Decorative and Functional Finishes by Low Temperature Arc Vapor Deposition

Klaus Brondum, Vapor Technologies, Inc., Longmont, Colorado ,80503, USA

Abstract

The process of Low Temperature Arc Vapor Deposition (LTAVD) occurs in a highly controlled vacuum environment. It is used to deposit adherent and dense metal and ceramic type coatings on suitable substrates. LTAVD operates at both high and low temperatures, which enables the coating of traditional metal substrates, as well as, heat-sensitive substrates such as plastics and zinc. LTAVD coatings have both durable and cosmetic characteristics that make it possible to produce finishes not achievable by current methods alone. This paper addresses performance comparisons for a number of nickel chrome coating stacks for decorative and functional use based on combinations of plating and PVD processing.

Klaus Brondum,
Vapor Technologies, Inc.,
6400 Dry Creek Pkwy,
Longmont, Colorado ,80503, USA
Phone 303 652 8500
Fax 303 652 8600
E-mail kbrondum@vaportech.com
Web www.vaportech.com

Introduction

Conventional processing of parts for cosmetic coating begins with a part formed from a base material, followed by a surface refinement that may take the form of polishing, brushing or grid blasting followed by a layer of nickel chrome plating. High-end products often add a Physical Vapor Deposition (PVD) top coat that simulates the appearance of metallic finishes ranging from stainless steel, bronze, brass over gold and a range of grays. These coatings are deposited directly onto the chrome plated surface. Popular coatings incorporate Zr, Ti and their alloys, nitrides, carbides and oxides. The success of these coatings is based on their ability to achieve the appearance desired by the customer and their superior durability. A schematic process flow describing the steps for PVD-coated part preparation is shown in Figure 1.

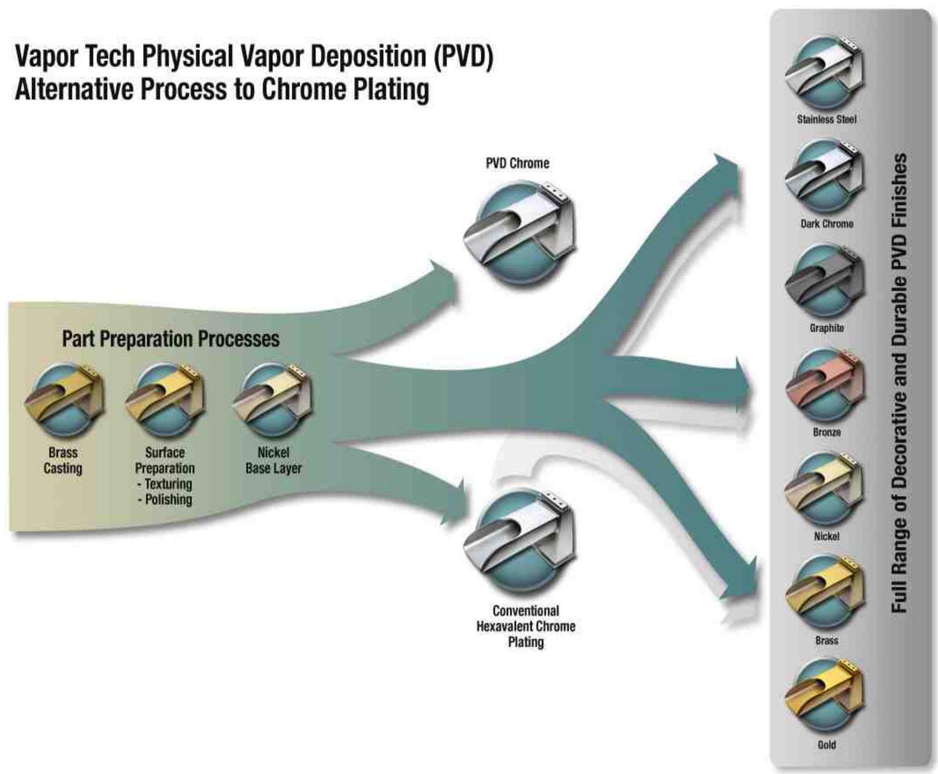

Figure 1. *Schematic process flow for vertically integrated plating and PVD resulting in a palette of appearances.*

