How Contaminants Affect the Quality of PVD Coatings and their Effects on Process Parameters

Z. Wang and M. Akkaoui, Tanury Industries, Lincoln, RI

ABSTRACT

Adhesion, scratch resistance and durability are all key factors in thin film coatings. The functionality of the coating and wear characteristics are greatly dependent upon these key factors. It was found that adhesion and scratch resistance performance were enhanced by adjusting the thickness of the plated chrome layer. The substrate studied was brass, coated with nickel and chromium via electroplating. The heavier the chrome plating, the higher the probability of coating failure. We utilized a Glow Discharge Spectrometer (GDS) to graph of the coating composition versus the thickness of the coating. The analysis showed a higher amount of oxygen at the ZrCN interface as the chrome layer became heavier. At one micron of chrome, the PVD coating failed adhesion and scratch resistance. The failure was due to hydrocarbon out gassing emitted from the chrome plate base. The oxygen out gas shows up as a contaminant on the GDS graph. In order to solve the problem, the electroplating process, cleaning process and several PVD coating parameters required modification. This paper will discuss these experiments and their results.

INTRODUCTION

The adhesion and scratch resistance play important roles for thin film behaviors by PVD. The substrates used most of time for PVD are very wide materials such as: aluminum, zinc, copper, brass, bronze, nickel silver, zinc, HSS/steel, sintered metals, stainless steel, inox, nickel/titanium, silver, gold, platinum and synthetic materials such as plastics. Oftentimes, customers require coatings using physical vapor deposition because they are concerned about the durability and scratch resistance of the products. In fact, many manufactures will offer the end user a life time warranty because the positive wear characteristics of PVD. In our particular application, the chrome layer which we are applying the PVD layer provides enhanced corrosion performance for product in the field. Normally, the chrome layer is deposited by electrochemistry plating. Simply stated, the chrome provides the corrosion barrier and the PVD film provided high wearability. The biggest challenge is combining the electroplating and PVD coating layers; these two layers should be matched and optimized in order to get the best adhesion. We need to decide the best interlayer to use in order to get the most stable chemical bond at the subsurface. Also, we need to find the most effective chemical or mechanical method that will activate the substrate surface in order to clean the coating. Finally, we need to be able to form linkages between the coating layer and the surface. All of this is necessary to achieve optimization.

Statement of the Problem

We encountered a problem when the ZrCN coating we were testing failed a standard wear test. For the application, the coating time and thickness settings are normally adequate to pass the testing. Typically, one (1) micron of ZrCN is sufficient to pass the test as normally applied. In our problem, the parts coated were failing 50% of the recommended time sequence. Puzzled by this result, we set out to determine what variables were in the process from the beginning of the manufacturing process to the final coating process that could affect this test negatively.

PVD LAYER DEPOSITION

The “ arc vapor deposition” process was used to deposit the ZrCN films. Figure 1 shows the inside of a batch coater and Figure 2 illustrates the basic operating principle of the coating machine. In the top left of the picture is the Arc power supply; it applies a high current on the metalized target in order to vaporize the target material. The DC bias power supply at the top right provides a negative charge to the product being coated to increase adhesion.

Here a few steps to this process [2]:

1. After loading the deposition chamber the parts were heated over to 100ºC to remove residual water molecules and other organic particles on the surface in order to assist adhesion.
2. Then, pump down the chamber to a base pressure less than 3.0×10^{-5} Torr.
3. Next, argon plasma treatment is used to clean the parts through bombardment to take out dust, oxides and contaminants. This is necessary to improve the adhesion of thin film layer to the substrate;
4. In order to raise adhesion, the transition zone process or clean process will be applied before the coating process. Here, ions bombard the substrates in order to heat the substrates and dislodge any remaining impurities. Some of the ions are embedded in the surface of the substrates, creating an interlayer to enhance adhesion. Sometimes, chemical bonds will form at this layer.

55th Annual Technical Conference Proceedings, Santa Clara, CA April 28–May 3, 2012 ISSN 0737-5921

5. A layer of pure metal adheres the substrates to promote wear and corrosion resistance.
6. Arc deposition of the Zirconium Carbon Nitride layer (~1500 nm thick) in a mixed argon, nitrogen and acetylene gas atmosphere occurs.

