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A review on the environment friendly electroplating of Cr (III) & Cr (VI)

Md. Saiful Islam*, Md. Jahid Hasan, Promita Poroma, Sraboni Akter

Department of Applied Chemistry and Chemical Engineering, University of Rajshahi, Rajshahi-6205, Bangladesh.

**Corresponding author: e-mail address: saiful@ru.ac.bd; ORCID: https://orcid.org/0000-0002-5825-296X

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ABSTRACT

Chromium plating process is the most effective way of protecting the base material against hostile environment or improving surface properties of base material. There are several problems with traditional chrome plating. Traditional process uses toxic acid baths and may cause various health conditions. The baths employed contain chromic acid in which the chromium is in the hexavalent state. Hexavalent chromium has been proved to have toxic, mutagenic and cancerogenic effects for human health. As a result, In Europe, the implementation of the reach initiative will increase fees on companies still using Cr (VI) in 2017 and will require action plans to phase out Cr (VI) in the future. This has left the plating industry in a very delicate position with dark future prospects unless new solutions that are both effective and environmentally friendly are discovered. Superchrome Physical Vapor Deposition coating ahead of looming industry regulatory actions that will drive towards the removal of hazardous hexavalent chromium compounds. These new sputtered chromium coatings do not require a protective paint top coat to pass exterior automotive trim specifications. Visually the chromium coatings match those of electroplated decorative chromium in color and appearance.

1. Introduction

Chromium electroplating is widely utilized in industry due to its unique and remarkable attributes such as low friction coefficient, exceptional wear resistance, outstanding corrosion resistance, and visual appeal [1, 2]. Numerous components comprise electroplated chromium coating on base substrate. A thin layer decorative chromium on 35-50 microns of leveling and supports metals under film formed from chemical bath and rinses (**Fig. 2**). However, there are indication that chromium can be very harmful to animals and even humans, as well as being recognized as carcinogen [3, 4]. Chromium has two stable oxidation states: trivalent Cr (III) and hexavalent Cr (VI), despite Cr (VI) is potentially more toxic, cancer-causing, and mutagenic [5]. The release of Cr-ion from conventional chrome plating decorative/metal/alloy generates numerous kinds of health and environmental issues. In China, the metal finishing industry was responsible for the highest amount of chromium discharge in 2010 (**Fig. 1**). Deposition processes comprise electroplated finishes like hard chromium, cadmium, nickel which are the most important source of pollution in all countries [6] .

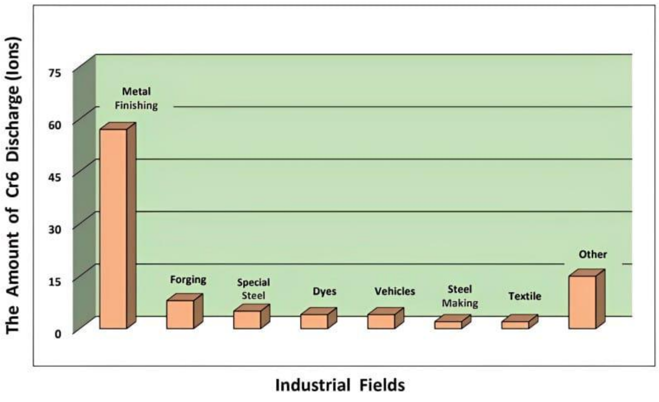

Figure 1. The discharge of chromium from different industries in the year of 2010 in China [7].

The decorative top layer is a thin film of electroplated chromium. However, this electroplated coating of chromium comprises several stages involving chemical baths and rinses [8].

