USING PHYSICAL VAPOR DEPOSITION TO OPTIMIZE SURFACE PROPERTIES Thin film cathodic arc PVD coatings offer an easy and economical way to optimize

surface properties without changing bulk performance. *David Bell and Viktor Khominich, Phygen Coatings Inc., Minneapolis Steve Midson, The Midson Group, Denver*

any engineering components require surface properties that are significantly different than bulk material properties. For example, superior wear resistance might be required on the surface, while the bulk material might call for easy machinability. Often, both properties are not attainable in one material, necessitating a compromise of specifying a material with only moderate wear resistance and moderate machinability to make the component. Surface engineering technologies, however, allow the properties and performance of a component's surface to be modified and controlled independent of its bulk. There are a number of different surface engineering technologies available, including weld overlay, surface hardening, and hard coatings, but physical vapor deposition (PVD) offers a straightforward and inexpensive approach to optimize surface properties without changing bulk performance.

PVD SPECIFICS

Physical vapor deposition involves vaporizing atoms from a solid source and transporting and depositing them onto a substrate. PVD can produce different categories of coatings including single elements such as titanium and diamond-like carbon (DLC), alloys (e.g., Al-Cr), and compounds (e.g., CrN and TiC). The most commonly used PVD coatings are metal nitrides such as CrN, TiAlN, and AlCrN, which are produced by admitting low-pressure nitrogen gas into the PVD chamber. This enables vaporized metallic atoms to react with the nitrogen gas during deposition on the substrate. Typically, PVD coating processes are performed at temperatures below 600°C, which enables depositing the coating onto a fully hardened steel without compromising the hardness of the steel substrate through over-tempering. PVD coatings are typically 1 to 6 µm thick.

Cathodic arc evaporation (CAE), a commonly used PVD process, involves evaporation and ionization of atoms from the target (source) material through the use of a high current-density arc. CAE produces high density coatings with extremely high adhesion and cohesion. However, one drawback of CAE is ejection of relatively large macroparticles (about 2 to 10 µm diameter) from the target material, which can become incorporated into the coating (Fig. 1a). Macroparticles form when unwanted droplets of liquid metal splash from the arc source and land on the substrate during coating growth. As the size of these macroparticles is similar to the PVD coating thickness, and because they are poorly adhered to the substrate, they negatively impact the coating's integrity, performance, and overall life.

This article describes a modified cathodic arc process called arc plasma acceleration (APA), which enables production of high density, thin film coatings containing minimal macroparticles.



Fig. 1 — (a) CrN coating produced using conventional cathodic arc evaporation (CAE) process contains detrimental metallic Cr macroparticle inclusions (white) and dark pores of various sizes; (b) CrN coating produced using the arc plasma acceleration process is essentially free of macroparticles.

ADVANCED MATERIALS & PROCESSES | SEPTEMBER 2018

ARC PLASMA ACCELERATION

The APA technique is a modified cathodic arc vapor deposition process patented by Phygen Coatings Inc.^[1] The process uses a magnetic field generator to create a field with a distinctive cusp shape, which provides enhanced trapping of plasma particles generated from the cathodic source. The contoured field creates an electron trap with an aperture through which plasma ions are directed at the substrate; the plasma deposition rate is higher per unit of magnetic field strength than can be obtained with conventional designs. The APA process enables control over coating growth, both via the intensity of ion bombardment (through plasma density control) and the energy of arriving particles (through the substrate bias potential). It is necessary to ensure that a large number of ions bombard the surface with a velocity in a specific range, and by tuning that range, crystalline configurations with weaker bonding can be minimized while preserving the strongest bonds. This phenomenon results in growth of a dense, highly textured coating with an excellent metallurgical bond to the substrate (Fig. 2).

Another benefit of the APA approach for producing CAE coatings is that the volume fraction of macroparticles within the coating is significantly reduced (Fig. 1b), and both average macroparticle size and volume fraction are significantly reduced compared

with conventional CAE techniques. Decreasing the volume fraction of macroparticle defects within a coating can improve performance and significantly extend coating life.

Typical properties of CrN and AlCrN coatings produced using the APA process are listed in Table 1. The APA process is also used to produce CrN-DLC and CrN-SiC bilayer coatings (Fig. 3). Properties of CrN-DLC and CrN-SiC bilayer coatings are listed in Table 1 as well.

COATING PERFORMANCE

PVD coatings are used in many applications where surface performance is crucial. As noted previously, one of the main benefits of thin film coatings is the ability to modify surface behavior independent of bulk performance. This is illustrated in several examples using both single-layer and bilayer coatings produced by the APA process.

