity gives the coating the ability to absorb and retain oil which makes it useful for machine tools [16, 17]. For examples, hydraulic tubes as used for aircraft undercarriages and on earth moving equipment, aircraft engine cylinders, diesel engines and on piston rings [14,18].

While many industries continue to seek viable alternatives to hard chromium, it is still a struggle to have an alternative matching all the properties offered by EHC coatings [19]. Thermal spraying is a leading technology for replacing EHC as it can provide higher tribological resistance coatings than EHC. Electroplating with Cr(VI) free electrolyte solutions is cost competitive, since the same infrastructure as EHC can be utilised. Other technologies being considered include electroless nickel alloy plating and vapour deposition; the former has an advantage for internal coatings due to the 'line-of-sight' limitations with many vapour deposition techniques and the latter can offer much higher hardness and good wear resistance.

This review will include a description of the methods, examples of the typical coatings and recorded tribological performance in controlled service environments.

3. Alternative Coating Techniques

Traditionally, electroplating has been the dominant technique to produce wear resistant chromium coatings since it offers moderate cost and the ability to produce a hard, durable finish at a variety of scales using relatively simple facilities. A wide range of alternative techniques and rival coating materials have developed over the last twenty years, as indicated in Figure 2. While it remains difficult to match the versatility and convenience of electroplated chromium layers, environmental restrictions and intense research efforts have provided alternative coatings.

3.1 Thermal spraying

The family of thermal spray processes and their development since the invention of thermal spray in 1910 has recently been reviewed in detail by Ang *et al* [20]. All thermal spray processes rely on the principle of softening and/or melting a feedstock, typically a powder (size from 5 to 150 µm) or wire, and projecting the resultant softened or molten droplets onto a substrate to build up a layer of well bonded pancake-shaped "splats" [21]. The necessary thermal energy can be provided by electrical means (e.g. by the generation of an arc or a gas plasma) or via combustion. The lower energy processes, i.e. flame and arc spray have lower cost but generally higher porosity (3-10%) and oxide levels and lower bond strengths (14-41 MPa) [22]. To reduce porosity and improve bonding, high energy processes and in particular high velocity particle impacts are required. The high energy process - plasma spray can expose the feedstock powder to temperatures above 12000°C and produce a good metallurgical bonding strength between the substrate and coating. As indicated in Figure 3, the high flame temperature may also increase phase transformation or oxidation of materials [19]. For example, WC may decarburise to W_2C, W_3C or W and react with Co forming intermetallic, $Co_xW_yC_z$ phases during flight [23]. These new phases are generally brittle and considered detrimental to the wear performance [23-26]. Moderate temperatures are crucial to deposit thermally sensitive materials; at a relatively low temperature, the thermal decomposition reactions will be prevented or reduced. High velocity spray was pioneered by Browning in 1982 who utilised an oxygen-fuel mixture expanding in a combustion chamber and accelerating through a convergent-divergent nozzle to deposit a powder feedstock [27] which powder is injected into a hot gas stream and accelerated onto a substrate at high velocities and moderate gas temperatures (2600-3000°C) [22]. The resultant coating is generally dense with a high bond strength (48-62 MPa) and low porosity (<1-2%). It has been a dominant thermal spraying process for hard chromium replacement coatings [20].

Cermet coatings, which consist of carbide phases to provide wear resistance and metallic metal/alloy as binder to impart a level of toughness, often perform better than EHC in tribological performance. WC–Co and Cr_3C_2–NiCr are mostly widely used as hard coating materials applied by thermal spray processes. As shown in Table 1, the HVOF-deposited WC-Co and Cr_3C_2-NiCr exhibit lower friction coefficients and wear rates than EHCs. The abrasive wear rate is one order of magnitude lower than that of hard chromium [28]. The relationships between constituents, microstructure and properties for WC-Co cemented hard metals have been well established. WC-Co(Cr) coatings can withstand a service temperature under 450-

550 °C compared to maximum temperatures of 200°C for EHC [19]. Cr_3C_2–NiCr coatings are more resistant to high temperature oxidation, and can operate at temperatures up to 850°C although they have a slightly poorer tribological performance than WC-Co(Cr) [27]. Cr_3C_2–NiCr coatings have been successfully applied to steam turbine blades and to boiler tubes, which are subject to harsh tribocorrosion [29].

Nanostructured coatings can potentially exhibit improved hardness, toughness, and wear resistance over conventional [30]. The increase in hardness is attributed to the decrease in grain size. Nanostructured particles ($\leq$100 nm), however, cannot be thermally sprayed because of their low mass, the lack of inertia and momentum required to impact on the substrate. In order to spray nanometre or submicrometre particles using a conventional thermal spray, the particles have to be agglomerated and spray-dried into larger size particles (>5 μm). The optimum structure contains molten splat in micrometre-size to ensure the adhesion/cohesion and partially molten splat to keep their nanometre-sized zones [31]. Optimisation of these coatings has resulted in microstructures with negligible porosity and high fracture toughness but contradiction on tribology. The HVOF-sprayed nanostructured TiO_2 and Al_2O_3-13TiO_2 coatings have a reduction in the abrasion wear levels of approximately 60% and 90%, respectively in comparison with the conventional plasma spray [32]. It has been reported that nanostructured WC-12Co coatings exhibited <5 times higher wear resistances and lower friction coefficients than conventional coatings [33]. A similar trend was reported for nanostructured WC-12Co coatings which have 5-10 times lower wear resistance and higher levels of decomposition due to enhanced kinetics of dissolution of the small WC particles into the molten binder during at a shorter spraying distance [26, 34].

The use of solid suspensions in liquid feeds provides a newer merged thermal spray for nanostructured coatings. The sub-micrometre or nanosized particles are dissolved in a liquid, usually water and alcohol based, then injected by high velocity gas onto a substrate. During thermal spraying, suspensions droplets will vaporise gradually followed by the de-agglomerated particles are accelerated and partially or completely melted. The pioneers in this field were Karthekeyan *et al.* [35] for solutions in plasmas. Porosity of coatings is achieved as low as <0.2% when particle velocities were increased over supersonic speed [36]. Figure 4a) shows the cross-sectional image of nanostructured TiO_2 coatings via HVOF. The grey zones are partially molten nanosized TiO_2 particles embedded in the molten TiO_2 matrix. No pores are observed, compared to the large number of pores in conventional HVOF coatings in Figure 4b). The planar view shows the nanostructured TiO_2 with crack free on the suspension HVOF coating in Figure 4c). In contrast, a network of fine cracks can be clearly resolved in the close-up plane view on the conventional HVOF coating in Figure 4d). A similar trend was observed that the suspension HVOF sprayed WC-12Co and Al_2O_3 coatings have much lower pores and have higher hardness, lower friction coefficient and wear loss, in comparison to the conventional HVOF coatings [37, 38]. Moreover, suspension spraying can result in lower as-sprayed surface roughness and deposit thinner coatings because of the relatively smaller powder particle size. Suspension HVOF is limited mostly to oxide materials (TiO_2, Al_2O_3, Cr_2O_3, etc.) [39] due to metals such as Co can be dissolved which influences the stability of the suspension [40]. Nanoparticles having a high density, such as WC (15.7 g cm^{-3}), are difficult to maintain in a stable suspension, in comparison to other carbides, such as TiC (4.93 g cm^{-3}) and Cr_3C_2 (6.68 g cm^{-3}).

The main limitation of thermal spraying (including HVOF) is that it is a line-of-sight application technique. For example, it is very difficult to apply thermal spray coatings to small inner diameters and to deep or blind holes and some complex geometries [41]. The sprayed surface is often rough (3-15 μm). Machining is then required, which is expensive because of their high hardness. HVOF is about 50% higher in cost than EHC coating for these types of aerospace applications also due to significant capital investment required and the use of expensive powder feedstock [42]. HVOF is most cost-effective for coating of large components, rather than for films of a few microns thickness.

3.2 Vapour Deposition

3.2.1 Physical vapour deposition (PVD)

PVD is a thin-film coating process which involves physically depositing atoms, ions or molecules of a coating species onto a substrate. The target materials can be evaporated by electric heater or sputtered by generation of plasma between the coating species and the substrate, in a vacuum at working pressure (typically 0.1 to 1 Pa). Reactive gases such as nitrogen may be introduced into the vacuum chamber with sputtered metals to create ceramic compounds. The temperature of the substrate being coated is typically in the range of 200-400 °C. Commonly, the film is less than 5 μm thick, with a relatively slow mean deposition rate of 1-3 μm h^{-1}.