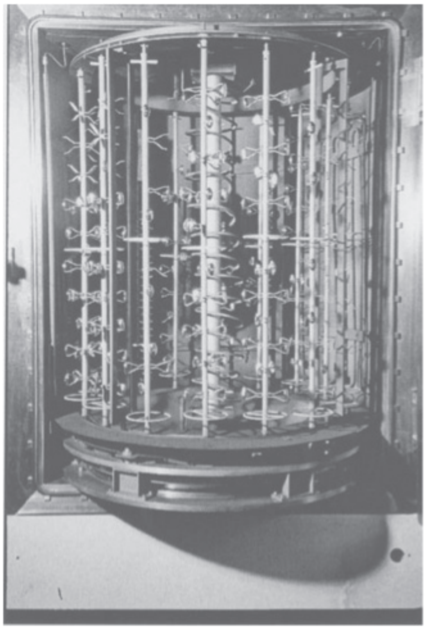


Figure 1: The inside of a batch coater from Vapor Technologies [1].

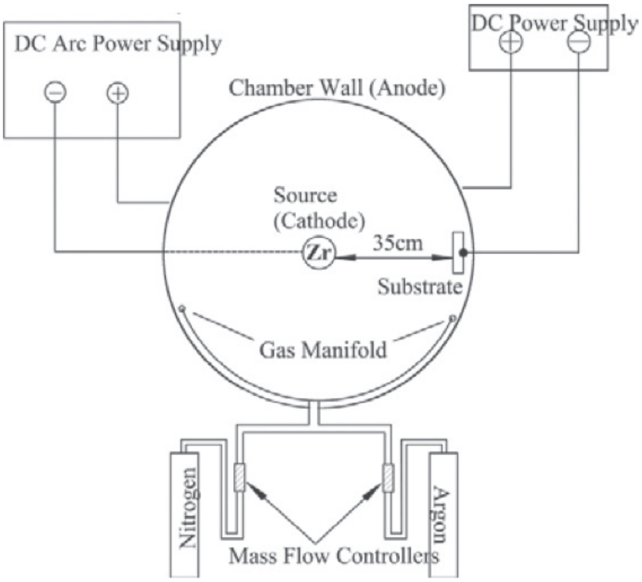


Figure 2: Schematic drawing for the basic operating principle of the coated machine. It includes Arc power supply that applies a current that vaporizes the metalized target, and the DC bias power supply that adds a negative charge to the coated parts to increase adhesion [1].

Figure 3 depicts the detailed layers of electrochemistry plating and the PVD layers. The material consists of many layers. Layers include the substrate brass, nickel plating and chromium plating. Also, there are thinner PVD interlayer's that increase adhesion. The thicker pure metal layer reduces potential cracking through growth of the gradient molecular structure. At the top, there is the compound layer (ZrCN) where we modify the ratio between argon, carbon and nitrogen to produce the desired film characteristics.

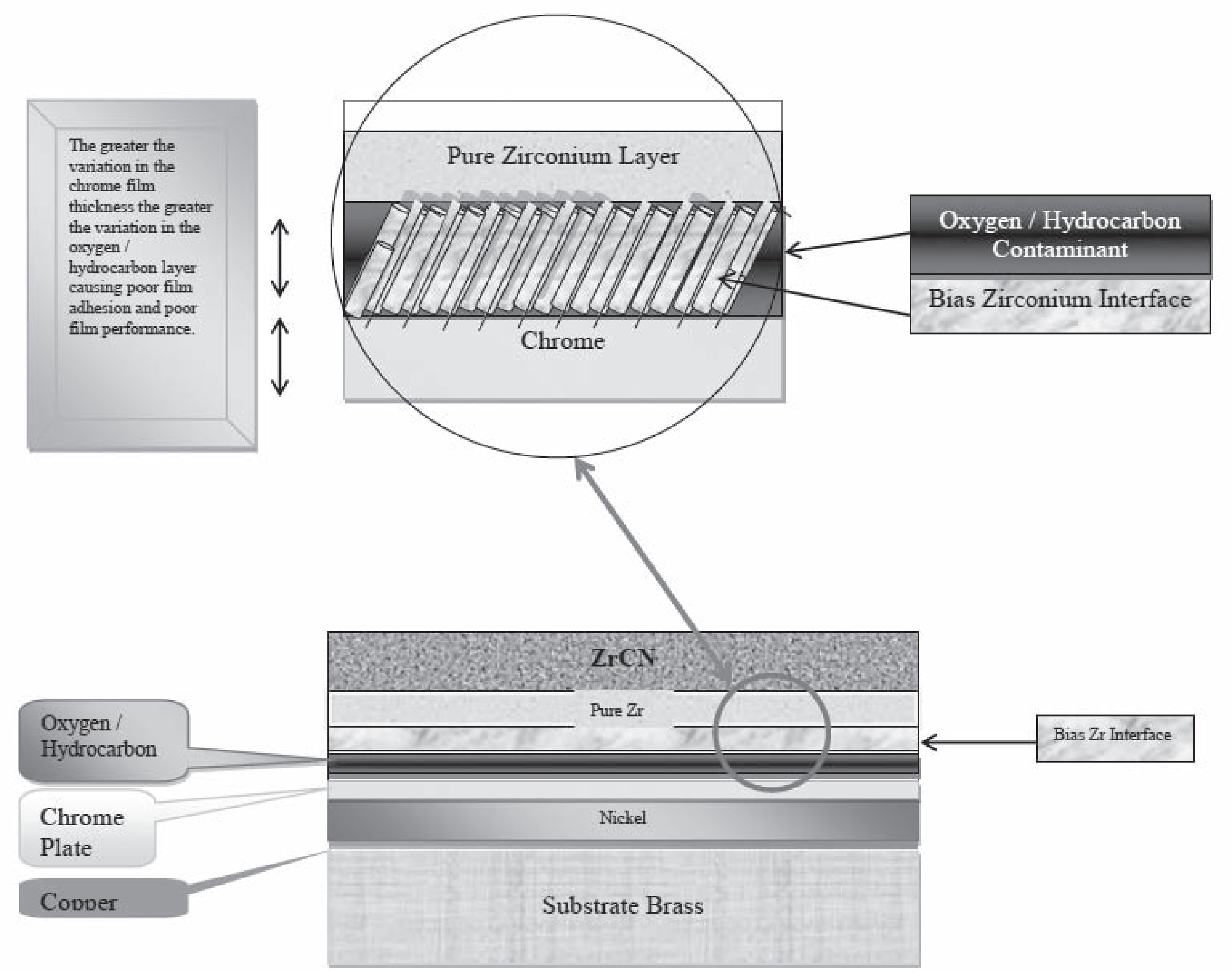
GLOW DISCHARGE SPECTROMETER (GDS) TECHNIQUE