Corrosion protection. For many applications, PVD coatings cannot provide



Fig. 2 — Coatings produced using the arc plasma acceleration method are dense and free of defects as illustrated in this cross section of a $3-\mu m$ thick CrN coating deposited on an AISI 4340 alloy steel substrate.



Fig. 3 — SEM micrographs showing cross sections through bilayer PVD coatings deposited onto AISI 4340 alloy steel substrates using the arc plasma-acceleration process. In (a), CrN-DLC coating; (b) CrN-SiC coating (in each image, the left-hand side is viewed using secondary electrons, while the right-hand side is viewed in electron-backscattered mode).

TABLE 1 – PROPERTIES OF ARC PLASMA ACCELERATION COATINGS

Coating compound (product name)	Typical coating thickness, μm	Nanoindentation hardness, GPa	Maximum operating temperature (based on oxidation resistance), °C	Adhesion strength (by scratch test) Critical load, N
CrN (FortiPhy)	3-6	22-26	800-850	110-120
CrN(a) (FortiPhy Plus)	3-6	23-27	825-875	112-135
AlCrN (CertiPhy)	3-6	31-35	~950	115-130
AlCrN(a) (CertiPhy Plus)	3-6	31-35	~950	115-130
CrN-DLC	~2 each layer	23	~350	80-105
CrN-SiC	~2 each layer	30	>600	89-90

(a) Duplex coating where substrate material is plasma ion nitride prior to coating for improved mechanical support.

adequate corrosion protection due to the presence of defects within the coatings, such as macroparticles, pits, and flakes. These defects originate during the deposition process along with a columnar growth structure that often is not entirely dense. However, the U.S. Army Armament Research, Development and Engineering Center at Benet Laboratories^[2] recently evaluated the corrosion protection of steel substrates by several coatings produced using the APA process. Tests were performed in accordance with the GM9540P specification^[3] involving 30 cycles of 16-hour exposure to chloride solutions at 50°C. Results show that a CrN coating and a CrN-SiC bilayer coating exhibit significantly better corrosion resistance than an electroplated chromium coating (12 and 40 µm thick), and equivalent corrosion resistance to a 40-µm thick electroless high-phosphorous nickel plate. Figure 4 shows the surface of the PVD CrN coating following accelerated corrosion testing, which exhibited a significantly smaller amount of corrosion than steel substrates with electroplated chromium coatings.

The excellent corrosion protection of APA CrN and CrN-SiC coatings is attributed to their lower concentration of defects^[2] and dense structure. For example, APA coatings were found to contain a macroparticle density of 3.5×10^3 / mm³, which is four to eight times lower than values typically found in coatings produced using conventional cathodic arc processes^[2]. In addition, the macroparticles were significantly smaller; average and maximum particle sizes were 0.67 and 4.2 µm, respectively, two to 16 times smaller than particles within coatings made using conventional cathodic arc processes^[2].

Applications requiring solid lubricants. Coefficient of friction (CoF) measurements were performed at Benet Labs on several APA coatings by sliding coatings against 6-mm alumina balls at room temperature using a ballon-disk tribometer^[2]. Results shown in Table 2 reveal that two bilayer coatings (CrN-DLC and CrN-SiC) have lower CoF values than single-layer CrN PVD coatings, electroless Ni-P, and electroplated Cr coatings. The bilayer coatings are suitable in applications requiring solid lubricants^[2].

Wear resistance. PVD coatings have excellent wear resistance due to their high as-deposited hardness. Table 3 shows wear rates from ball-on-disk tribometer tests of the three PVD coatings produced using the APA process, conventional Ni-P and Cr coatings, and bare AISI 4340 alloy steel substrate. The PVD coatings have significantly lower wear rates.

Metal forming and casting tools. PVD coatings are also commonly applied to metal forming and casting tools, such as stamping tools and core pins used in die casting. A driveshaft housing produced at Mercury Castings, Fond du Lac, Wis., provides an example of the benefits of using PVD coatings^[4]. Casting production involves the use of



Fig. 4 — Surface of samples following accelerated corrosion tests consisting of 30 cycles of 16 h exposure to chloride solutions at 50°C in accordance with specification $GM9540P^{[2]}$: (a) APA CrN coating, (b) 40-µm thick electroplated Cr coating, and (c) 12-µm thick electroplated Cr coating. several long cores, and when using uncoated H13 tool steel cores, the aluminum die casting alloy rapidly solders to the steel core (Fig. 5), creating high loads during casting ejection, which causes the entire housing to bend. Applying a 5- μ m AlCrN coating using the APA process to the core eliminates soldering (Fig. 5), avoids bending the casting during core pull, and eliminates the need for 100% inspection of the castings.