PVD ceramic coatings are widely used for cutting tool applications because of their high hardness and outstanding wear resistance. They have been developed over thirty years to realise four coating generations: (a) single metal nitride PVD coatings e.g. TiN, CrN or ZrN, (b) alloyed elements improving oxidation resistance, e.g. TiAlN, (c) multilayers with the layer spacing less than 10 nm and (d) nanocomposite coatings [43]. The hardness of titanium nitride is typically higher than 20 GPa. Improvements in oxidation resistance are achieved by co-depositing elements such as Al, Cr with the TiN. The addition of Al prevents other elements being oxidised by formation of a stable aluminium oxide on top surface. Small levels of chromium increase the density of the oxide, tending to migrate to grain boundaries and prevent the substrate elements from diffusing up through the coating as the temperature rises. Incorporation of carbon into transition metal nitrides by magnetron sputtering yields important wear resistant materials. Carbon also shows a remarkable influence on columnar growth, leading to finer grain size. As shown in Table 2, a TiN modified TiAlVCN nanocomposite has exhibited a very low wear rate 1×10^{-8} mm^3 N^{-1} m^{-1} against hard alumina [44]. This is 1000 times lower a wear rate than the EHC performance. Multilayered coatings can further improve the hardness, corrosion resistance, oxidation resistance and toughness compared to single layers of the same materials. One example is that the multilayer coatings of alternating nanoscale (of period 3–5 nm) TiAlN and VN layers have exhibited superior hardness and sliding wear rate of 1.3×10^{-8} mm^3 N^{-1} m^{-1} against an alumina ball counterpart [45]. The cross-section of the multilayer coating is shown in Figure 5a).

Hard, wear resistant and low friction diamond-like carbon (DLC) coatings are often applied in automotive engines to achieve friction reduction on engine components (tribology). Their wear rate is reported to be a thousand times lower than uncoated CoCr [46], with the useful life extending from 12–15 years to over 50 years. DLC coatings are superior for the machining of cast and wrought aluminium and coating of plastic injection molds due to their low coefficient of friction and non-stick properties. Codeposition of strong and weak, carbide-forming metals will further increase wear resistance and reduce residual stress. Figure 5b) shows

nanocrystalline WC carbide particles embedded in aluminium doped amorphous DLC. As shown in Table 2, the friction coefficient of DLC against steel is 10 times less than EHC [44, 47-51]. Vetter has contributed a review of boron-doped diamond (BDD) coatings [52].

The emerging technique of pulsed magnetron deposition has been comprehensively reviewed [53]. High power pulsed magnetron sputtering (HPPMS) is a physical vapour deposition technique in which the power is applied to the target in pulses of low duty cycle (<10%) and frequency (<10 kHz) leading to pulse target power densities of several kW cm^{-2}. The resultant ultra-dense plasmas have a high degree of ionization of the sputtered atoms and unusual transport of ionized species, with respect to the target. These features enable the deposition of dense and smooth coatings on substrates of complex-shape. Examples of materials deposited by HPPMS include tailored metal oxides and nitrides.

3.2.2 Chemical Vapour Deposition (CVD)

CVD films are formed by chemical reactions within a gas mixture on a heated substrate. The surface is usually maintained above 600 °C [15] in the reaction chamber, to assist the chemical reactions with decomposed reactant gases such as $TiCl_4$, SiH_4, NH_3, C_xH_y. The 'hot' processes create diffusion bonding between the film coating and the substrate and thus is much stronger than the bond created through the PVD process. CVD coatings provide an excellent wear resistance but are limited to heat resistant substrates.

DLC films by PVD are produced at very slow rate (<1 μm h^{-1}) and accompanied by high residual stresses, limiting the coating thickness to a few micrometres. Thicker coatings are obviously advantageous for tribological applications. A novel technique for depositing thick diamond-like carbon-based films has been developed and patented by Sub-one who utilised plasma enhanced CVD (PECVD) technology to generate high density hollow cathode plasma [51]. The coating thickness can reach as thick as 80 μm and the deposition temperature on the substrate is below 200°C, due to the use of a gaseous plasma.

Both PVD and CVD techniques produce coatings of high hardness (2-3 times higher than EHC) and low sliding rates against mild steel (at least one magnitude of order lower than EHC) but have a number of limitations [54]:

- Relatively thin (below a few μm) coatings are normally deposited at temperatures of >200°C in PVD and >600°C in CVD so the latter is unsuitable for use on a heat sensitive substrate. Chromium deposition is considered as a 'cold' process in PVD terms, with the operating temperature typically being 50-60°C; however, the high density hollow cathode plasma CVD techniques can produce a thick diamond like carbon, DLC layer up to 80 μm;
- PVD and CVD are relatively expensive and require a sealed, controlled gas atmosphere or a vacuum which limits the size and shape of items that can be coated; it also necessitates use of a customised gas-sealed chamber;
- PVD is a line-of-sight process and requires the substrate surface to be easily accessible. CVD process uses various gases to deposit anywhere the gas can contact the substrate. The latter can be used for coating non-line-of-sight substrate geometries, such as an internal tube.

3.3 Electrodeposition from other baths

Electrodeposition is traditional, versatile, widely practised and economically competitive. Electroplating from baths free of hexavalent chromium can be carried out using existing hard chromium plating hardware, significantly reducing the cost. In addition, quite a number of benefits associated with hard chromium plating are retained, such as freedom from line-of-sight limitations, dimensional consistency, good coating adhesion and surface finish [55]. However, chromium electroplating which avoids chromic acid baths tend to be more expensive, less tolerant to impurities and more difficult to maintain; their development has taken some 50 years. The electrodeposition alternative to EHC includes trivalent chromium, Ni and Co based alloy coatings. It is important to realise, however, that electrodeposition is also capable of depositing a wide variety of polymer, ceramic and metal-composite coatings, including nanostructured materials [56, 57].

3.3.1 Trivalent chromium plating

Trivalent chromium plating using $Cr_2(SO_4)_3$ and $CrCl_3$ as the main components of Cr^{3+} plating baths, with significantly less detrimental human health effects, has been considered as a promising replacement for Cr (VI) technology for decorative applications since the 1970s. Development of early trivalent baths, before 1980, are considered elsewhere [3]. It is until the early 2000s, for commercially functional (thick) chromium coating by trivalent processes. Trivalent chromium processes have a much greater throwing power leading to two and three times faster than hexavalent chromium processes at much lower current densities [18]. The challenges for trivalent chromium plating involving much more complex than hexavalent chromium, the need for environmentally friendly trivalent chrome is urgent with tightening regulations on hazardous substances, e.g., in the U.S. and EU. Many efforts have been made to develop functional trivalent chromium in aqueous or ionic electrolytes. In an aqueous electrolyte, examples include pulse and pulse reverse waveforms applied to the electrodeposition of functional and decorative chromium coatings [58]. In mixed, water-ionic liquid electrolytes, Khani and Brennecke [59] successfully electrodeposited a composite coating of thick trivalent chromium via the addition of cation surfactant, cation polymer, and ceramic particles to the bath. In 2017, Atotech launched its first commercial trivalent thick chromium (BluCr®) which is similar to hexavalent hard chrome, utilizing mixed metal oxide or graphite inert anodes for plating [60]. Hydroxide sludge disposal costs are significantly reduced due to the low level of chromium salt/oxides of 4-20 g dm-3 vs. 150-300 g dm-3 for a hexavalent bath [58].

Compared to hard chromium plating, the trivalent process claims advantages in terms of cathode efficiency, throwing power and disposal cost. However, trivalent chromium deposits also have significant drawbacks:

(1) The as-deposited coating from Cr^{3+} is amorphous and appears a darker, less optically reflective surface [61] due to absorbed carbon.

(2) The thickness of the coatings is limited to less than a few μm due to the formation of a cathode salt film constituted of chromium hydroxide or chromium oxide during the plating process [62]. This restricts their applications for anti-wear and other functional purposes [3, 4] although the oxidation can be reduced by using pulsed current [4], decreasing the pH [63] or adding strong buffers into trivalent chromium electrolytes [64].