It is of highest importance that all of the layers of the coating stack are designed to meet the part's requirements from the points of view of corrosion, wear and cosmetic appearance. The PVD process supports the creation of very sophisticated coating stacks. In fact, most standard PVD coating stacks have, but are not limited to, up to 5 distinct layers. These layers are chosen to address the overall performance goals required for any given application.

The chrome part of the coating stack is typically deposited in-line with nickel plating and is considered far more cost effective than the alternative PVD-based Cr processing. While this is true historically, interest in PVD Cr processing has gained significant momentum due to general uncertainty about the future for hex chrome based plating chemistry. Legislative changes as well as awareness among customers and changing preferences affect this attitude.

PVD processing is accomplished in a plasma created from a mixture of evaporated metal, metal ions and gasses such as argon, nitrogen, oxygen and methane. While a number of technologies for metal evaporation and ionization are commercially available, the technology utilizing centrally mounted target has proven superior for a number of reasons including, high throughput, high and low temperature processing, general reliability and versatility. A schematic of the LTAVD equipment is shown in Figure 2.

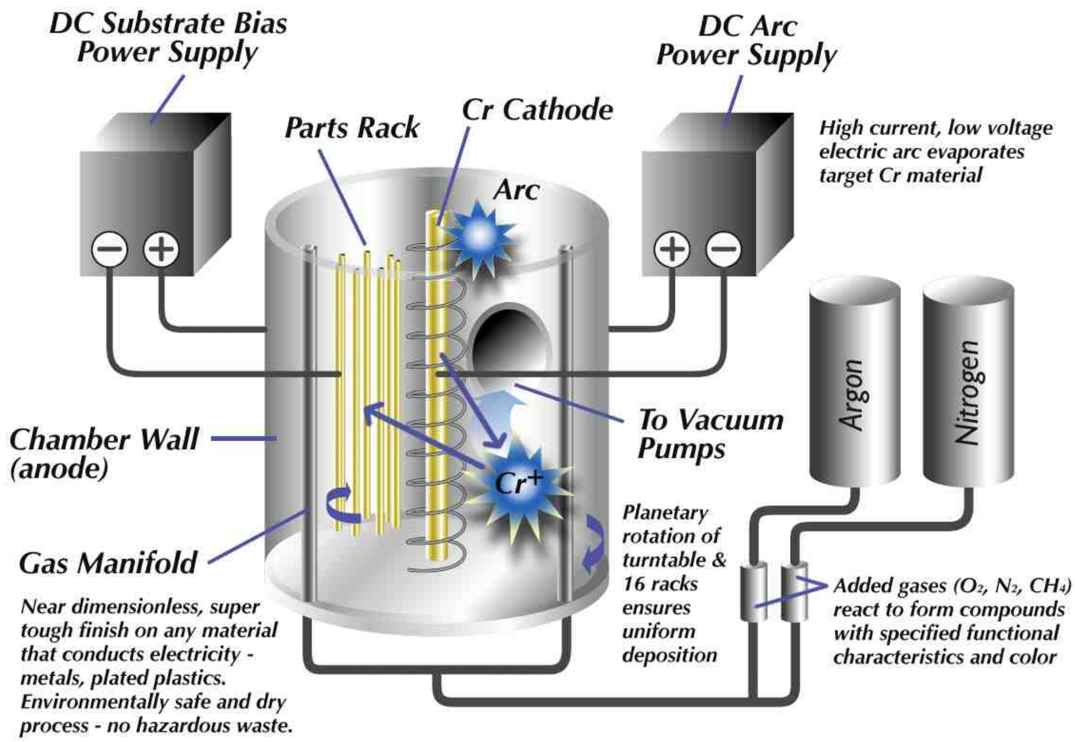

Figure 2. *Schematic VT 1500 LTAVD chamber*

Experimental

Carbon steel (ASTM A36) and brass coupons were plated in a conventional plating line which was used to apply three coating stacks consisting of varying nickel base coats and a top coat of chrome plated from hexavalent chrome bath (Hex Cr, Cr plating). The plating was completed by an outside vendor. A total of 140, 10 x 10 cm coupons were plated in a so-called sandwich configuration with a fixed spacing of 10 mm allowing for determination of throwing and covering power (TP_{10}, CP_{10}) as described previously[1]. Two thirds of the chrome plated plates were stripped in an anodic alkaline solution and then re-coated in a VT1500 LTAVD chamber equipped with centrally-mounted chromium target applying chromium (Cr) and chromium nitride (CrN).