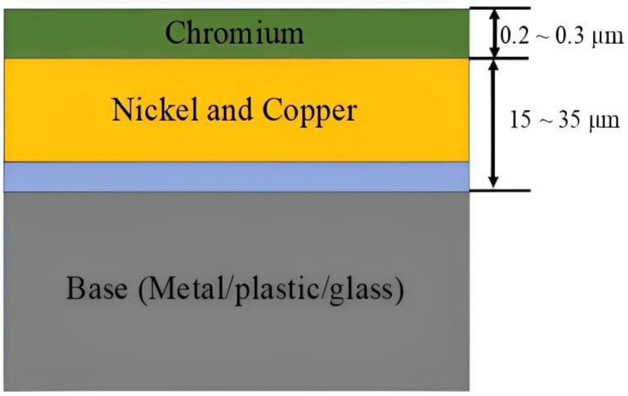

Figure 2. Electroplated chrome stack.

A variety of reasons including its wear and corrosion resistance, traditional hard chrome plating has been frequently utilized [9]. Alternative methods, such as HVOF-sprayed coatings, demonstrate promise as a replacement for traditional chrome plating processes, providing good corrosion resistance and highly adherent coatings with low porosity [10]. Furthermore, laser clad coatings have been investigated as an alternative for chrome electroplating, with surface hardness in the 1000 Hv range [11]. Furthermore, HVOF coatings have been established as a viable alternative to hard chrome plating for pistons and valves, with much reduced specific wear rates when compared to typical hard chrome plating [12]. Additionally WC-Co-Cr coatings sprayed using the HVOF technique have been suggested to replace hard chrome plating, especially for aircraft landing gear, with the goal of extending the gear's operational lifetime [13]. Also, nanodiamond chrome coatings have been identified to outperform the technical properties of hard chromium plating, broadening the spectrum of use for chrome plating [14]. Simillarly, thermal spray methods, particularly high velocity oxyfuel (HVOF) thermal spraying, are commonly regarded as capable of replacing hard chrome plating for a wide range of industrial components [15].

2. Replacement of existing chromeplating methods

In recent years, substantial research has been conducted on the limitations of various chrome plating processes. As prospective substitutes for standard chrome plating methods, HVOF-sprayed coatings, laser clad coatings, nanodiamond chrome coatings, and thermal spray technologies have all been investigated.These techniques, however, are not without boundaries. HVOF-sprayed coatings have demonstrated potential for replacing traditional chrome plating techniques. However, one of the key difficulties of thermal spraying, including HVOF, is that it is a line-of-sight application technique, limiting its use in specific settings [16]. Moreover, decarburization of WC into W2C, W3C, and even metallic W phases can degrade coating characteristics, minimizing its application to temperatures below 450-530°C [12]. Laser clad coatings have also been investigated as a possible replacement for chrome electroplating. However, the industrial implementation of laser cladding technology is limited by its shortcomings, which need to be addressed for wider adoption [17]. In addition the use of chrome plating and other surface engineering processes for thick coatings can be inefficient and expensive, with actual process limits [11]. Nanodiamond chrome coatings outperformed chromia-only coatings in terms of tribological performance. However, the tribological performance gain is minor, with specific wear rates falling by 20% and the coefficient of friction falling by 15% [18]. Thermal spray technologies, especially HVOF thermal spraying, have been widely viewed as capable of replacing hard chrome plating. The HVOF/HVAF process offers better mechanical properties, relatively lower porosity, and a lower degree of decarburization, making it an attractive alternative to hard chrome plating [19]. However, the main limitation of HVOF compared to other thermal spray techniques is the ability to accelerate the melted powder particles of the feedstock material at a relatively large velocity, which permits the formation of a fairly dense microstructure [20].

Over the past decade, engineers have been working to replace outdated, environmentally harmful technology with advanced dry coating methods, aiming to provide high-quality and cost-effective production coatings that meet specific standards, thereby promoting a more environmentally friendly approach.

Physical vapor deposition (PVD) is usually regarded as a method capable of replacing chrome plating among the various currently available technologies [8]. A clear paint top coating with or without color tinting was applied as a safeguard the base coating from wear and tear and environmental damage (**Fig. 3**).