(3) Trivalent chromium baths are more sensitive to foreign ion contamination than hexavalent chromium plating [62] and less tolerant of impurities routinely arising from substrates or longer term process carry-over.

3.3.2 Non-chromium nanocrystalline coatings

Electrodeposited nickel and cobalt based coatings have been considered as potential replacements for hard chromium [65, 66]. The first bath to deposit nickel was formulated by Watts in 1916. It contained nickel sulphate to provide nickel ions, nickel chloride or sodium chloride) to assist the dissolution of the nickel anode and boric acid as a pH buffering agent, as listed in Table 3. The Ni hardness prepared by Watts is under 200 HV which is much lower than that of EHC. One way to increase hardness is to reduce grain size according to the Hall-Petch effect. The grain refinement depends on the formation of new nuclei which can be improved by a low surface diffusion rate and high overpotential [67]. When adsorbed on the surface, surfactants, such as saccharin have been proven to be an effective additive for grain refinement in nickel electrodeposition [18,68,69]. Nanocrystalline Ni coatings (grain size <100 nm) have a typical hardness of 450 HV [68] which is 2-4 times that of deposits from a Watts nickel bath.

Cobalt based coatings have been intensively investigated recently due to their hexagonal-close-packed (hcp) structure and very low stacking fault energy (SFE) which lead to an intrinsically low coefficient of friction [70]. With the increase of cobalt content from Ni rich to Co rich coatings, the structure changes from face-centred-cubic (fcc) to hcp and the corresponding coefficient of friction is reduced from 0.45 to 0.2 which is only one-third of hard chromium [71], as shown in Table 4.

Ni/Co-P alloys are important tribological coatings. Similarly, their nanograined coatings exhibit enhanced hardness up to 600 HV. However, they are heat treatable, when their hardness becomes comparable to that of hard chromium. An example is that the hardness of Ni-Co-P coatings increases by up to 40% after heat treatment [6]. Figure 6a) shows the variation of hardness with annealing temperatures. The as-deposited Co-Ni-P coating has a microhardness of 602±15 HV, which is lower than as-deposited hard chromium. As the heat treatment temperature reaches 400°C, the microhardness increases to 980±65 HV, where the formation of precipitate $Ni_{12}P_5$ precipitates takes place during hardening [6]. The coefficient of friction of both the as-deposited and the heat-treated Co-Ni-P coatings is approximately 0.3 (only half that of hard chromium coatings). Without cobalt, a Ni-P coating with the same surface P content (25 at. %) has a higher coefficient of friction (0.5) under the same test conditions. The minimum wear rate of Co-Ni-P coatings (2.8×10^{-6} $mm^3 N^{-1} m^{-1}$) was achieved after annealing at 400°C and is 4-7 times lower than that of hard chromium coatings.

Recent reviews of electrodeposited and electroless coatings to offer selective hard chromium alternatives include electrodeposited:
a) nanostructured Ni or Co coatings [72]
b) Ni-P alloys [73],
c) Ni-P-included particle composite coatings [74],
d) Ni-Co alloys [75, 76] and their composite coatings [76, 77] and
e) electodeposited Ni-Co-P ternary alloy coatings [78].

a) Corrosion of nanocrystalline nickel and cobalt
Deposits having micron sized nickel grains are amongst the most important coating materials due to their good corrosion resistance and ease of application. Nanocrystalline nickel, Ni-Co and Ni-Co-P coatings [72, 76, 78] exhibit a reduced corrosion rate compared to coarse (micrometre sized) grained nickel coatings in acid (H_2SO_4 / HCl) [79] and alkaline (NaOH

solutions [80] due to the formation of passive films. Cobalt coatings can readily form protective passive films in alkaline NaOH but not in acidic H_2SO_4 solutions [81] and consequently, the higher grain boundary density of nanocrystalline cobalt coatings accelerates corrosion in acid, due to the presence of a larger number of active sites for preferential attack.

By the formation of a dense oxidation ceramic film during the heat treatment, the coating corrosion can be improved further. The polarisation curves measured in 3.5% w/v NaCl for the Co-Ni-P coatings in Figure 6b) show that the corrosion potential positively increases from - 558 mV to -348 mV *vs.* SCE as the annealing temperature is increased [61, 64]. Electrodeposited composite coatings containing included hard particles, such as SiC, TiO_2 and Al_2O_3, have been reported to increase hardness and improve wear resistant and anti-corrosion properties, which broadens their applications [82].

b) Variation of coating composition

It has been observed during the plating of Ni-P, Co-P and Co-Ni-P that initially formed crystalline surface structures gradually transformed to an amorphous structure with the increase of phosphorus contents. Current density [83], plating bath composition [84], solution pH [85] and bath temperature [86] all exert an effect. Figures 6a) and 6b) show the compositional evolution and SEM cross-sectional view, respectively, of an 'as-deposited' Co-Ni-P sample plated for 75 minutes. The coating structure changes from initial columnar crystals to a very fine amorphous structure. The corresponding phosphorus content increases from 7% at, to 26 % at.; the amorphous structure appeared at a phosphorus content of >12% at. [6, 87]. The mechanism is believed to reduce the residual stress and improve the coating tribological performance. It is amazing that such a similar structure can be traced in nature: the feature of Staffa cliff in Scotland as shown in Figure 6c). Composite coatings incorporating hard particles, such as SiC, TiO_2 and Al_2O_3, have been reported to increase hardness and improve wear resistance and anti-corrosion properties [88].

c) Direct and pulsed current control

Electroplating can be powered by direct current (DC) or pulsed current. In comparison to DC plating, pulsed current plating enhances the initiation of nuclei and then the number of grains which result in finer grained deposit with better properties than conventionally plated coatings [2]. The simplest form uses interrupted DC current to electroplate parts. This is accomplished with a series of DC current pulses, which may be of equal amplitude and duration in the same direction, separated by periods of zero current. During the current off period, metal ions from the bulk of plating solution diffuse near the cathode. The potential or current can be regulated by amplitude, duration and polarity, and thus it is possible to control the deposited film composition and thickness. In comparison to direct current plating, pulse current plating enhances the initiation of nuclei and then the number of grains which results in finer grained deposit with better properties than conventionally plated coatings [3-5].

Nanostructured cobalt-phosphorus (Nanovate™ CO) has been developed to coat steel bars and tubing for applications currently serviced by EHC in the fluid power market [89]. The commercially available nCoP coating is prepared by pulsed current plating. It deposits at a much higher current efficiency (approx. 90%). The coating has lower sliding wear rate and a lower coefficient of friction against steel, as shown in Table 5 [90].
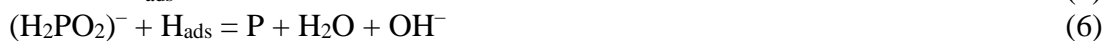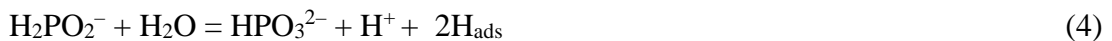
d) Possible health risks associated with nickel and cobalt compared to hexavalent chromium

It is generally accepted that the nickel and cobalt solute salts used in the electroplating industry have a much lower carcinogenic potency than hexavalent chromium. Indeed, nickel sulphate via inhalation is not carcinogenic, but may induce adverse effects in asthma suffers caused by inhaling the mist or on skin sensitisation caused by skin contact. However, the cobalt salts - cobalt dichloride and cobalt sulphate have been categorized as 'substances of very high concern (SVHC) under REACH and have been nominated as candidates for Annex XIV, although they have not so far been added to Annex XIV [91], as listed in Table 6. So, cobalt based plating may face stricter regulation in the long run. Nickel plating may have a definite future but boric acid, which is commonly added to the nickel plating as a pH buffer, has to be replaced as this substance has also been nominated as a candidate of SVHC. NaH_2PO_2 or H_3PO_4, have been successfully used for pH buffering and as a source of phosphorus for Co-Ni-P coatings (Table 3), and may be used in Ni-P plating.

3.4 Electroless Deposition

Since the discovery of electroless deposition in 1946 by Brenner and Riddell [92], the autocatalytic deposition of pure nickel using hydrazine as the reducing agent has become well established. Electroless deposition is relatively fast rate (<20 μm h^{-1}) but relies on an autocatalytic surface reaction, the coating thickness usually being restricted to several microns over a deposition time of several hours. For tribological applications several binary Ni-P, Ni-B, ternary Ni-P-B, Ni-W-P, Ni-Co-P etc. coatings have been developed [93]. Figure 8 shows the general market for electroless nickel based coatings, the main applications of electroless nickel coatings being based on their properties including wear and corrosion resistance (55%) and electromagnetic interference (18%).