CASS performance was performed according to ASTM B-368 and evaluated according to ASTM B-537-70. An elementary profile was established via Glow Discharge Spectroscopy (GDS) LECO Model SA2000, color characterized in L*a*b* space and color difference in terms of ΔE using Minolta CM 508d, D65 light source, 10^o observation angle. Abrasion resistance was established via Taber model 5150 abrader using CS 10 wheel and 1000 g loads and inspected visually for coating break through.
Hardness and modulus profiles were established via nano indentation (CSEM) using Rockwell C indenter in indentation sweeps ranging from 20-300 mN.

Results and discussion

Plating stack

The plating stack was targeted at a total nickel thickness of 25 microns with a top coat of 0.25 microns of Cr. This plating stack is appropriate for service condition 3 (severe) as specified in ASTM B 456. The coating stacks are summarized in Table 1.

Table 1 *Designed experiment matrix. Coating stack*

Ni\Cr	Hex Cr	PVD Cr	PVD CrN
Bright Nickel	x	xx	xx
Duplex Nickel	x	xx	xx
Micro Porous Nickel	x	xx	xx

Note *x, original Hex Cr plating, xx, top re-coat applied via PVD*

A typical duplex plating stack would look like this in GDS:

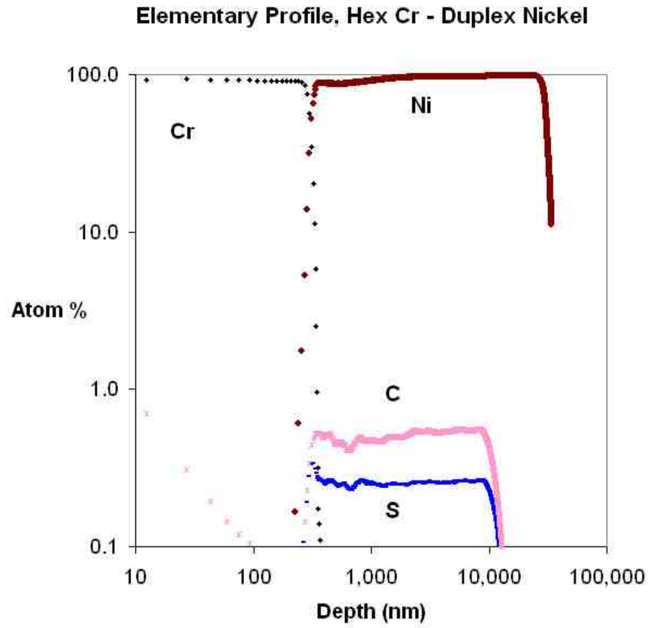

Figure 3. *Elementary profile of chrome plated duplex nickel. Double logarithmic scale. Notice the top chrome layer (250nm) followed by a high sulfur content in the upper half of the coating stack corresponding to a bright nickel layer. The deeper portion of the nickel layer show carbon and sulfur levels below 0.1 atom percent characteristic of a matte nickel.*

Two thirds of the samples were stripped of chrome and recoated. An example of a CrN coated sample is shown in Figure 4. The outermost chrome layer determines color while the innermost serves adhesion purposes.