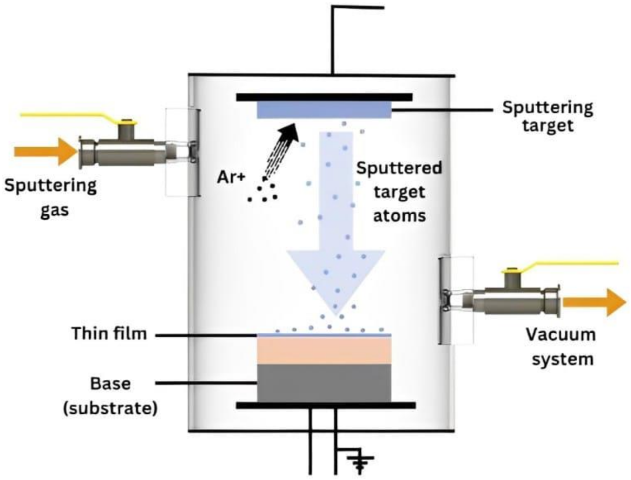

Figure 3. Schamatic diagram of PVD method

Following the arrangement of the substrates mounted on the holders' vacuum chamber, the deposition process comprises the four critical steps shown in **Fig. 4**:

- The first step, Ramp Up, involves assembling the vacuum chamber by continually raising the temperature, which is induced by a tubular heating and an interchangeable control system; at an identical time, the vacuum pumps are activated to decrease the pressure inside the chamber [21].

- The second step, Etching, has been defined by cathodic cleaning. Ions from plasma etching attacking the substrate to get rid of contaminations on the outside of the substrate [22, 23].

- The third stages, coating, occurs. The substance that needs to be coated is projected onto the surface of the substrate [21].

- The final step, the ramp downstage, corresponds to the vacuum chamber going back to its normal pressure and temperature [21].

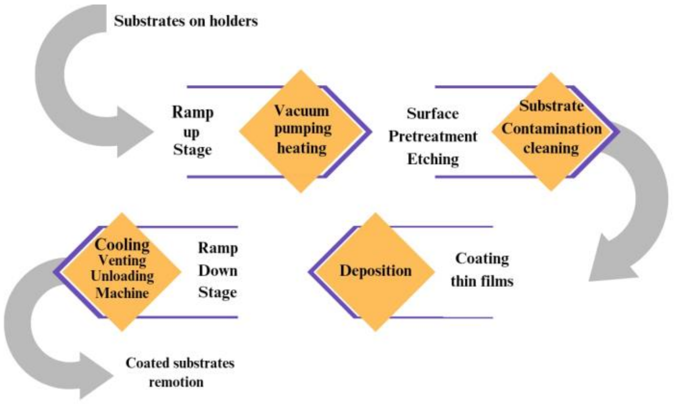

Figure 4. The processing flow for a classic PVD sputtering process.

Moreover, it is important to note that PVD is regarded as one of the methods of applying not only metallized layer, but also alloys and ceramics. With an almost infinite variety of chemical composition therefore controllable protective, mechanical and wear resistive characteristics [24]. PVD can produce coating with excellent adhesion, uniform structure graduated layers, properties, designed controlled morphology of materials with a variety of properties, etc. [25-29]. In conventional Plating, whether decorative or harsh, is a time-consuming procedure that includes immersion in many chemical baths and results with considerable metal loss, which may be quantified by examining the characteristics of chrome plating waste water. In the waste water of the plating business, the concentration of Cr (VI) in the effluent is substantially greater than the authorized limit of 0.1 mg/L [30]; **Table 1** shows the Physicochemical characterization of chrome plating waste-water.

TABLE 1. Physicochemical characterization of chrome plating waste-water.