The instrument we used to evaluate and diagnose the coating film is called the Glow Discharge Spectrometer (GDS). The layers of the coating were sputtered out and the elements of the coating which were emitted into the instrument were analyzed in real time. The plots are coating composition (atomic percent as vertical axis) versus depth into the coating (microns as horizontal axis). Essentially, the curve gives the cross-section view of the coating. The top of the coating is on the left side. You can match the elements to their colors. Notice the zirconium (blue line), carbon (purple line), and nitrogen (red line). Notice that Zr represents 70% of the atomic percentage while there were very low C, N and O contents. After the zirconium layer, there is the Cr plating (orange line) and finally the Ni plating (yellow line). It is very interesting that some oxygen (green line) 40% by atomic at the very top surface to 8% by atomic at the top coating layer) was found during the experiment.

RESULTS AND DISCUSSIONS

We produced two sets of samples with different Cr plating thicknesses. One is thinner with 0.20 microns (called sample 1) and another one is thicker with 0.80 microns (called sample 2). Both samples were coated with a ZrCN layer. Sample 1 passed the wearability test; whereas, Sample 2 failed the wearability test. Our wearability test involved 50,000 forceful strokes on the coating surface.

Figure 4 shows the GDS plot for sample 1 (thinner Cr plating thickness with 0.20 microns). The depth is between 0 to 0.5 microns. Between 0 and 0.12 microns, Zr(57% by atomic)/C(20% by atomic)/N(16% by atomic)/O(7% by atomic) could be found. This corresponds to the top compound PVD layer as indicated by Figure 3. After that, when depth was between 0.12 and 0.14 microns, pure Zr (peak on the curve) existed as the interlayer. If the samples continued to sputter, the Cr plating layer could be found between 0.15 and 0.35 microns. The Cr layer thickness is 0.20 microns. At 0.38 microns, the Ni plating layer starts to be exposed.



The greater the variation in the chrome film thickness the greater the variation in the oxygen / hydrocarbon layer causing poor film adhesion and poor film performance.

Figure 3: Chrome Interface Complexity.

Figure 5a showed the GDS plot for sample 2 (thicker Cr plating thickness with 0.80 microns). Figure 5b is a close up of Sample 2(zoom-in for Figure 5a.). Figure 5b represented the same development for Zr/C/N/O between 0 and 0.12 microns depth. The heavy Cr plating layer could be seen from Figure 5a. The thickness is 1.1 microns (between 0.12 and 1.2 microns). The very different point is that at the depth 0.14 microns, 11% Oxygen by atomic percentage existed instead of 6% from Sample 1. We must realize that the change in oxygen levels changed the wearability of the coating. We can conclude that ZrCNO coating is not effective in increasing adhesion.

Question?
Why does a high abundance of oxygen relate to a heavy Cr plating layer and where does this Oxygen come from?