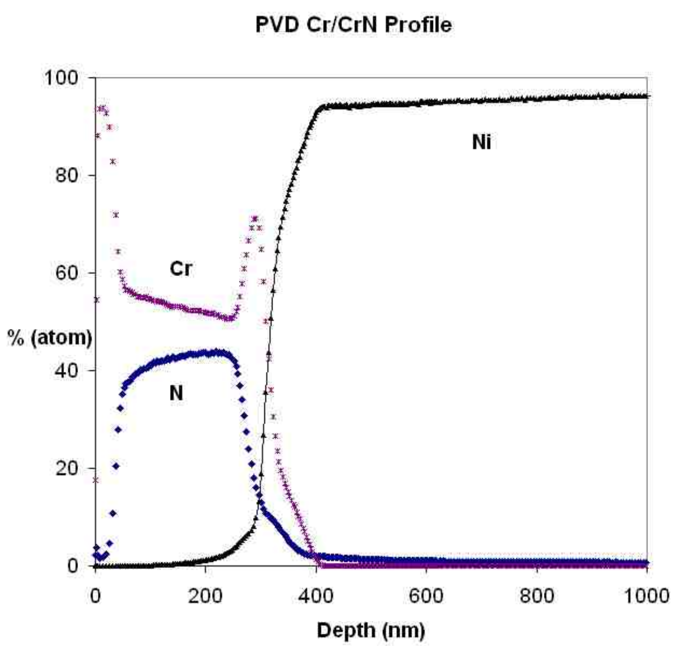

Figure 4. *Detail from elementary profile of a CrN coated sample. Notice CrN sandwiched between two pure layers of Cr.*

Corrosion performance

According to ASTM B 456, combinations of nickel thickness and thin chrome top layers improve corrosion resistance as function of increasing nickel thickness. Corrosion resistance can be improved further if one or more of the following strategies are pursued:

1. Start out with a noble nickel layer (semi bright nickel) followed by a less noble nickel (bright nickel) in combination - called duplex nickel - ending up with thin chrome top layer.
2. Start out with a bright nickel layer followed by a thin micro porous nickel layer, ending up with thin chrome top layer (micro porous).
3. Increase the number of cracks in any given chrome layer (micro cracked).

In addition, a chrome layer produced via a hex chrome process will have a somewhat improved corrosion resistance on uncoated surfaces due to a chromate conversion coating effect.

Table 2 below, shows the averaged corrosion performance of 45 nickel chrome stacks on steel basis material after 24, 48 and 96 hours. It should be noted that, given a pass criteria of rating 9 (< 0.1% attacked surface area), most of the samples pass 24 hour CASS test.

Table 2. *CASS performance*

CASS 24 hours

Ni\Cr	Hex Cr	PVD Cr	PVD CrN	Totals
Bright Nickel	9.2	8.6	9.0	8.9
Duplex Nickel	8.4	9.4	9.8	9.2
Micro Porous Nickel	8.8	10.0	9.2	9.3
Totals	8.8	9.3	9.3	9.2

CASS 48 Hours

Ni\Cr	Hex Cr	PVD Cr	PVD CrN	Totals
Bright Nickel	8.0	6.4	7.8	7.4
Duplex Nickel	8.0	8.6	9.4	8.7
Micro Porous Nickel	7.2	9.0	8.0	8.1
Totals	7.7	8.0	8.4	8.0

CASS 96 Hours

Ni\Cr	Hex Cr	PVD Cr	PVD CrN	Totals
Bright Nickel	7.0	5.8	6.6	6.5
Duplex Nickel	7.0	7.8	8.8	7.9
Micro Porous Nickel	6.0	8.2	6.4	6.9
Totals	6.7	7.3	7.3	7.1

Note. *The ASTM B-537-70 standard outlines a rating scale from 1 to 10. 10, 9, 8 being no corrosion, 0.1% and 0.25% corroded area respectively.*

The samples showed corrosion as result of pinhole defects bleeding red rust from steel nickel interface. Other types, like nickel corrosion, were not observed.