Recent research has taken the concept of coatings on forming and casting tools even further, with the goal of eliminating the need to lubricate dies used to produce die castings. During die casting, a water based organic lubricant is applied to the hot faces of the steel casting die prior to each shot to prevent the aluminum castings from soldering (sticking) to the die. However, a number of undesirable outcomes can arise from applying these lubricants, including lower casting quality (higher residual porosity), shorter die life, and effluents that need to be disposed of.

TABLE 2 – STEADY-STATE COEFFICIENT OF FRICTION FOR SELECT COATINGS^[2]

Coating	Average steady-state coefficient of friction
CrN-DLC	$\textbf{0.07}\pm\textbf{0.01}$
CrN-SiC	0.07 ± 0.01
CrN	$\textbf{0.28}\pm\textbf{0.02}$
Ni-P	$\textbf{0.23}\pm\textbf{0.02}$
Cr	$\textbf{0.55}\pm\textbf{0.09}$

TABLE 3 – WEAR RATES OF SELECT COATINGS^[2]

Coating	Wear rate, mm³/N m
CrN	$5.30 imes10^{-7}$
CrN-DLC	$7.32 imes 10^{-7}$
CrN-SiC	$7.90 imes 10^{-7}$
Ni-P	$25.5 imes10^{-7}$
Cr	$263 imes 10^{-7}$
Uncoated AISI 4340	556×10^{-7}
alloy steel	



Fig. 5 — Steel slide inserts used in the production of a die cast driveshaft housing after 1256 shots^[4]. The upper core with a 5-µm thick AlCrN coating shows no soldering, while the lower uncoated insert shows soldering.

The research objective was to identify permanent PVD thin film coatings that could be applied to the hot faces of the die and eliminate the need for conventional lubrication. Following extensive laboratory testing at the Colorado School of Mines^[5], an AlCrN coating was selected and applied to the entire die used to produce balance shaft housings. As illustrated in Fig. 6, all surfaces of the steel die contacted by the liquid aluminum were coated, including the shot block, runners, cavity insert and chill vent on the ejector side of the die, and the runners, cavity insert, and chill block (not shown) on the cover side of the die.

Plant trials demonstrate that the AlCrN coating enables a reduction of about 85% in the use of conventional organic lubricant, improves cycle time by about 12%, and improves the internal quality of the die castings. The coating is also expected to extend the life of the casting tool. To date, roughly 20,000 castings have been produced using the AlCrN coated tool, so details of extended die life are not yet available^[5].

SUMMARY

Thin film cathodic arc PVD coatings have excellent commercial potential for a number of markets, as they enable surface properties to be modified and optimized independent of the material's bulk performance. However, many cathodic arc processes suffer from the presence of defects within the coating thickness, limiting commercial application. The arc plasma acceleration process reduces the size and number of macroparticles and other defects in the coating. This process should open up new applications and markets for PVD coatings,

including corrosion protection, wear resistance, reduction of die lubrication, and life extension of forming tools. ~AM&P

For more information: David Bell is president and CEO of Phygen Coatings Inc., 1400 Marshall St. NE, Minneapolis,

MN 55413, 612.331.4224, tech@phygen.com, www. phygen.com.

References

1. V.N. Khominich, Arc Plasma Acceleration: A Method for Improving Coating Quality by Decreasing Macro Particle Inclusions, *37th ICMCTF*, San Diego, 2010.

2. C.P. Mulligan, et al., CrN, CrN/SiC and CrN/DLC Coatings Deposited by a Novel Plasma Acceleration Process: Processing and Properties, *Matls. and Manufac. Proc.*, 29, p 1037-1043, 2014.

3. General Motors Engineering Standard 9540P, General Motors Corp., Detroit, 1997.

4. Z. Gay, et al., Study of Structural Aluminum Casting Operations Using



Fig. 6 — 3D models of die cast balance shaft housing die: (left) ejector side and (right) cover side. An AlCrN coating applied to the entire die reduced the need for lubricant and improved both production cycle time and die casting quality.

CertiPhy Plus Coatings, Paper No. T14-061, NADCA 2014 Congress.

5. B. Wang, et al., Results from a Series of Plant Trials to Evaluate the Impact of PVD Processed AlCrN Thin-Film Die Coatings to Minimize Die Lubrication, Paper number T17-083, NADCA 2017 Congress.



www.masterbond.com