A Comparison of Hexavalent & Trivalent Chromium for Use as a Base Material for Decorative PVD Coatings

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Decorative Cr/Ni or Cr/Ni/Cu electroplated layers on brass, zinc or ABS plastic are standard finishes for use on plumbing fixtures, door hardware and automotive trim. The chromium layer is typically plated from a hexavalent chromium bath, but because of environmental concerns, an alternative such as trivalent chromium would be of interest as a replacement. Zirconium nitride (ZrN) deposited by a PVD method on top of these plated layers can offer an attractive brass-like finish and provides excellent wear, corrosion and chemical-resistant properties. This report will present experimental results of a comparison of the performance of ZrN thin films on both types of chromium deposits. In particular, the research will focus on the corrosion and wear resistance of the coating on these different plating stacks.

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INTRODUCTION

The use of decorative coatings deposited by a physical vapor deposition (PVD) method has been embraced by a number of industries within the last ten years, primarily with plumbing fixtures, door hardware and automotive trim. The most common of these PVD coatings in use has been zirconium nitride (ZrN) which imparts a brass-like color and provides exceptional scratch and chemical resistance. These finishes are generally applied to parts made of brass, zinc or ABS plastic which have been plated with standard decorative Cr/Ni or Cr/Ni/Cu layers. While most parts for these applications have been plated with chromium from a hexavalent bath, there has been a recent increase in the occurrence of parts plated with trivalent chromium because of environmental concerns with hexavalent chromium. For this reason it is of interest to understand how these PVD coatings perform on trivalent chromium in comparison to hexavalent chromium.

Corrosion comparisons between hexavalent and trivalent chromium have been reported in a number of papers, particularly those by Snyder[1] on early trivalent baths and more recent electrochemical studies by Lansdell and Farr.[2] Outdoor exposure and accelerated corrosion testing such as CASS and Corrodkote showed little difference in performance of the two chromium deposits. Electrochemical evaluation of the two chromium types told a different story and showed that the hexavalent chromium had superior corrosion resistance. No studies have been found that compare the corrosion performance of PVD coatings on the two electrodeposits.

The mechanical performance of a hard PVD coating is very dependent on the compatibility with the base material it is coated upon. The adhesive strength or interfacial toughness between the coating and the base material is one of the most influential features affecting the ultimate performance of the coating. Studies of the differences in the microstructure between hexavalent and trivalent chromium by Willis and Hammond[3] have shown that there are significant differences in the deposits. Hexavalent chromium is highly crystalline and pore free while trivalent chromium is amorphous and has a microporous structure. Hexavalent chromium deposits also tend to have a higher metallic purity with higher chromium oxide content[4] while trivalent chromium has higher levels of metallic impurities such as iron, copper, nickel, zinc and lead.[5,6] These differences in the deposits lead one to suspect that the compatibility with PVD coatings will differ as well.

Another factor influencing the performance of a hard coating is the base material hardness. The relatively high hardness of chromium plating is one of the reasons these PVD coatings have been so successful on plated parts. Fortunately, there is very little difference in hardness of the two types of chromium deposits. Microhardness measurements of both types of chromium deposits have been reported to have values around 1000 HV measured on thick samples.[4,7]

Hexavalent and trivalent chromium have been deposited onto brass test panels and then coated with ZrN by a cathodic arc PVD process. These samples were evaluated for corrosion resistance using copper-accelerated acetic acid-salt spray (CASS) and electrochemical methods. The hardness of the chromium was measured using nanoindentation and the adhesive strength of the ZrN was measured by a micro-scratch technique. Wear resistance was measured by Taber abrasion.

EXPERIMENTAL

Electrodeposition

The 60/40 brass test coupons were prepared for electroplating by going through a clean soak for 10 minutes at a temperature of 140ºF followed by an electroclean for 1 minute at 20 A/ft^2. The coupons were then etched in a 10% H_2SO_4 acid dip. Bright nickel was deposited at 30 A/ft^2 for 20 minutes for a thickness of 10µm (0.0004"). The hexavalent chromium coupons were plated at 175 A/ft^2 and 115ºF for 3 minutes for a 0.25µm (0.000010") deposit. The trivalent chromium samples were plated at 100 A/ft^2 and 95ºF for 2 minutes for a 0.38µm (0.000015") deposit.