Parameter	Value	Unit	ref.
pH	3-9	-	[31]
Electrical conductivity at 25^{0}C	6000.0	µS/cm	[32]
Total chromium	112.49	mg/L	[33]
Hexavelant Chromium	50.1	mg/L	[32]
Nickel	15.2	mg/L	[32]
Zinc	3.6	mg/L	[32]
Copper	0.2	mg/L	[32]
Chemical oxygen demand	25.5	mg/L	[32]

The amount of metal loss in superchrome PVD technique is extremely small as it is not required multiple chemical baths as well as vacuum plating. There are no atmospheric discharges of any type during the processing processes. There are no pigments or residues to deal with in this modern technique, which uses benign metals, inert gas, a vacuum, controlled temperature, and time. There is some dust as a result of chamber cleaning, but it creates no disposal issues.

3. Improvement of PVD coating technology

PVD coatings generated through Arc Bond Sputtering (ABS TM) technology, such as CrN/NbN films, have been shown to have limitations such as macro droplets, porosity, and less dense structures [34]. Growth deficiencies in PVD coatings have been observed as a limiting factor, affecting the coatings' tribological properties [35]. Furthermore, the thickness of PVD coatings is limited, which limits their use in some situations [16]. Also, unsupported and mechanically incompliant ceramic coatings, such as TiN, can promote the formation of many crack sites, leading to premature failure of the substrate and a reduction in endurance limit [36]. Moreover, the effect of coating structure, hardness, plastic deformation residence, and stresses on erosion and wear resistance has been examined, showing that these characteristics can restrict the efficiency of PVD coatings in specific applications [37]. The application of PVD coatings on polymer surfaces or template structures on plastic substrates might be difficult due to the high synthesis temperature required for metal ALD (Atomic Layer Deposition) [38]. Furthermore, metal layer adherence on ABS, PVC, and PVC/ABS blends surfaces necessitates higher temperatures, immersion time, and etching solution concentration, indicating adhesion process challenges [39].

Addressing the correlations between variables such as thermal expansion, stress management, adhesion, surface smoothness, and durability are critical to the success of PVD chromium. Traditional PVD Coating (**Fig. 5**) uses regulated ion and heat energy throughout the film deposition process [8]. A 15-25 micrometer broad UV prime base coat was established on the base of this PVD coating. After that, a 0.04-0.1 micrometer broad layer of PVD metal coating was formed on the previously applied UV prime base coat, and finally, a top layer of UV prime base coat was developed on the PVD metal coating layer.

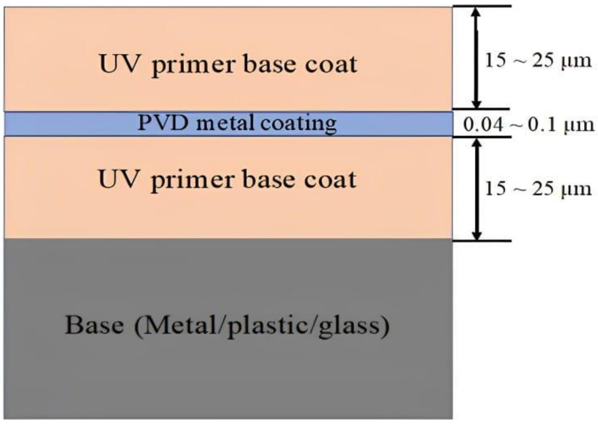

Figure 5. PVD Metallizing (Traditional Triple Stack:Base Coat/PVD/Top Cost)

Traditional PVD chrome plating can be improved by using a UV prime base coat with a thickness ranging from 15 to 50 micrometer and then develop a top layer of PVD metal coating with a thickness range of 0.3-1.15 micrometers. This improved variant of PVD chrome plating is referred to as superchrome PVD coating (**Fig. 6**).

