# Decorative PVD coatings as an environmentally clean alternative to chrome plating

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***Abstract.*** *The objective of this work is to conduct applied research and development to demonstrate that metal or ceramic coatings deposited by Physical Vapor Deposition (PVD) are equivalent or superior in performance and are a cost-effective alternative to chrome plating in decorative applications. Chromium plating is commercially used to produce wear-resistant and decorative coatings, but the plating bath contains hexavalent chromium, which has adverse health and environmental effects. The present study describes and compares the mechanical and tribological properties of TiN, AlTiN, ZrN and ZrCN coatings deposited by CAPVD (cathodic arc plasma physical vapor deposition), on nickel plated aluminium substrates. The properties of the above mentioned PVD coatings have been compared with the properties of conventional chromium plating.*

**Keywords**: *Physical vapour deposition, Decorative coating, Mechanical properties, Tribology, Adhesion.*

## 1. INTRODUCTION

The increasing environmental and worker safety pressures on chrome plating are leading many industries to adopt alternatives. Chromium plating is commercially used to produce wear-resistant and decorative coatings [1, 2], but the plating bath contains hexavalent chromium and produces large volumes of chrome-contaminated toxic waste, which have adverse health and environmental effects. For this reason, the use of hexavalent chromium is being limited.

It has not been until the last decade that strong activity aimed towards systematically replacing this “dirty” technology with high performance dry coating “clean” methods. Engineers faced the difficult problem of finding an appropriate alternative coating technology, which would offer quality and cost-effective production coatings according to the available standard in each case.

Among the many available technologies the processes that are most widely viewed as being capable of replacing chrome plating are the physical vapour deposition (PVD) and chemical vapour deposition (CVD) techniques, which are used to produce functional hard coatings or decorative thin films [3, 4].

Deposited PVD coatings can have a wide colour range, for example, titanium nitride (TiN) is gold coloured, and titanium carbonitride ($TiC_xN_y$) can vary in colour from gold to purple to black depending on the composition. Zirconium nitride (ZrN) has the colour of brass and is much more wear and scratch resistant than brass. Decorative/wear coatings are used on door hardware, plumbing fixtures, fashion items, marine hardware, and other such applications.

## 2. EXPERIMENTAL DETAILS

### A. Coating deposition

The coatings studied in this research were TiN, TiAlN, ZrN and ZrCN deposited by PVD/CAPVD (cathodic arc plasma physical vapour deposition) on a nickel plated aluminium 6063 substrate with a thickness around 0.5 µm. PVD decorative coatings are by their nature very thin, and do not act as a corrosion barrier. Therefore, the decorative PVD coatings should be applied on top of the corrosion resistant nickel electroplated coating. The properties of the above mentioned PVD coatings have been compared with the properties of conventional chromium plating on a nickel plated aluminium substrate.

Prior to deposition of the PVD coatings all samples were cleaned in a cleaning line composed of a series of ultrasonically agitated aqueous alkali solutions, deionised water baths, and drying. Finally the nickel plated aluminium substrates were cleaned in alcohol using ultrasonic agitation.

A compact MIDAS 450 system (Millennium Coatings S.L.) equipped with three advanced controlled arc cathodes in a chamber volume of 1 $m^3$ was used for coating deposition. A photograph of the inside of typical equipment used to deposit the PVD coatings is shown in Fig.1 and the deposition conditions are summarized in Table 1. The arc is initiated by a striker at one end of the cathode. The arc movement is directed by the polarity of the cathode and a magnetic field generated by a water-cooled coil surrounding the cathode.

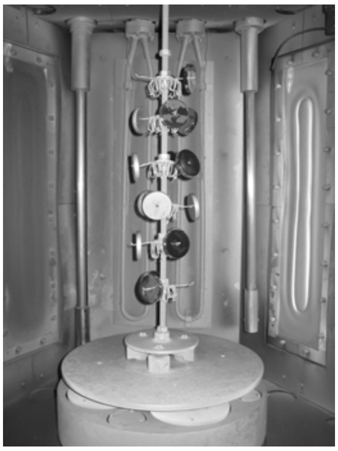

Figure 1. Photograph of the inside of the cathodic arc plasma physical vapour deposition system used to deposit PVD coatings.