Physical Vapor Deposition

The ZrN films were deposited in a VT-1500 LTAVD chamber using a water-cooled cylindrical zirconium target. A schematic of the deposition chamber is shown in Figure 1. The parts were rotated in 2-axis planetary motion around the centrally positioned target while process gases were introduced through two manifolds controlled by mass flow controllers. The arc was powered by high current DC power supplies and the substrates were biased using a 30kW DC power supply. Temperature control was provided by resistive heaters mounted on the walls of the chamber.

The process began with a 20 minute preheat to 150ºC which began when the chamber reached a base pressure of 2.0e-5 Torr. The test coupons then went through a two-step surface preparation before deposition begins. First, the parts go through an argon ion etch cleaning (glow discharge) by applying a 400V bias to the substrates in 25.0 mTorr of argon. The second step is a metal ion bombardment (high bias) where the arc is struck on the zirconium target while the 400V remains applied to the parts at an argon pressure of 5.0 mTorr.

Deposition began with a thin Zr metal adhesion layer (~.06µm) applied at 5.0 mTorr with a 460A arc current and a 70V substrate bias. The process continued with the addition of nitrogen to react with the zirconium to form the ZrN layer which comprised the remainder of the coating. The final thickness of the PVD layer was 0.32µm.

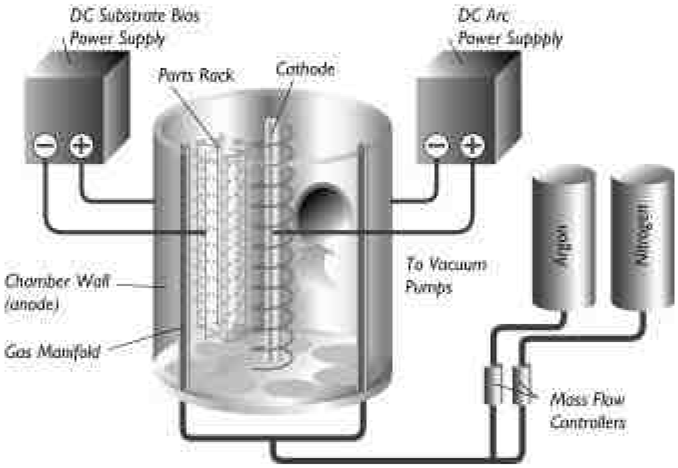

Figure 1. Schematic of LTAVD chamber used for ZrN deposition.

CORROSION TESTING

Electrochemical

Potentiodynamic polarization tests were used to make quantitative measurements of a coating's resistance to corrosion. Experiments were carried out using a Solartron Electrochemical Interface SI 1287 and a 1255B Frequency Response Analyzer. CASS solution was used as the electrolyte and was comprised of 5% NaCl with 0.25 g/l copper chloride and 1.5 ml/l glacial acetic acid. The reference electrode was Ag/AgCl saturated KCl and the counter electrode was platinum. Coupons were placed in a flat cell with 5.0 cm^2 exposed to the electrolyte. A lugin capillary between the reference electrode and working electrode was used to reduce the IR drop.

The coupons were exposed to the electrolyte for one hour to equilibrate the open circuit potential (OCP) before the sweep began. Polarization began at 25 mV below the OCP and terminated when the anodic current reached 100 mA/cm^2. This termination point was chosen because at this point pits generally become visually detectable. The sweep rate of the potential was controlled to 0.17 mV/sec. Samples with and without the ZrN coating were evaluated and the plots of the polarization responses are seen in Figure 2 and the data can be found in Table 1. The i_{corr} value is the current density at the OCP and is also known as the passive corrosion rate. The pitting potential is the voltage at the end point of 100 mA/cm^2.