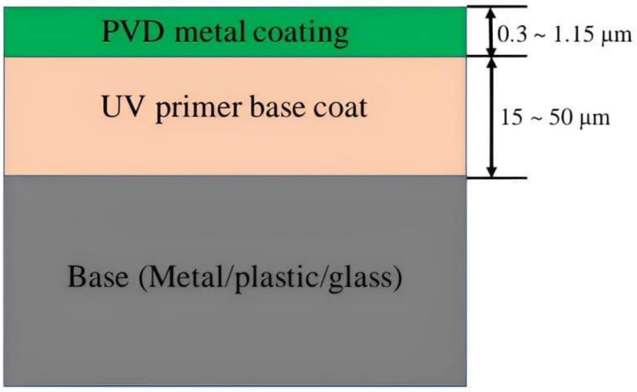

Figure 6. 0.3 ~ 1.15 µm 15 ~ 50 µm Superchrome PVD coating (Double Stack: Base Coat/PVD)

A wide range of UV primer base coat thicknesses (usually 15 to 50 micrometers) is employed for several fundamental reasons:

(a) Enhanced Adhesion: The thicker UV primer layer produces a rougher surface texture, which improves mechanical interaction between the primer and the underlying substrate (often plastic). This enhanced adhesion is critical to SuperChrome PVD's high durability and scratch resistance, particularly on non-metallic materials.

(b) Stress Mitigation: The thicker primer functions as a buffer zone between the base substrate and the PVD metal coating, reducing stress. This accommodates any changes in thermal expansion between the two materials, lowering stress and avoiding the coating from cracking or peeling over time.

(c) Light Control and Color Effects: To create diverse optical effects, the UV primer can be made with different pigments and refractive indices. For instance, a thicker primer with specific pigmentation can enhance the brightness and depth of the final chrome finish. Additionally, colored primers can be used to create unique chrome shades like black chrome or bronze chrome.

(d) Surface Imperfection Coverage: The larger priming coat can aid in the masking of tiny defects on the underlying substrate, giving in a smoother and more visually acceptable final finish. This is particularly advantageous for applications requiring a high-quality chrome appearance.

In terms of aesthetics, performance, cost optimization, and functional qualities, the extensive selection of metal coatings offered in Superchrome PVD gives substantial advantages.

4. Improvement of superchrome PVD coating

4.1. For polymer/plastic base

A number of methods can be used to improve the Superchrome PVD coating for plastic or polymer bases. Lugscheider et al. demonstrated that using combined pulsed magnetron sputtering, which is more effective than direct current or pulsed sputter procedures, can improve the adhesion between PVD coating and polymer substrate [40]. Additionally, it was proposed that the PVD coating can be improved by utilizing a thin conformal oxide layer produced via atomic layer deposition (ALD) as an interlayer, which improves the coating's adhesion to the polymer substrate [38]. Furthermore, adding a plasticizer to the coating formulation has been demonstrated to increase the plastic behavior of the films as well as their mechanical properties [41]. This is in line with the findings of, who found that adding a plasticizer reduces film stiffness by reducing intermolecular tensions and enhancing molecular chain mobility [42].

UV curing capabilities of Superchrome PVD coating can be enhanced by utilizing type II photo initiator. A conventional UV curing process on base substrate show in **Fig. 7**.

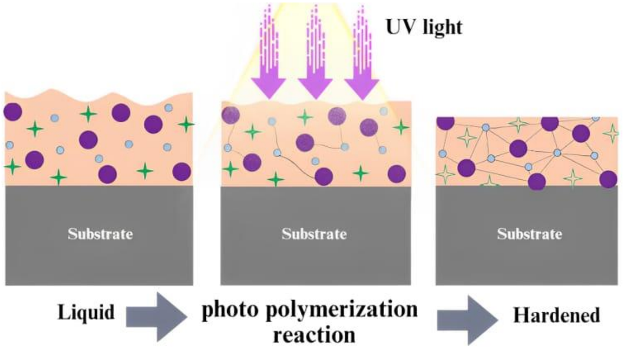

Figure 7. The mechanism of UV curing on substrate

Type-II systems (for example, benzophenone/tertiary amine) have a more complex initiating process. The excited benzophenone begins a quick electron transfer from the lone pair of tertiary amines, which is followed by a delayed proton transfer process, delivering the H-donor radical for polymerization initiation (**Fig. 8**).