Ni-P alloys are one of the most common autocatalytic nickel deposits, and have various applications in aircraft, automotive, marine and electronics industries. Alloys containing a range of phosphorus contents, ranging from 2-14% wt., depending on bath composition and temperature are common. Nickel deposition via oxidation of hypophosphite ions can be followed by the 'atomic' (adsorbed) hydrogen mechanism [93]:

$$H_2PO_2^- + H_2O = HPO_3^{2-} + H^+ + 2H_{ads} \qquad (4)$$
$$Ni^{2+} + 2 H_{ads} = Ni + 2H^+ \qquad (5)$$
$$(H_2PO_2)^- + H_{ads} = P + H_2O + OH^- \qquad (6)$$

These reactions take place at catalytically active surfaces at relatively high temperatures (95°C) in aqueous solution such that evaporation and heat loss need to be considered. In addition to metallic nickel and non-metallic phosphorus, atomic hydrogen is released as the result of the catalytic dehydrogenation of hypophosphite adsorbed at the surface of the work-piece. The hardness of as-deposited Ni-P coatings ranges from 490 HV to 660 HV depending on the phosphorus content, and can be significantly increased from 880 HV to 1080 HV after annealing at 400°C due to precipitation hardening by the intermetallic compound Ni_3P [94], as shown in Table 7 [95]. Thanks to their high hardness and good ductility, the wear resistance is similar to that of hard chromium plating [88].

Electroless Ni-B plating, usually involving a biborane reducing agent in the bath, is another process which can produce coatings with higher hardness, typically between 650-750 HV. After heat treatment, a hardness of 1200 HV can be obtained by precipitating the Ni_3B intermetallic compound. The Ni-B coatings also exhibit lower coefficient of friction and wear

rates against a steel ball in lubricated wear tests [88]. The Ni-P and Ni-B alloys have already gained 95% of the industrial production market due to excellent hardness, anti-corrosion and tribological properties [96]. In the field of tribology, nickel based composite coatings can be divided into two major categories, i.e., lubricating composite coatings and wear-resistant composite coatings. The former have been developed by co-depositing solid lubricating particles such as MoS_2 and PTFE [93] and the latter have co-deposited hard particles such as BN, SiC, Al_2O_3, B_4C and diamond. The disadvantage is that the process requires high standards of quality control of surface preparation and plating solution because of unstable baths [94]. Complexing agents are added to prevent the oxidation of reduced nickel and to control pH. Inhibitors are also added to prevent the decomposition of the solutions in the bath.

Electroplating and electroless deposition processes are commonly used to deposit a surface layer from an aqueous solution. In electroplating, the desired reaction of metal deposition from reduction of soluble metal ions, takes place directly at the cathode surface. The anode uses an inert material or the same metal being plated in order to continuously replenish the ions in the electrolyte bath. In contrast, electroless plating involves a spontaneous, autocatalytic reduction of metallic ions in an aqueous solution by a reducing agent in the bath to deposit the metal at open-circuit without the use of external electrical power. The advantages of electroless plating include the uniformity of thickness on a substrate and the ability to deposit onto complex geometrical surfaces and internal tubular components [95]. The downside is that it is usually more expensive and slower to create a thick coating and less cost-effective due to difficulties in controlling solution stability. Compared to electroless plating, electrodeposition has the advantages of lower cost, a faster deposition rate and more stable, tolerant baths; over 95% of metal industrially deposited is by electroplating [96].

The porosity of coatings is often critical to tribological applications, especially regarding corrosion resistance, but coating porosity is poorly appreciated by many in the modern coatings community. Substrate mechanical finishing, surface roughness and pre-treatment are particularly important in electroplating and electroless deposition where the case of nickel coatings on steel have received special attention, e.g. [97]. Through-porosity via ionically communicating pores in the coating to the substrate, which can critically determine the lifetime and performance of corrosion protection coatings can be detected by a wide range of imaging and electrochemical techniques. Through-porosity has been well-documented in electrodeposited coatings, despite difficulties in detecting and quantifying its presence by simple imaging [98] and electrochemical monitoring [99] techniques. However, coating porosity has been poorly considered in many other types of coating. For example, it is very difficult to adequately cover high surface roughness of the substrate by vacuum techniques such as CVD, PVD and plasma vapour deposition, despite their versatility in coating small, specialised components of regular shape by metals, alloys and composites.

4 Summary

Due to the rising health concerns and costs associated with complying with international regulations regarding exposure to an acid mist of Cr (VI) and disposal of waste plating baths and rinses, there is a strong drive to find an alternative to EHC coatings. This review has considered both non-aqueous deposition processes including thermal spray, vapour deposition and aqueous electrochemical deposition including trivalent chromium plating, non-chromium electrodeposited nanocrystalline coatings and electroless nickel-based coatings and has discussed their suitability for replacing EHC. Coatings deposited via these processes have demonstrated potential to provide equivalent or better properties for anti-wear and/or anti-

corrosion purposes. Each of these processes has advantages and limitations, which can be summarised as follows:

(1) Geometry of the substrate: HVOF and PVD are line-of-sight coating processes, while CVD, electrodeposition and electroless deposition are not limited by line-of-sight geometries.

(2) Coating thickness: HVOF, 0.05-2.5 mm; Electrodeposition, 0.1-500 μm; Electroless deposition, <10 μm; PVD, <5 μm; CVD, <80 μm.

(3) Deposition rate: HVOF, 1-9 kg h^{-1}; Electrodeposition, 20-50 μm h^{-1}; Electroless deposition, <20 μm h^{-1}; PVD, <1 μm h^{-1}.

(4) Operating temperature: HVOF, 2600-3000°C; Electrodeposition, 15-60°C; Electroless deposition, 60-100°C; PVD, 200-400°C; CVD >600°C (exceptional: PECVD working temperature is in the range of PVD).

(5) Hardness: HVOF, carbide cermet >1200 HV; Electrodeposition, 400-1000 HV; Electroless deposits, 250-800 HV; PVD/PVD, 1000-3000 HV.

(6) Porosity: HVOF sprayed coatings, <1% (carbide); the rest are dense.

(7) Surface finish: HVOF sparing tends to result in a surface roughness in the micrometre range, while the other techniques are capable of realising a smoother finish, sometimes on the nanometre scale.

It is generally considered that electroplating technology is cost effective. Alternative coatings by electrodeposition can often utilise existing EHC infrastructure. Cobalt based electroplating is facing stricter regulation but nickel plating can fulfil present environmental requirements. It has been demonstrated that a heat treated Ni-P electrodeposit can show comparable performance to EHC. Hard ceramic particles added into Ni based electrodeposit can achieve higher hardness and lower abrasive wear rate [56]. Pulsed plating favours nucleation of new grains over the growth of existing ones, resulting in an ultra-fine grain structure and high corrosion resistance.

HVOF requires significant capital expenditures, special application on equipment and personnel training. However, it also offers outstanding tribological properties. WC-CoCr and Cr$_3$C$_2$-25%NiCr cermet coatings have generally been accepted as suitable alternatives for hard chrome. The ceramic coatings by Suspension HVOF have a dense, few defect and improved tribocorrosion resistance in comparison with conventional HVOF. Little research has been carried out on nanosized cermet coating using Suspension HVOF due to the restricted commercially available of suitable nanosized cermet particles.

PVD / CVD use a vacuum chamber thus the size and dimension of components are restricted. On the other hand, the vapour technique deposits extremely hard coatings, e.g. TiAlVCN and superior low friction coating, such as DLC, which have been successfully applied to facings in the tool industry.

Figure 9a) shows alternative coatings to electroplated hard chromium (EHC), showing the application technique and examples of coating materials. Wet, electrochemical deposition includes electroless deposition and electrodeposition from non-hexavalent Cr baths, while dry coating techniques include thermal spraying and vapour phase deposition. Application sectors are indicated in Figure 9b).

5. Further Research & Development

1. A close comparison of the characteristics and performance of typical thicknesses, alternative coatings to electroplated hard chromium, with respect to wear resistance and corrosion under controlled environmental and load conditions is needed. This includes dry and wet conditions and multiple cycles.