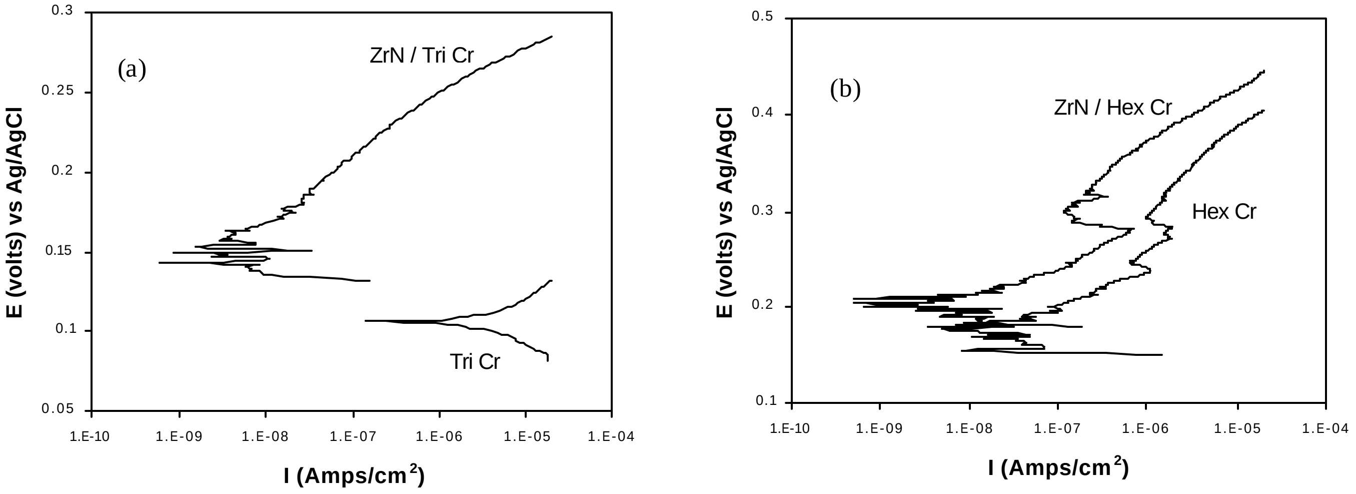

Figure 2. Potentiodynamic responses for as-received Cr/Ni/Brass samples versus ZrN coated Cr/Ni/Brass for (a) trivalent Cr and (b) hexavalent Cr.

Table 1. Potentiodynamic Sweep Data.

	OCP ($V_{Ag/AgCl}$)	i_{corr} (A/cm^2)	Pitting Potential ($V_{Ag/AgCl}$)
Cr(Tri)/Ni/Brass	0.11	$2.3x10^{-7}$	0.14
Cr(Hex)/Ni/Brass	0.18	$3.5x10^{-9}$	0.40
ZrN/Cr(Tri)/Ni/Brass	0.14	$6.5x10^{-10}$	0.27
ZrN/Cr(Hex)/Ni/Brass	0.18	$2.8x10^{-10}$	0.44

Both the plots and the data show that the deposition of the ZrN on the trivalent chromium resulted in increases in the OCP and pitting potential and a decrease in the i_{corr}, all of which indicate significantly improved corrosion resistance. ZrN on hexavalent chromium resulted in an increase in corrosion resistance as well but it was minor as compared to the improvement seen with trivalent chromium.

CASS

Samples were evaluated in a CASS fog chamber maintained as per ASTM B368–97. The samples were evaluated both visually and by microscopic examination for defect (pit) measurement. Digital images were taken at a magnification of 100x and then imported to imaging software that measured the size of the surface defects and calculated a percentage of the area the defects covered. The as-received chromium plated samples were put in CASS for a total of 40 hours and measured every four hours. The ZrN coated samples were left in CASS for a total of 196 hours and measured every 16-20 hours. Plots of the data generated from the images can bee seen in Figures 3 and 4.