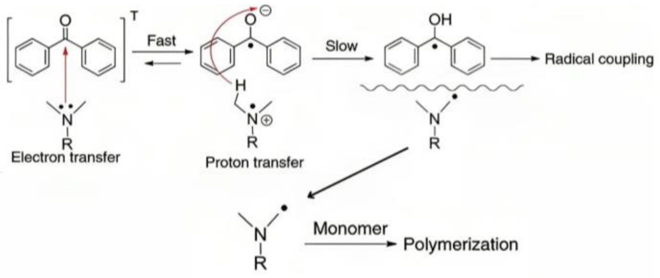

Figure 8. Photoinitiating mechanisms of Type-II

Even in the absence of multiacrylates, the use of a type II initiator in the photopolymerization of monoacrylate increased the surface hardness, heat resistance, and solvent resistance of the UVcurable coatings. It also discovered that it is possible to improve the adherence onto the substrate and warpage of the coated film, which are the most serious issues with standard UV-curable coatings based on multiacrylates [43].

4.2. For metal/metal alloy base

PVD coating has the potential to improve the attributes of metals and metal alloys in a variety of ways. For starters, it can improve high-temperature resistance by decreasing substrate oxidation [44]. Second, by regulating the stress distribution inside the coating, PVD coatings can increase the cutting performance and longevity of hard alloy cutting blades. Third, electrophoretic deposition (EPD) coatings applied via PVD can improve magnesium and related alloys' corrosion resistance, biocompatibility, wear resistance, and mechanical qualities [45]. Finally, when compared to uncoated tools, nanostructured TiN/CrN coatings applied via PVD can greatly boost the longevity of metalworking tools such as cutters and drills [46].

A thick layer of UV primer base coat can increase the adhesion between UV ink layers, increase the application range of a bottom coating, and boost the performance of the combined bottom, UV ink, and top coating to form a final coating that has improved the properties of metal or metal alloys. On the other hand, a thick layer of PVD metal coating can also improve the properties of metal or metal alloys by enhancing corrosion resistance (**Fig. 9**), abrasion during forming, phosphatinga nd paint adhesion.

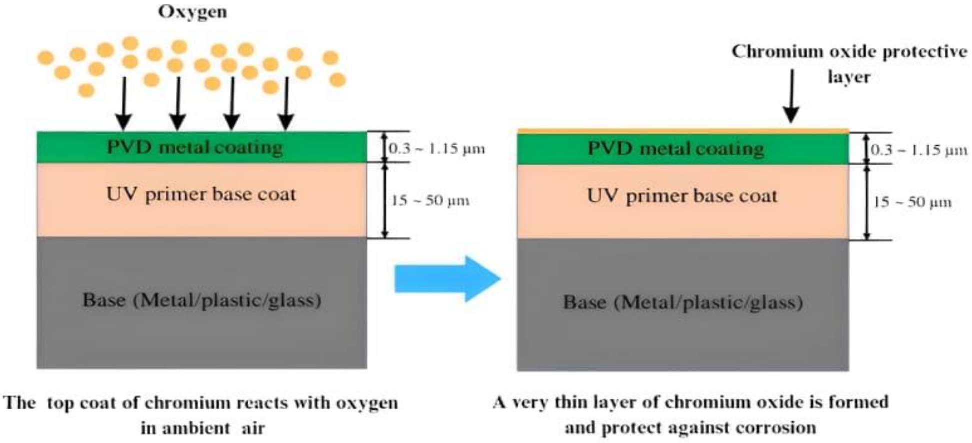

Figure 9. Corrosion resistance mechanism of superchrome PVD coating

The primary defense mechanism is the development of a thick layer of PVD chromium top coat on the surface of the substrate.By serving as a physical barrier, this layer successfully protects the metal underneath from corrosive conditions. This passive layer is highly impermeable to aggressive ions and prevents further oxidation of the underlying metal.