Figure 6 provides evidence that the oxygen source could be from the heavier chrome layer itself. It might be created by electrochemistry plating, which has the potential to produces hydrocarbons under heat. . To stop hydrocarbon production, the parts need to be washed and cleaned very well and the heat in the chamber must be controlled. To diminish oxygen production, different coating parameters that lower the bias power and reduce coating power are used in order to drop heat produced during the coating process. Our results illustrate that the heavier the chrome plating, the higher the probability of hydrocarbon / oxygen out gassing increasing the risk of poor coating performance.

CONCLUSIONS

This experiment found that adhesion and scratch resistance performance were enhanced by adjusting the chrome layer thickness. The heavier the chrome plating, the higher the probability of coating failure. The Glow Discharge Spectrometer (GDS) analysis showed a higher abundance of oxygen as the chrome layer became heavier. At one micron of chrome the PVD coating failed adhesion and scratch resistance.

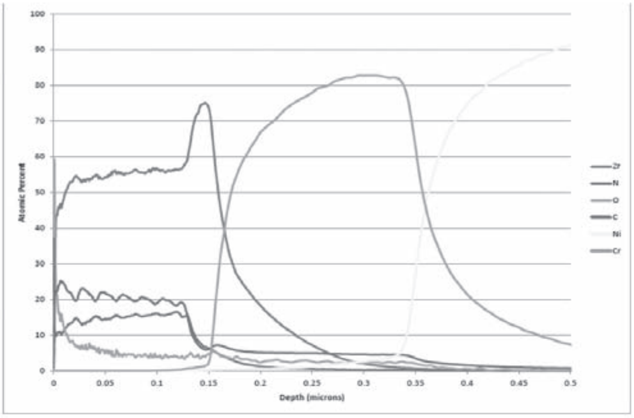


Figure 4: Atomic percentage vs. Depth Sample 1.

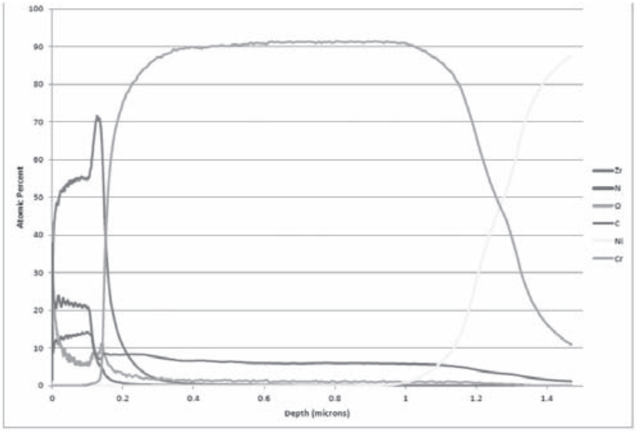


Figure 5a: Atomic Percent vs. Depth Sample 2.

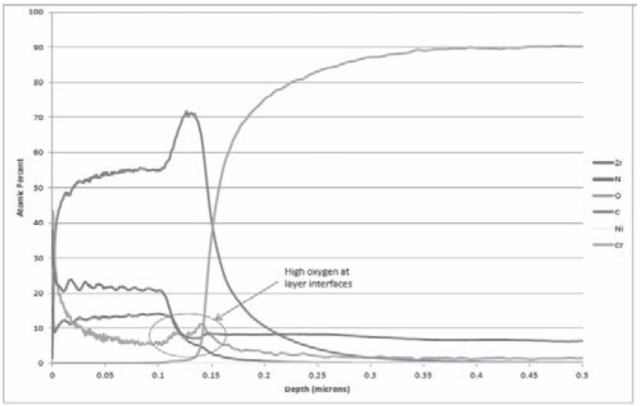


Figure 5b: Zoom-up on Figure 5a.

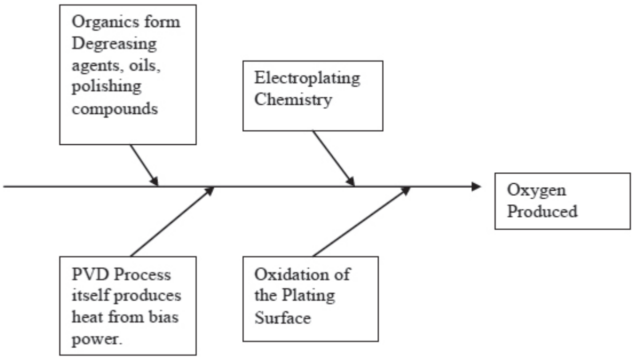


Figure 6: Fish bone for analyzing where oxygen comes from.

The failure was due to hydrocarbon contamination during the plating process. This same PVD coating passed adhesion and scratch resistance testing over a lower thickness of electroplated chrome.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. Bryce Anton of Vapor Technologies, Colorado, USA and his group for analyzing the samples of the Glow Discharge Spectrometer (GDS).

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