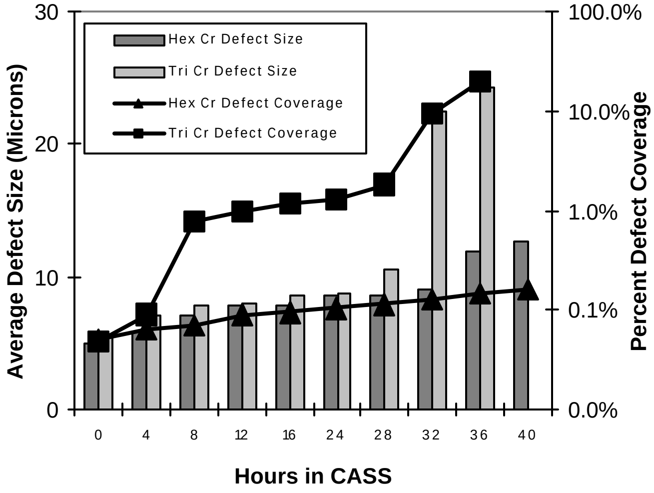

Figure 4. Plot of CASS results on as-received chromium plating throughout 40 hours of testing.

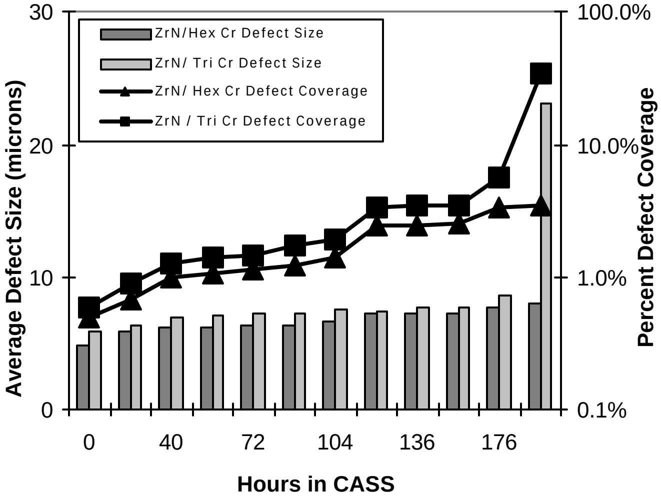

Figure 4. Plot of CASS results on ZrN coated chromium plating throughout 196 hours of testing.

The as-received hexavalent chromium samples performed quite well though all 40 hours of testing. The defect size remained small and just gradually increased while the coverage remained minor. The trivalent chromium behaved somewhat differently in that the defect size remained equal to that of the hexavalent chromium but there was a large increase in the defect coverage area at around 8 hours and then another large increase at 32 hours. The second increase at 32 hours was the point at which the corrosion became visually apparent and was judged to be the point of failure. The hexavalent chromium was still passable after 40 hours but was not tested to failure.

The test coupons coated with ZrN were able to last considerably longer in CASS testing. Both the trivalent and hexavalent chromium behaved more or less the same until the 196 hour point was reached and the ZrN coated trivalent chromium experienced a leap in both defect size and percent area coverage. At this point the ZrN coated trivalent was considered to be failed while the hexavalent sample remained acceptable. Again, the hexavalent chromium was not tested to failure.

MECHANICAL TESTING

Nanohardness

Hardness was measured on the raw, as-received Cr plated samples and also on coated samples where the ZrN layer had been stripped away to reveal the underlying Cr. The ZrN was stripped to determine if the PVD process had an effect on the plating because it is known that annealing trivalent chromium at high temperatures will increase its hardness.[5] Measurements were made using a CSEM nano-hardness tester equipped with a Berkovich indenter. Indentation penetration depths were limited from 1/7th to 1/10th of the total thickness of the top layer to reduce substrate effects on the measurements. Results found in Table 2 are reported as the averages of five clean indentations.

Table 2. Nanohardness Measurements.