2. Determination of coating porosity, particularly with respect to through porosity in thin (<10 μm) coatings from a wide range of application techniques, including electrochemical deposition, vacuum deposition and thermal spraying.

3. Published case studies on competitive coating performance are extremely important in establishing the practical benefits and limitations of various coatings and their application techniques.

4. As electrodeposited coatings continue to provide versatile and cost effective coatings, environmentally acceptable chromium electroplating baths continue to be important but practical acceptance of such electrolytes infers electrolytes which are stable, water tolerant/compatible and have acceptable obtainability, storage, handling, health, safety and environmental disposal. Such constraints limit the choice to, e.g., trivalent chromium baths, more practical ionic liquid baths (such as choline chloride based ones) or composite electrodeposition baths involving metals other than Cr and Cd (including diverse composite baths).

5. Techniques applied to the examination of coatings before and after controlled service use should be complementary and include imaging (optical, electron and x-ray), surface profiling, phase and composition analysis (XRD, ED and EDX), tribometer and electrochemical corrosion (LPR, EIS, porosity and ageing) studies under controlled environment/sample flow and loading conditions.

6. It is probable that increased testing of chromium electroplated coatings will become mandatory, especially in aerospace and environmentally sensitive sectors of industry, worldwide [100].

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No potential conflict of interests was reported by the authors.

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Tables

Table 1. Tribological high velocity oxygen fuel, HVOF / plasma sprayed coatings (380 to 490 μm thickness) as alternatives to electrodeposited hard chromium, EHC [28]

Coating composition /wt.	Hardness / HV	Coefficient of friction (dry against Al_2O_3 ball)	Coefficient of friction (dry against steel ball)	Sliding wear rate (against Al_2O_3 ball) / 10^{-6} mm^3 N^{-1} m^{-1}	Sand abrasive wear rate / 10^{-4} mm^3 N^{-1} m^{-1}
EHC	800 to 1000	0.70	-	9-11	11.4
WC-17%Co	1240±116	0.37	0.78	-	0.9
WC-10%Co-4%Cr	1369±114	0.40	0.76	-	1.27
Cr_3C_2-25%NiCr	786±123	0.55	0.72	5.5	2.04
Cr_2O_3 plasma sprayed	962±112	0.35	0.57	-	11.3

Table 2. Tribological vapour deposited coatings (of approximate thickness of 1 μm) as alternatives to electrodeposited hard chromium

Coating	Hardness / HV	Coefficient of friction (dry)	Sliding wear rate / 10^{-6} mm^3 N^{-1} m^{-1} (counterpart)	Ref
TiN	2000-3000	0.5	0.1 (steel)	[48]
TiAlN/VN	2600	0.44	0.013 (Al_2O_3)	[45]
TiAlVCN	2900	0.4	0.01 (Al_2O_3)	[44]
DLC (a-C^{SP3})	1710	0.12	0.85 (steel)	[47]
DLC-WC-Al	1820	0.05	0.18 (steel)	[47]
GLC (a-C^{SP2})	2300	0.05	0.45 (Si_3N_4)	[49]
Graphit-iC^{TM} (a-C^{SP2}:Cr)	1500-2500	0.1	0.05 (WC-Co)	[50]
Dymon-iC^{TM} (a-C^{SP3}:H)	1200-1800	0.07	0.025 (WC-Co)	[50]
InnerArmor DLC	1000-2500	<0.08	0.5	[51]

Table 3. Typical electrolytes for Ni and Co based coatings

	Parameter	Microstructured Ni from Watts bath	Nanostructured Ni [68]	Nanostructured Co-Ni [68]	Nanostructured Co-Ni-P [6]
Bath composition	$NiSO_4.6H_2O$	240-300 g dm^{-3}	250 g dm^{-3}	200 g dm^{-3}	40 g dm^{-3}
	$NiCl_2.6H_2O$	30-90 g dm^{-3}	45 g dm^{-3}	-	-
	H_3BO_3	30-45 g dm^{-3}	40 g dm^{-3}	30 g dm^{-3}	-
	$CoSO_4.7H_2O$	-	-	100 g dm^{-3}	40 g dm^{-3}
	NaCl	-	-	20 g dm^{-3}	-
	NaH_2PO_2	-	-	-	20 g dm^{-3}
	additives	No	Yes	Yes	Yes
Operating Conditions	Temperature / ºC	40-65	45	45	45
	Current density / A dm^{-2}	2-10	4	4	5
	pH	3.0-4.5	4.5	2-4	2-3
Hardness / HV			130-200	450	500	600

Table 4. Tribological properties of electrodeposited coatings as alternatives to Electroplated hard chromium, EHC (dry sliding against an AISI-52100 stainless steel counterpart).

Coating	Hardness / HV	Coefficient of friction	Wear rate against steel / 10^{-6} mm^3 N^{-1} m^{-1}	Corrosion current density, j_{corr} / 10^{-6} A cm^{-2}
EHC	800-1000	0.7	20	3.30
Ni-P as-deposited [65]	550	0.45	38	
Ni-P annealed at 400°C [65]	1000	0.45	33	7.99
Ni-25%Co [71]	490±10	0.45	230	5.5
Co-17%Ni [71]	475±10	0.2	2.8	6.85
Co-Ni-P [5]	600±15	0.3	6	3.58
Co-Ni-P annealed at 400°C [6]	980±65	0.3	2.8	1.44

Table 5. Comparison of pulsed electroplated Co-P and electroplated hard chromium, EHC processes [90]

	Pulsed electroplated Co-P	electroplated hard chromium, EHC
Deposition method	Pulsed electroplating Co-2-5 wt%P.	Direct (smooth direct current) electroplating
% Current efficiency	85-95	15-35
Average deposition rate / $\mu m \, h^{-1}$	50-200	12.5-25
Hardness / HV	600 – 700 as-deposited, 1,000-1,200 HV after 400°C heat treatment	800-1,200
Wear volume loss (Pin-on-disc against Al_2O_3 pin)	$6 – 7 \times 10^{-6}$ $mm^3 \, N^{-1} \, m^{-1}$	$9 – 11 \times 10^{-6}$ $mm^3 \, N^{-1} \, m^{-1}$
Coefficient of friction (Pin-on-disc against Al_2O_3 pin)	0.4 - 0.5	0.7
Abrasive wear rate $mm^{3/} \, N^{-1} \, m^{-1}$	11×10^{-3}	11×10^{-4} mm^3
Appearance	Pit/pore/crack free	Microcracked
Microstructure	Nanocrystalline (5-15 nm grain size)	<1 μm to several μm grain size
Appearance	Pit, pore and crack free	Microcracked

Table 6. A candidate list of substances of very high concern for authorisation [91]

Substance Name	EC Number	CAS Number	Date of inclusion	Reason for inclusion
Cobalt dichloride	231-589-4	7646-79-9	20/06/2011	Carcinogenic and toxic to reproduction
Cobalt sulphate	233-334-2	10124-43-3	15/12/2010	Carcinogenic and toxic to reproduction
Boric acid	233-139-2, 234-343-4	10043-35-3, 11113-50-1	18/06/2010	Toxic to reproduction

Table 7. Electroless nickel coatings as possible alternatives to electrodeposited hard chromium in tribological applications. After Broman [95].