It has been demonstrated that adding elements like Al, Ti, and B to PVD coatings enhances their corrosion resistance and wear resistance [47]. When applied to a range of metallic substrates for different industrial uses, the usage of PVD coatings, especially CrN coatings, has demonstrated improved wear and corrosion properties [48]. In addition, utilizing multilayer coatings with various plasma nitride layers has been designed to further improve corrosion and wear resistance [49].

5. Discussions

SuperChrome PVD Coating does not negatively impact the environment and gives a rich, deep Cr (VI) appearance [8]. Paint top coat is not necessary for this coating procedure. Moveover, Trivalent chrome plating has also replaced traditional chrome plating [50]. The environmental and health risks associated with hexavalent chromium ions have drawn attention to trivalent chromium plating as a more sustainable option [51]. However, it's crucial to remember that there's research associating lung cancer risk to trivalent chromium exposure [52]. Despite the possible health hazards, the increased awareness of environmental and health issues is driving interest in trivalent chromium baths as a substitute for the extremely hazardous hexavalent chromium baths [53]. Numerous difficulties arise when using trivalent chromium plating, especially when trying to retain the material's aesthetic appeal and achieve exceptional corrosion resistance [54, 55]. There are questions regarding the longevity of trivalent chromium coatings because it has been seen that they crack and spall, particularly after extended conversion treatment [51]. Furthermore, high trivalent chromium levels can cause visible stains, which distract from the material's aesthetic appeal [55].

The Black Nickel-Chromium plating process is a further chrome plating method that has gained popularity because of its distinct benefits, which include good wear resistance, corrosion resistance, lubricity, acceptable ductility, electric conduction, and high hardness [56]. Nevertheless, this plating procedure has many drawbacks and issues. Due to strict laws that have been implemented to phase out hexavalent chromium or limit its usage in the plating sector, regulatory, technological, and economic challenges have been investigated [57]. The hazards to the environment and human health that come with nickel and chromium exposure highlight the limitations of black nickel-chromium plating. For example, a study on the health hazards connected with eating cow meat in an urban Nigerian population discovered that the concentrations of nickel were below the allowable limit, suggesting that there may be health problems related to exposure to these metals [58].

The plasma-assisted chemical vapor deposition (PACVD) process is another method of chrome plating that has been extensively used in many industries, including the manufacture of semiconductors, because it can deposit thin films with desired properties at low temperatures and high deposition rates [59]. PACVD plating does have certain benefits, but it also has some drawbacks and difficulties. As shown in the case of BN films, one of the main drawbacks of PACVD plating is the possibility of reliability problems including film peeling off the substrate and cracking [60].

When it comes to chromium or alloys containing chromium, laser cladding is a technology that shows promise for producing coatings that are resistant to wear. Nevertheless, there are some restrictions on the process itself. A notable obstacle is the generation of residual stress as a result of thermal shrinkage, rapid cooling, and variations in the substrate's and cladding material's coefficients of thermal expansion [61]. Furthermore, there are particular restrictions and difficulties when using laser cladding on magnesium alloys [62]. Moreover, it has been demonstrated that the high expense of purchasing laser equipment and the inefficiency of laser sources are barriers to coating application, repair, and quick prototyping [63].

High-Density Chrome Plating (HDCP) has been widely used in various industrial applications due to its desirable properties such as low friction, chemical inertness, high surface hardness, and high wear resistance [64]. Nonetheless, research has shown that effluent from the chrome plating industry contains hazardous materials, including significant quantities of F-53B, a Chinese substitute for PFOS, raising concerns about HDCP's potential effects on the environment [65]. Research has demonstrated that there are erratic correlations between HDCP and lipid profiles, such as total cholesterol, HDL-C, and low-density lipoprotein cholesterol (LDL-C) [66-67]. Moreover, Observed between HDCP and triglycerides, apolipoprotein A1, and high-density lipoprotein cholesterol [67]. These results emphasize that HDCP may include some health hazards thus it's essential to look into coating solutions that don't have similar concerns.