Sample	Hardness, Hv (Vickers)
Trivalent Cr, as-received	1070 ± 70
Trivalent Cr, ZrN stripped	1110 ± 70
Hexavalent Cr, as-received	1170 ± 100
Hexavalent Cr, ZrN stripped	1150 ± 60

These results confirm that very little difference in the hardness exists between the two materials. The hexavalent chromium may be slightly harder than the trivalent chromium but it cannot be determined for certain due to variation in the measurement technique. If this is the case it may be due to the fact that hexavalent chromium has a higher degree of tensile stress than trivalent chromium.[5] These values are in relative agreement with measurements taken from thick chromium deposits. It can also be seen that this PVD process does not appear to have any effect on the hardness of the chromium.

Micro-Scratch

Adhesion strength of the film/substrate interface is measured using a CSEM Micro-Scratch tester. A 20µm diamond tip is scratched across the film with a progressively increasing load. The applied load at the point of coating failure is a relative measure of the adhesion strength. The critical loads can be determined from plots of acoustic emission, frictional force, penetration depth or by visual observation. Two critical loads are determined from each scratch in the coating. The first critical load, L_{C1}, is the point at which the first crack appears across the entire width of the scratch. The second critical load, L_{C2}, is the point at which the tip breaks through the coating into the substrate. The instrument was set up to make scratches with a length of 30 mm at a velocity of 10 mm/min with a maximum applied load of 30N at a loading rate of 10 N/min. Ten scratches were made on each sample and critical load values were averaged and are found in Table 3.

Table 3. Micro-Scratch Measurements.

Sample	L_{C1} (N)	L_{C2} (N)
ZrN / Cr (Tri)	6.97 ± 0.52	25.12 ± 1.51
ZrN / Cr (hex)	8.16 ± 0.86	25.34 ± 2.48

These micro-scratch results indicate little difference in the adhesion of the ZrN on the two Cr finishes. The slight increase in L_{C1} for the hexavalent samples may be due to the slightly higher hardness that the hexavalent Cr exhibits.

Taber Abrasion

Abrasion resistance of a coating is dependant on a number of properties of the coating and substrate including the hardness of both materials, adhesive strength between the coating and substrate and the friction coefficient of the coating to name but a few. By using identical ZrN coatings on substrates with similar hardness, a measurement of the wear resistance can give a relative measurement of the adhesion of the coating. Wear resistance was measured using a Taber Abraser. The coating to be tested is mounted face-up on a turntable while two abrasive wheels are placed upon the coating with a fixed pressure. As the turntable rotates, the abrading wheels turn in such a way that a sliding action against the coating occurs. The wheels used in these test were Calibrase CS-17 (rubber with aluminum oxide particles) and were weighted down with 1000g on each wheel.

The wear resistance of the coating was determined by the number of cycles the turntable rotates until the wheels breakthrough to the substrate. The ZrN on trivalent chromium was able to last an average of 1450 cycles while the ZrN on hexavalent chromium lasted an average of 1375 cycles. Any result greater than 1000 cycles is considered a passable coating under these aggressive test conditions. The difference in performance between the two plating types is not significant.

CONCLUSION

The purpose of this study was to compare the performance of ZrN coated trivalent and hexavalent chromium. It is of interest to determine if trivalent chromium could be used as a direct replacement for hexavalent chromium in decorative and functional applications. To make this evaluation it was necessary to perform side-by-side comparisons of the corrosion resistance and the mechanical properties of the deposited ZrN. It was found from both electrochemical and CASS testing that the trivalent chromium is more susceptible to corrosive attack than hexavalent chromium. Although the corrosion resistance was not as good as hexavalent chromium, it would be sufficient for most decorative and functional applications. From the adhesion and wear resistance evaluations it was found that there was essentially no difference in the behavior in which the ZrN performed on the two electrodeposits.

The findings from this study are a good indication that trivalent chromium will be able to replace hexavalent chromium in most applications where PVD deposited ZrN coatings are used.

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