Previous to the coating deposition step, the substrate was metal ion pre-treated (metal ion etching), which results in a better coating adhesion [5]. In the surface pre-treatment step, metal ions generated from an arc discharge sustained on one of the targets are accelerated towards the substrate due to the applied high bias voltage (-350 V), which produces surface etching and implantation. The duration of the metal ion etching step was shortened to 4-5 min. The subsequent coating was deposited by reactive cathodic arc plasma physical vapour deposition using pure titanium, pure zirconium and titanium-aluminium (Ti50Al50) rectangular targets and nitrogen, acetylene and argon atmospheres (see Table 1). In all cases a first deposition of a very thin metallic interface layer for adhesion promotion was performed. The coating deposition temperature was maintained in the range 250-300ºC, which prevented softening of the nickel plated aluminium substrates. A negative substrate bias of - 30 V was applied to the racks in order to control the residual stress, colour and uniformity of the films. During the coating process all the relevant process parameters were continuously monitored and controlled by an automatic computer control system in order to obtain an excellent coating quality and reproducibility. The substrate bias, arc source current and flow of argon and reactive gases could affect the amount of nitrogen or carbo-nitrogen incorporated into the film and thus the final colour of the coating.

Table 1. Technological parameters of PVD deposition

|  | TiN | AlTiN | ZrN | ZrCN |
|---|---|---|---|---|
| Cathode | Pure Ti | Al$_{50}$Ti50 | Pure Zr | Pure Zr |
| Cathode Voltage (V) | 39 | 44 | 42 | 40 |
| Cathode current (A) | 150 | 130 | 160 | 150 |
| Substrate bias voltage (V) | - 30 | - 30 | - 30 | - 30 |
| Ar flow rate (sccm) | 25 | 20 | 23 | 21 |
| $N_2$ flow rate (sccm) | 83 | 70 | 77 | 89 |
| $C_2H_2$ flow rate (sccm) | --- | --- | --- | 7 |
| Background pressure (torr) | $7.6\ 10^{-5}$ | $7.1\ 10^{-5}$ | $8.3\ 10^{-5}$ | $7.5\ 10^{-5}$ |
| Operational pressure (torr) | $8.2\ 10^{-3}$ | $8.2\ 10^{-3}$ | $8.3\ 10^{-3}$ | $8.2\ 10^{-3}$ |
| Coating colour | Golden yellow | Grey anthracite | Brass coloured | Golden coloured |

B. Coating characterisation

The coating hardness was determined with an ultra-microhardness testing system, capable of measuring force versus displacement, using a Vickers diamond indentor (DIN 50359). On every sample the dynamic hardness measurements were carried out with a maximum applied load of 20 mN. Each average value was calculated from 25 different measurements, the anomalous values results from coating defects were discarded. Surface roughness measurements were performed with a Taylor-Hobson rugosimeter using a 0.8 mm cut-off.

Tribological evaluation of coated substrates was performed using a pin on disc tribometer, according to ASTM wear testing standard (G-99). The tests were carried out at the same linear speed (0.10 m/s) under dry and lubricated conditions and with an applied load of 2 and 10 N respectively. When testing was completed, the amount of material lost was evaluated by measuring the cross sectional area of the wear tracks using a rugosimeter–perfilometer. The average cross-section area of a wear track was calculated from at least eight measurements in each specimen. The wear volume and specific wear rate (SWR) were calculated according to the classic wear theory [6]. The friction coefficient was plotted as a function of the number of laps in the test. At least three different tests were conducted for each set of testing condition and material.

Two techniques were employed for adhesion evaluation of the coatings. Indentation tests using a standard Vickers hardness tester were primarily used to ensure the adhesion effectiveness after the substrate preparation stage, whereas scratch tests were performed to provide some quantitative information on the coating-substrate interface and to compare the adhesion/cohesion failure of different coatings. The scratch length was 5 mm and the applied load was varied between 5 and 50 N with a loading rate of 37.5 $N.min^{-1}$. Three scratch tests were performed to obtain the mean values. After the tests the coatings were evaluated using optical microscopy, evaluating at which critical load severe cracking and flaking started to occur (cohesive or adhesive failure).

## 3. RESULTS AND DISCUSSION

A. Mechanical properties

Micro-indentation experiments provide values of the applied load and the penetration depth for both loading and unloading processes. Ultra-microhardness values calculated from this method correspond to hardness values under load (Universal Hardness, HU) and to hardness determined after removal of the applied load (Plastic Hardness, Hplas). The unloading curve allowed by obtaining the elastic recovery and plastic deformation of the coating, additionally an estimated Young's modulus (E), was also calculated. Fig. 2 shows the typical load-displacement curves from microindentation experiments using a maximum applied load of 20 mN on the studied coatings.

Table 2 shows the average results of the micro-indentation tests and roughness parameters. The hardness values obtained for the AlTiN coating were the highest among the PVD coatings under study. The hardness of the TiN, ZrN and ZrCN coatings were quite close to each other, and hence the differences between them could be considered to be within the standard deviation interval. Furthermore, all studied PVD coatings presented higher hardness and elastic properties than conventional chromium plating.