Duplex and Micro Porous nickel coatings show a beneficial effect on small diameter pinhole corrosion and move the corrosion site away from steel - nickel interface. Therefore, the 24 hour rating is rather a measure of large pinhole density.

If the bar is lowered to a rating 8 (0.25% attacked surface) the superior performance of the duplex and micro porous nickel starts to show. In all instances, the PVD Cr and PVD CrN top coats show CASS performance comparable to Hex Cr - if not better.

Color Results

Hex Cr has a very desirable color as measured by customer preference. Its color is described as slightly blue. The small color shift between Hex chrome plated and PVD Cr coated shown in Figure 5 may not appear different to a trained observer before ΔE exceeds 2.

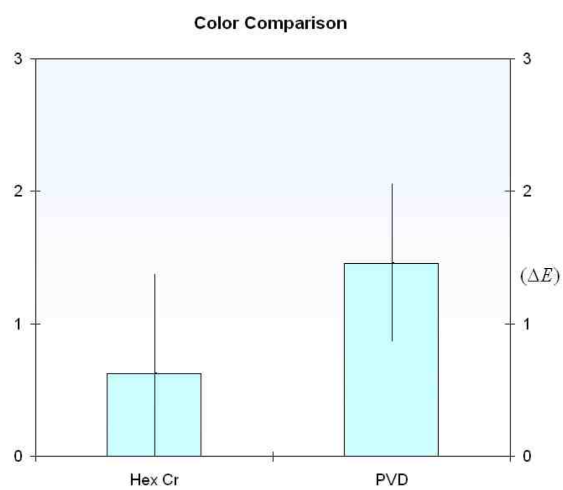

Figure 5. *Comparison of color difference using Hex Cr color reference as result of plating and PVD processing. A trained observed can distinguish a ΔE of no less than 2. The vertical line represents 2 standard deviations*

Throwing power, covering power

Throwing and covering power determines the complexity of parts geometries that can be coated and the density with which they can be mounted on racks. Table 3 shows values for plating and PVD processes obtained in this study using parallel plate approach.

Table 3. *Throwing power and covering power of nickel and chromium based coatings*

	Electroplating		PVD	
	Bright Ni	Hex Cr	Cr	CrN
TP	0.2	<< 0.1	0.2	0.1
CP	>3.5	~0.2	~2	~1
Thickness (µm)	25	0.25	0.25	0.25

The Hex chrome plating process is notorious for both poor throwing power and covering power, with both declining as impurities build up in the plating tank. Hex chrome plating of recessed areas calls for spacious rack mounting and in some cases secondary anodes adapted for the purpose. PVD processing of pure metals like Cr, Zr, Ti or their alloys, in general have TP and CP comparable to bright nickel and far better than Hex Cr. Reacted coatings, such as nitrides, carbides and oxides show intermediate values. While Hex chrome plating is the limiting factor for rack part spacing density, this is not the case for the PVD alternatives.

Hardness and elasticity

Hardness and elastic characteristics of the different top coatings are shown figures 6.