Coating	Hardness of as-deposited layer / HV	Hardness of heat-treated deposit / HV	Coefficient of friction (dry)	Abrasive wear resistance / 10^{-6} $mm^3 N^{-1} m^{-1}$
Electrodeposited hard chromium	800-1000	-	0.6-0.7	1.0-4.7
Ni-11%P	530	1050		11.6
Ni-10%P + 1%BN	785	-	-	-
Ni-7-10%P+ <50%MoS$_2$	675	-	0.85	>1.0-4.7
Ni-P+ 23-25%PTFE	250	400	-	<1.0-4.7
Ni-6-8%P +diamond	-	884-1161	-	1.3
Ni (4-6%)-Co-P	-	924	-	13.3
Ni (4-6%)-Co-P+ diamond	-	1135	-	2.1
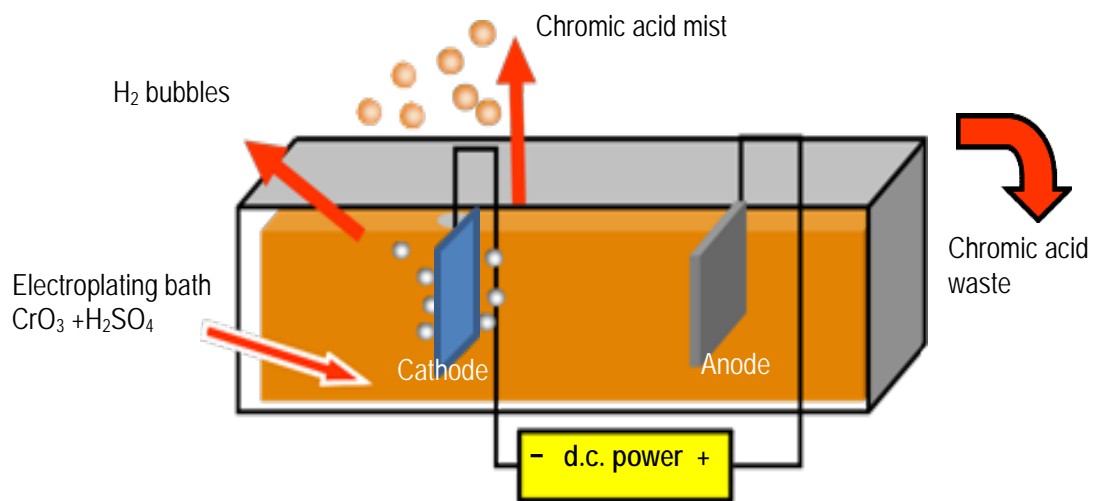
Figure 1   The principles of hard chromium plating. After Prado [7].
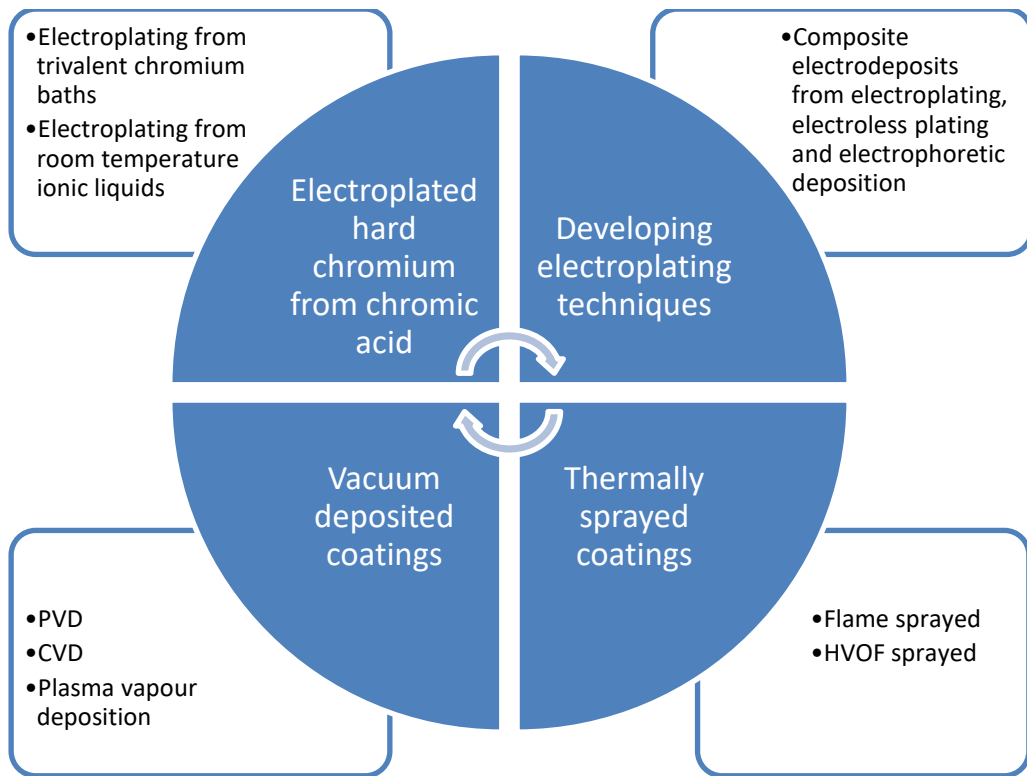
Figure 2   Alternative coating materials to hard chromium electroplating and their application techniques.
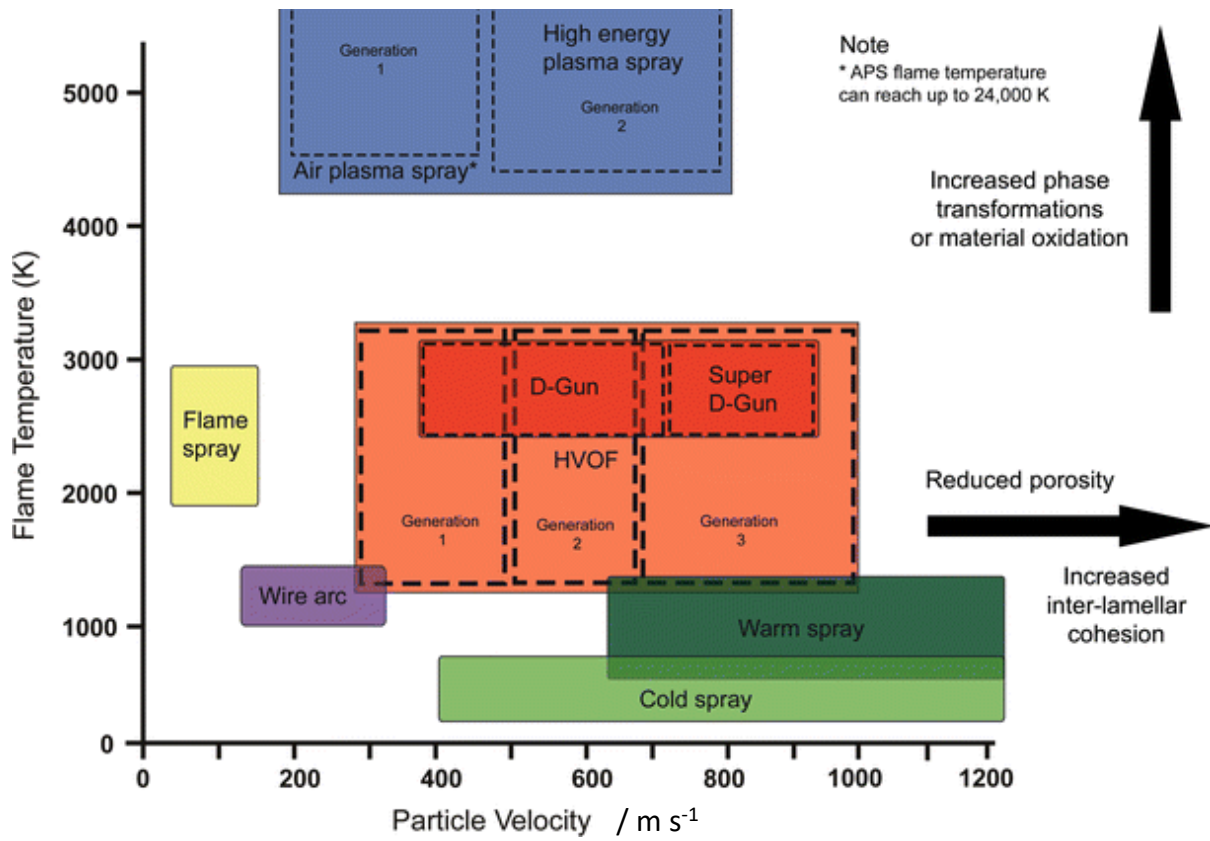
Figure 3   Classification of thermal spray processes, according to particle velocity and flame temperature. After [20].
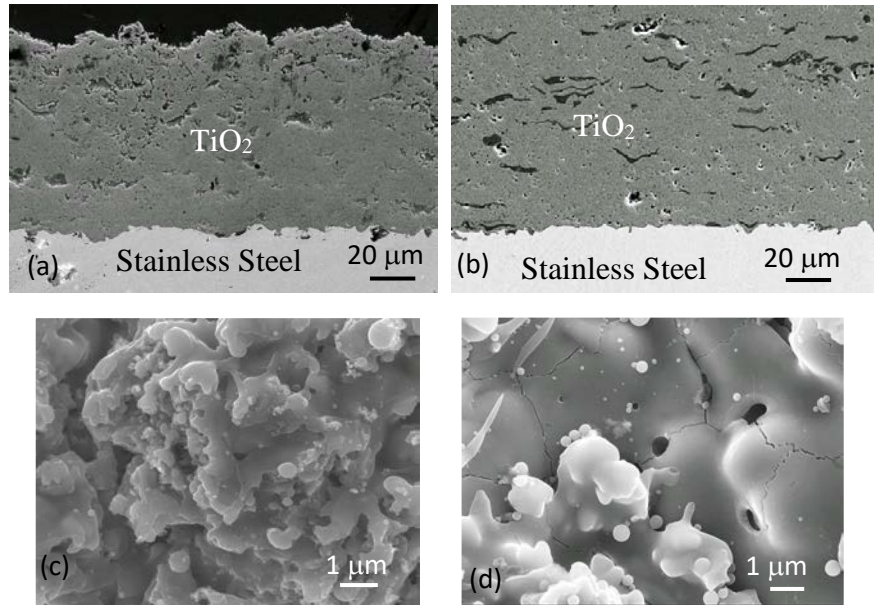
Figure 4   SEM micrographs of TiO$_2$ coatings. Cross-section view of the coatings by (a) S-HVOF spraying and (b) conventional HVOF spraying [40]. Close-up planar views of coatings from (c) S-HVOF and (d) conventional HVOF spraying. After [47].
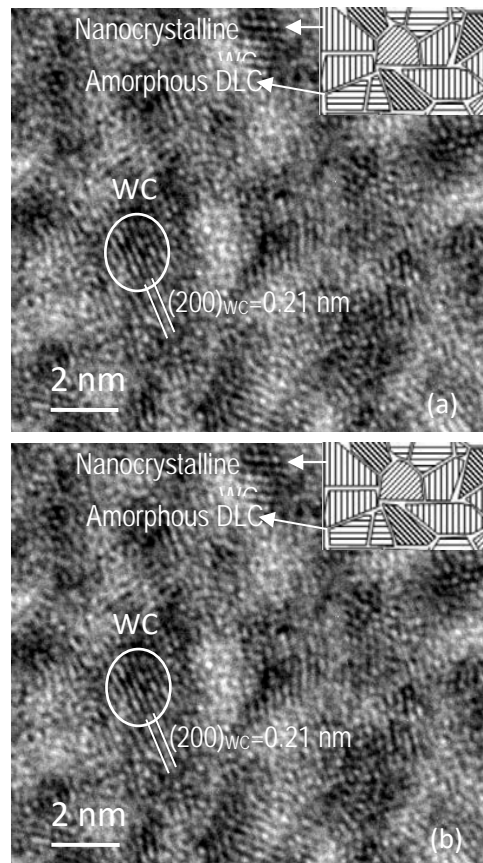
Figure 5 A TiAlN/VN multilayer coating. a) Cross-sectional TEM image, showing superlattice fringes of 4-5 nm [43]. b) High resolution TEM image of a DLC-Al-WC coating deposited by magnetron sputtering. The coefficient of friction against mild steel is 0.05 and the wear rate is 1.8×10^{-7} mm^3 N^{-1} m^{-1} under dry conditions. After [47].
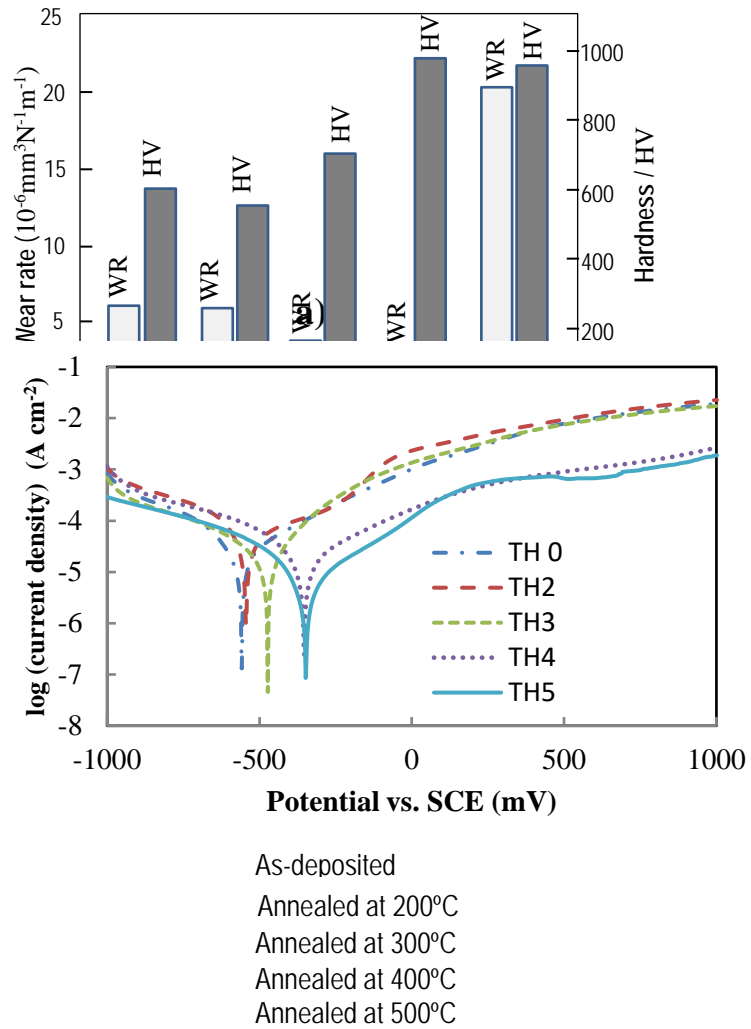
Figure 6   Co-Ni-P coatings, showing a) a comparison of hardness and dry sliding wear rates between annealed at different temperatures and hard chromium deposits. b) The corresponding polarisation curves of Co-Ni-P coating in 3.5% wt. NaCl solution. After [6].
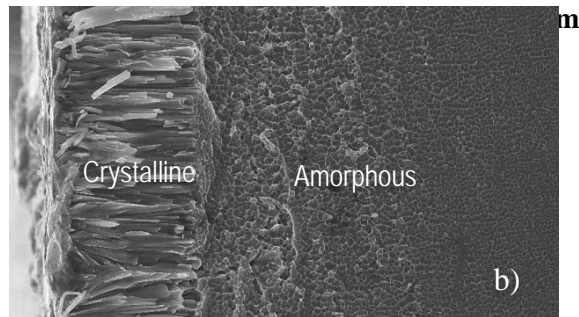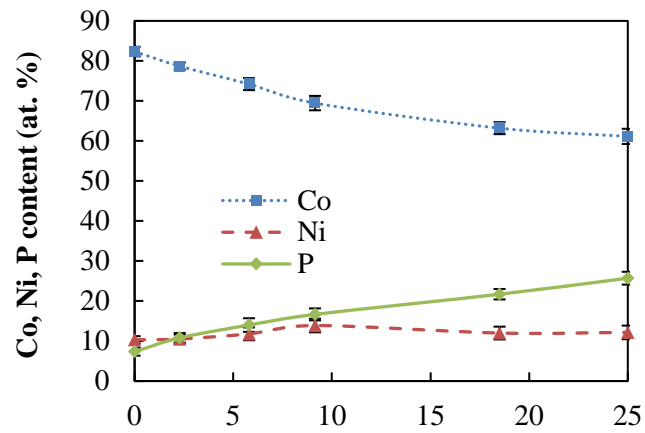
32