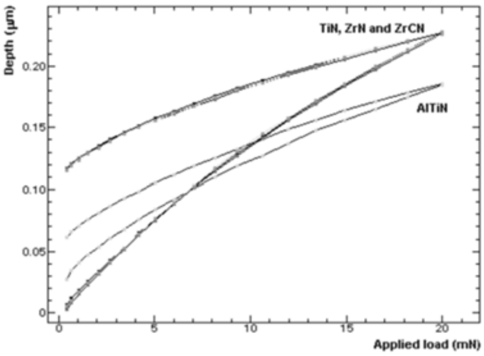

Figure 2. Loading and unloading curves for PVD coatings deposited onto nickel plated aluminium substrates (maximum applied load: 20 mN).

The measured values are lower than reported values obtained from ultra-microindentation or nanoindentation studies on coatings produced by arc evaporation on hard substrates [7-9]. This aspect can be explained by the influence the substrate has on the coating mechanical properties. To measure the coating hardness and effective Young's modulus without the influence of the substrate mechanical properties, the load should be set at a value that causes a penetration depth less than 10% of the coating thickness. The ultra-microindentation tests were carried out with a maximum load of 20 mN over deposited coatings with a nickel plated aluminium substrate, and this creating a penetration depth of around 0.2 µm, which is clearly higher than 10% of the film thickness. The use of lighter loads is not possible, because higher value dispersion is produced due to the superficial roughness effect and the limitations of the ultra-microhardness equipment employed. Nevertheless, the measured hardness values can be used for this comparative study.

Table 2. Mechanical and tribological properties and coating adhesion.

| | Chrom. plating | TiN | AlTiN | ZrN | ZrCN |
|---|---|---|---|---|---|
| HU (GPa) | 5.4 | 7.9 | 10.7 | 7.8 | 7.9 |
| Hplast (GPa) | 8.4 | 16.1 | 29.2 | 15.7 | 16.1 |
| $E/(1-\upsilon^2)$ GPa | 183 | 212 | 260 | 211 | 208 |
| Elastic rec. (%) | 32 | 46 | 77 | 46 | 47 |
| Ra | 0.009 | 0.012 | 0.024 | 0.013 | 0.013 |
| Friction coefficient[1] | 0.08 | 0.09 | 0.05 | 0.08 | 0.08 |
| Specific Wear Rate[1] ($m^3/m.N$ $x10^{-16}$) | 4,24 | 1,1 | 5,27 | 1,27 | 0,44 |
| Cycles $\mu \approx 0.6$ value[2] | 90 | 140 | 120 | 240 | 220 |
| Critical load failure ($L_c$) (Scratch test) (N) | 9 | 15 | 11 | 25 | 23 |

B. Tribological properties

Table 2 only shows the tribological properties of the studied coatings under lubricated environment. The pin on disc tests performed in dry conditions involves a drastic coating detachment after few cycles. The studied coatings exhibited a similar friction coefficient, during the initial test stages (i.e. $\tilde{\mu} \approx 0.12$), however the friction coefficient value increased with test duration, presumably due to wear or detachment of the coating. Table 2 also gives the number of laps during the test in which the friction coefficient exceeded 0.6. This value corresponds with the nickel underlayer and indicates the total elimination or detachment of the PVD coating.

The analysis of the wear tracks reveals that the increase of the friction coefficient observed during the test stem from the loss of adherence rather than from the coating abrasive wear. This is due to the large difference in hardness and elastic recovery between the substrate and the coatings. The large difference causes a larger plastic deformation in the substrate with respect to the coating and consequently produces an increase of the film stress, which results in coating fracture. Fig. 3 shows the wear track produced by the sliding of a WC-6%Co ball onto the ZrCN coating during the Pin on disc tests after 30000 laps, with an applied load of 10 N under lubricated conditions, where the wear process is observed to occur by the partial coating detachment. The wear process accelerates in pin on disc tests performed under dry conditions.

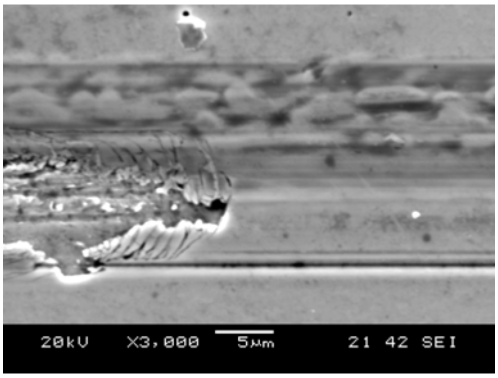

Figure 3. Wear track of ZrCN coating in Pin on disc test after 30000 laps, with an applied load of 10 N under lubricated conditions.