HVOF-sprayed coatings, demonstrate promise as a replacement for traditional chrome plating processes, providing good corrosion resistance and highly adherent coatings with low porosity [10]. However, one of the key difficulties of thermal spraying, including HVOF, is that it is a line-of-sight application technique, limiting its use in specific settings [16]. Moreover, decarburization of WC into W2C, W3C, and even metallic W phases can degrade coating characteristics, minimizing its application to temperatures below 450-530°C [12]. The main limitation of HVOF compared to other thermal spray techniques is the ability to accelerate the melted powder particles of the feedstock material at a relatively large velocity, which permits the formation of a fairly dense microstructure [20].

Pulsed Electrodeposition (PED) Chrome plating have been a subject of interest in the field of materials science and electrochemistry. The technique involves the repeated switching on and off of power with specific time intervals, and it has been successfully applied to deposit microcrystalline chromium from certain baths [68]. However, some parameters, like pH, bath temperature, and the presence of organic additives, can restrict the efficiency of PED for chrome plating [69].

On the other hand, a number of significant advantages make superchrome PVD an environmentally preferable option to conventional chrome plating:

- **No Discharge of Chromium:** Conventional chrome plating involves the use of hexavalent chromium liquid baths, which have the potential to leak or evaporate and contaminate the air, water, and soil. By entirely isolating the process and preventing any chromium discharge, Superchrome PVD, in contrast, operates within a vacuum chamber. This removes the possibility of contaminating the environment and exposing workers to hazardous compounds.

- **A Wide Layer of UV Primer Coat for Enhanced Adhesion:** The Superchrome PVD method consists of two steps. Applying a wide range of UV-cured primer coat in the initial phase greatly improves the adhesion between the base metal and the top PVD chrome layer. There is less chance of the top layer breaking or flaking as a result to this strong bond.

- **Reduces Waste and Emissions:** Superchrome's PVD process produces less waste than electroplating. There aren't any hazardous liquid byproducts or sludge that need to be disposed of separately. Furthermore, the vacuum atmosphere reduces emissions of volatile organic compounds (VOCs) and air pollution.

- **Energy Efficiency:** Compared to conventional chrome plating, superchrome PVD operates at lower temperatures, which means that less energy is used and less carbon is left behind.

- **Durable and Long-lasting:** Superchrome PVD coatings provide exceptional defense against wear, abrasion, and corrosion. Longer product lifespans result in fewer replacements being needed and the related environmental effects from manufacturing new products.

- **Recyclability:** The underlying substrate is unaffected and can be recycled at the end of its life cycle because of the thin film nature of the PVD coating. This reduces waste even further and encourages resource conservation.

- **Versatility:** Superchrome PVD can be used on a variety of materials, including plastics, which are frequently unsuitable for chrome plating using conventional techniques. This broadens the range of uses for which environmental friendly coating solutions are offered.

- **Cost effective:** PVD price has been shown to be up to 15% less expensive than electroplating when comparing the true cost per item produced between the two processes. These estimates take into account a number of variables, including the capital cost of the processing equipment, manpower, consumables, utilities, floor space, effluent disposal and management, and product scrap [8].

6. Conclusion

Superchrome PVD shines not only as a mirror-like finish but also as a symbol of environmental advancement. plastic substrates can have a chrome-like finish without the usage of hazardous hexavalent chromium compounds. It is made up of a chromium PVD layer that replaces the requirement for a top coat and a UV-cured base coat. Compared to conventional chrome plating, superchrome PVD offers a number of benefits, including safety, corrosion resistance, environmental friendliness, adaptability, and versatility in design. Superchrome PVD is a viable substitute for decorative applications in a variety of industries, particularly the automotive sector, where it can satisfy demanding standards for both performance and appearance.

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