b)

Figure 7.   A Co-Ni-P electrodeposited coating, showing a) distribution of Co, Ni and P content with thickness, b) SEM cross-sectional image of the as-deposited Co-Ni-P coating plated for 75 min; (from [6]) and c) an Inset showing the landscape of Staffa cliff, Scotland. The marked rectangle was enlarged and rotated clockwise by 90°. The structure is similar to that shown in (b).
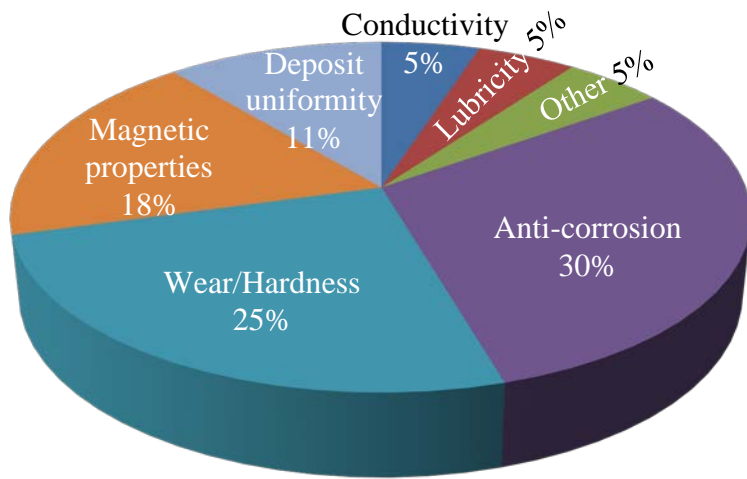
Figure 8   Market applications for electroless nickel deposits. After [85].