After the Pin on disc experiments the coating specific wear rate (see Table 2) was calculated from the measurement of the wear track area, according to ASTM wear testing standard G-99. Despite having the highest hardness, the AlTiN coating presents a high specific wear rate, probably as a consequence of residual stresses within the coating that lead to a higher adherence loss. On the other hand, it can be observed that from the studied PVD coatings, all the ones produced using cathodic arc plasma physical vapour deposition technique, with exception of the AlTiN coating,

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[1] Pin on disc test under lubricated conditions (10 N).

[2] Pin on disc test under dry conditions (2N). Cycles in the test in which friction coefficient exceeded 0.6 value.

have better tribological performance than the conventional chromium plating.

C. Coating adhesion

The critical load, i.e. the normal load at the first coating failure, was found to increase in the following order: conventional chromium plating, AlTiN, TiN, ZrCN and ZrN (see Table 2). In all coatings, the critical load corresponded to semicircular cohesive failures, which are typical for brittle materials (Fig. 4). For loads higher than the critical load the coatings showed large cracks, on both sides of the scratch (Fig. 5).

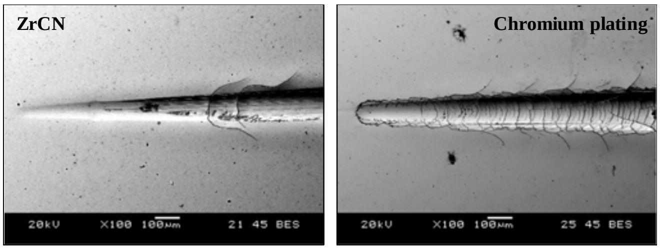

Figure 4. Representative examples of coating failures in scratch test: (a) ZrCN PVD coating and (b) conventional chromium plating.

For all PVD coatings the level of the critical normal load is probably sufficient for many applications. The evaluation of the coating adherence by this method produced satisfactory comparative results, which agree well with the number of laps during the pin on disc test in which the friction coefficient exceeded the 0.6 value.

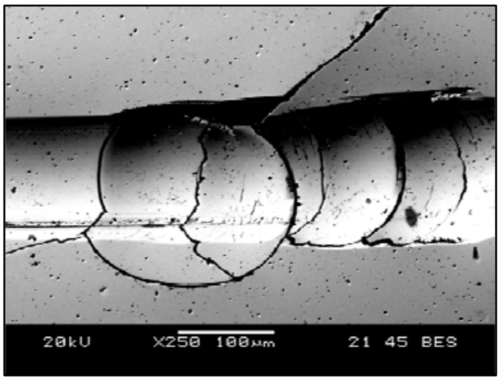

Figure 5. Large cracks observed on ZrN PVD coating in scratch test above the critical load failure ($L_c$).

Furthermore, Fig. 6 shows the optical micrographs of the indentations on the ZrCN PVD coating and conventional chromium plating, which were performed using a Vickers indenter under an applied load of 20 kgf. The adhesion of the coatings can be judged from the radial cracks generated on the edges of the Vickers indentation. The failure modes of the coatings appear similar with the formation of some radial cracks and slight plastic deformation of the coating around the indentations. PVD coatings seem to present a lower radial crack formation indicating that these coatings possess better adhesion to the nickel plated aluminium substrate than conventional chromium plating.

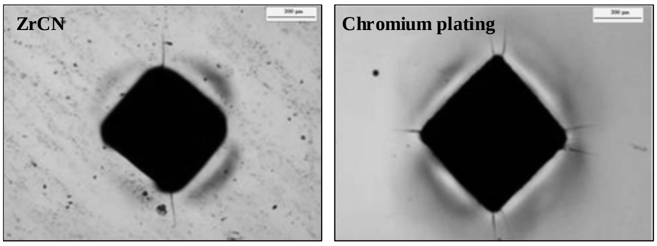

Figure 6. Failure cracks of (a) ZrCN PVD coating and (b) conventional chromium plating after Vickers indentation test.

## 3. CONCLUSIONS

The studied PVD ceramic coatings are better than the traditional chromium electroplated coating due to their superior hardness, adhesion and wear resistance. The PVD coatings can replace the decorative wear resistant coatings; in addition a wide colour range is available.

The introduction of PVD processes as a substitute for chromium plating in decorative applications represents a development towards an environmentally clean technology. Future successful applications of PVD coatings, as alternative to chromium plating, should considered collectively many factors like wear resistance, friction coefficient, costs and environmental issues.

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