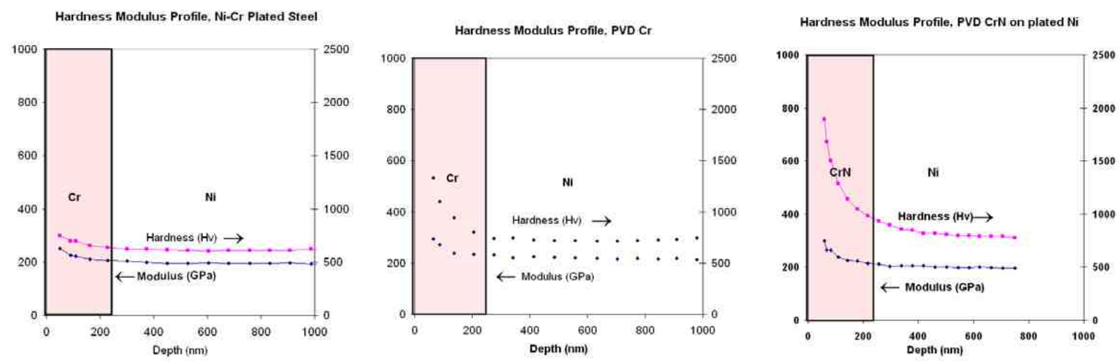

Figure 6*. Hardness and modulus profiles of left)Hex Cr plated bright nickel, center)PVD Cr coated bright nickel, right) PVD CrN coated bright nickel as found in nano hardness testing. Left scale modulus (MPa), right scale Vickers hardness (Hv)*

The hardness of a coating is determined by the penetration depth of a stylus. As a rule of thumb, only measurements from the upper 5-10% of the layer thickness represent the layer hardness and modulus, while the remainder represents a weighted average of the two layers. Our measurements show Cr hardness 800-1400Hv and CrN hardness up to 2200Hv. Bright nickel is about 800Hv. The corresponding moduli are between 250-300 MPa for Cr and CrN and 200 MPa for Ni.

Abrasion resistance.

It should be appreciated that even though very high hardness and modulus values can be found in literature for any given coating, in most cases characteristics like wear and friction performance under specified load conditions constitute the desired performance. These attributes are dictated by the characteristics of a combination of the top surface, its supporting layers and the substrate. The Taber abrasion test was developed to characterize wear performance of organic coatings and is here adopted to visualize wear performance of Cr and CrN surfaces. Wear rates of organic coatings are several orders of magnitude higher than for metallic coatings and ceramic coatings performs even better.

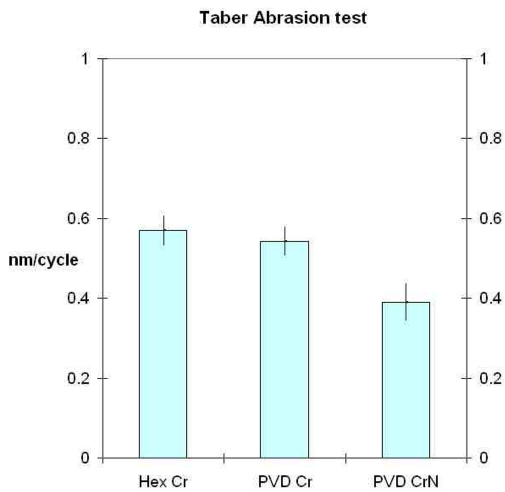

Figure 7. *Taber abrasion presented as thickness loss per cycle using CS10 wheel and 1 kg load. The vertical line represents 2 standard deviations.*

Figure 7 shows that while the Hex Cr and PVD Cr appear to have equivalent abrasion rates, the wear on PVD CrN is about 30% lower. This translates to a longer service life. It should be obvious that even lower abrasion rates can be achieved by PVD coating stack modifications without sacrificing the appearance or corrosion performance characteristics.

Conclusions

This investigation aims at comparing nickel chrome plating obtained from conventional plating processing and PVD coating stacks on steel via PVD processing. The findings show:

- Color of Cr PVD based coatings is indistinguishable from Hex chrome based plating.
- Corrosion test results indicate that Cr PVD top coats perform comparably or better than Hex Cr based platings.
- Throwing and covering power of PVD processing is superior to Hex Cr plating.
- PVD processing allows for tailoring of coating stacks to accommodate improved wear performance without sacrificing cosmetic and corrosion performance.

References

Throwing- and Covering-Power Assessment. PVD Application. *Klaus Brondum*, Proceedings SVC, 2003