Electrochemical deposition	• Electrodeposition, e.g., Ni-Co, Ni-W, Ni-SiC, Ni-diamond composites • Electroless deposition, e.g., Ni-B; Ni-P, Co-WC composites
HVOF spraying	• Binary alloys, e.g., Co-W • Complex alloys and composites, e.g., CoCr-WC$_2$, Cr$_3$C$_2$-NiCr
Vapour deposition	• CVD. e.g., DLC, TiAlVCN • PVD, e.g., TiAlN, TiAlVCN, BDD, DLC • Plasma vapour deposition, e.g., BDD, TiAlN

a)

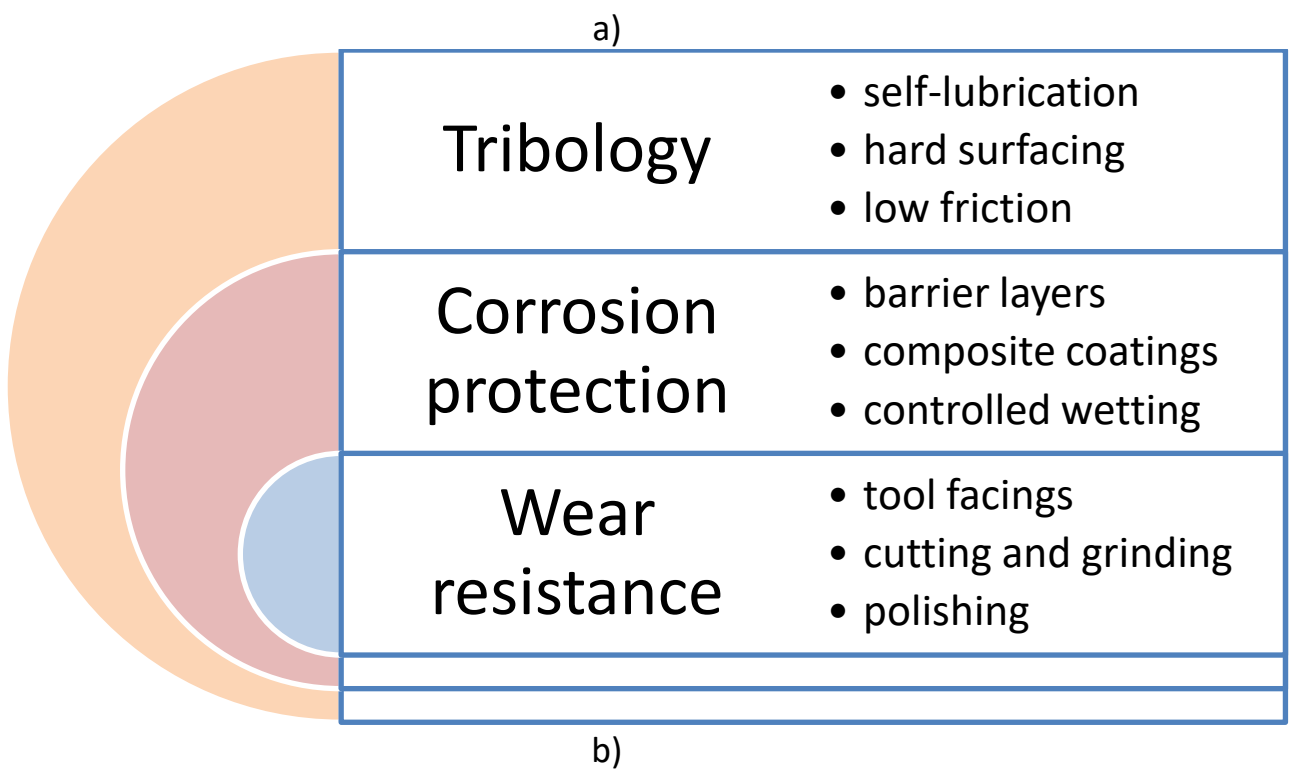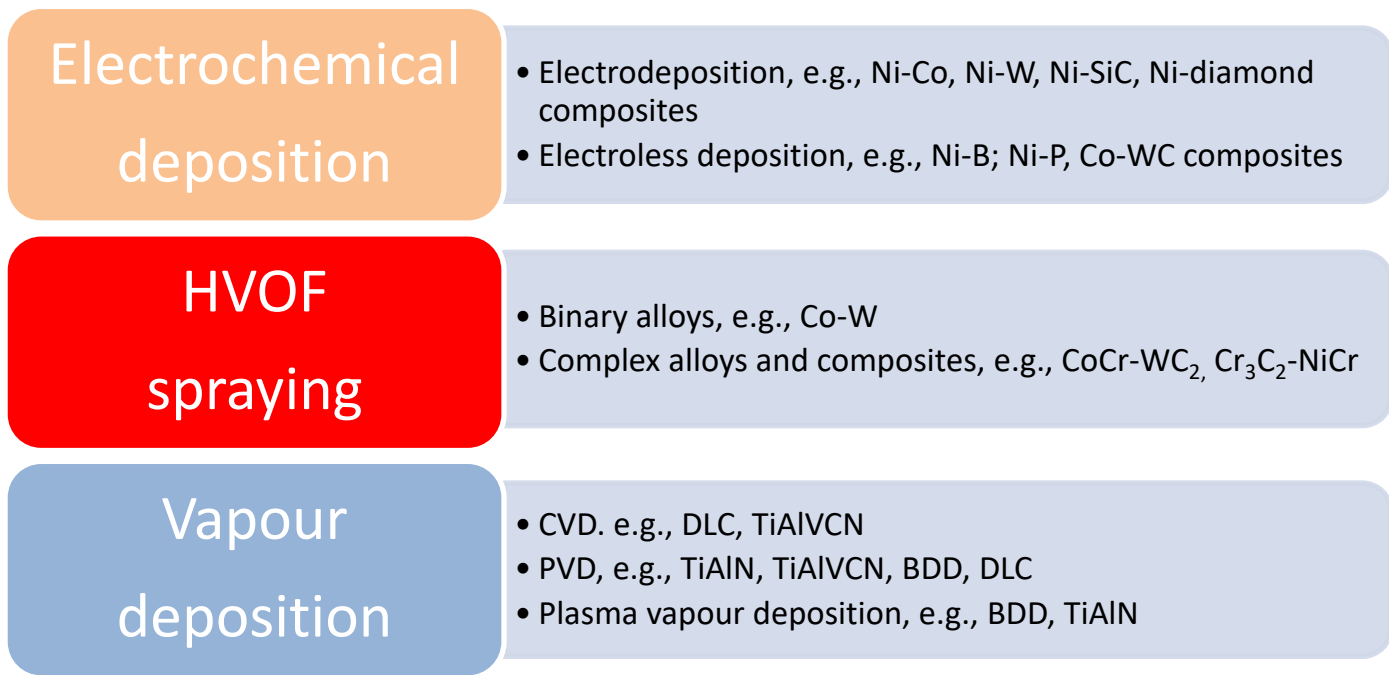| Tribology	• self-lubrication • hard surfacing • low friction
Corrosion protection	• barrier layers • composite coatings • controlled wetting
Wear resistance	• tool facings • cutting and grinding • polishing

b)

Figure 9   Examples of alternative coatings to electroplated hard chromium (EHC), a) wet (electrochemical) and dry application techniques and examples of deposited materials.

b) broad application sectors include tribology, corrosion protection and tool facings.