

High-Quality Physical Vapor Deposition Coatings for Corrosion Protection Applications

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This article describes using physical vapor deposition (PVD) coatings to provide corrosion protection for metallic substrates. Historically, the corrosion protection offered by PVD coatings has been inadequate due to the presence of defects in the coatings, including macroparticles, flakes, pores, and the porous columnar structure of the coatings. However, a modified PVD coating process was introduced that produces coatings containing a much lower number of macroparticles and other defects, thereby significantly improving corrosion resistance. A case study is presented where a CrN coating produced by the novel PVD process was used by the U.S. Army to replace conventional plated coatings.

Steel is one of the most important engineering materials due to its combination of low cost and excellent performance in strength, ductility, machinability, and formability.¹ However, the corrosion resistance of most steels is relatively poor in corrosive environments and to provide adequate corrosion resistance, steels often require the use of a protective coating. Commonly used coatings include paints, polymers, electroplating, conversion coatings, and galvanizing. These types of coatings suffer from problems that place

severe constraints on their application at high temperatures, lack of wear resistance, or environmental problems associated with the coatings themselves.

Another class of coatings that can be applied to steels are thin-film, hard coatings produced by physical vapor deposition (PVD) processes, such as cathodic arc evaporation (CAE). Examples of these types of PVD coatings include TiN, CrN, AlCrN, and TiAlN. These metal nitride coatings are chemically inert² and should, therefore, provide excellent corrosion protection for steel substrates. In practice, however, numerous studies have shown that the corrosion protection provided by most PVD coatings is relatively poor. The poor corrosion protection of PVD coatings has been related to defects in the coatings,^{1,3-4} such as macroparticles, flakes, pores, and the porous columnar structure of the coatings.¹ One potential solution is the use of thicker PVD coatings (up to 18 μm), which can provide better corrosion protection.^{3,5} However, in addition to the cost issue, high thickness PVD coatings can be problematic in many commercial applications, such as those requiring wear resistance due to the brittle nature of thick coatings.³ So PVD coatings are normally not thicker than 5 to 6 μm .

PVD coatings must be essentially defect-free to achieve their potential for providing excellent corrosion protection. The penetration of corrosive media through the coating to the substrate must be prevented⁶ by coatings with a dense, equiaxed grain structure.⁵ This article describes a

novel PVD application method called the arc plasma acceleration (APA) process that can produce thin-film coatings with very low-defect contents necessary to provide corrosion protection to metal substrates. Before describing the APA process in detail, it is worthwhile to provide a brief summary of PVD coating processes.

PVD Coating Processes

PVD involves the vaporization of atoms from a solid metallic source, and the transportation and deposition of these atoms onto a substrate of interest. Some of the most commonly used PVD coatings for wear protection are metal nitrides, which are produced by bleeding low pressures of nitrogen gas into the PVD deposition chamber, allowing the metallic atoms vaporized from the metal target to react with the nitrogen gas during deposition on the substrate. PVD coatings are normally ~1 to 6 μm in thickness (Figure 1).

A number of commercial PVD processes exist, and CAE is one of the most commonly used, as it produces coatings with extremely high levels of adhesion, cohesion, density, and hardness. One of the drawbacks of the cathodic arc process is the ejection from the target material of relatively large (~2 to 10 μm diameter) macroparticles,⁵ which can become incorporated into the coating (Figure 2[a]). These macroparticles form when unwanted droplets of liquid metal splashed from the arc source land on the substrate during coating growth. As these particles are similar in size to the thickness of the PVD coating, and often are poorly adhered to the substrate, they are detrimental to the coating's integrity, and significantly reduce corrosion protection.⁵

A modified CAE process called the APA process, patented by Phygen[†],⁷ can significantly reduce the number of macroparticles and other defects within the PVD coatings (Figure 2[b]), and thereby significantly improve corrosion resistance. The APA process utilizes a magnetic field generator that creates a magnetic field with a distinctive cusp shape, which provides enhanced trapping of the plasma particles generated from

[†]Trade name.

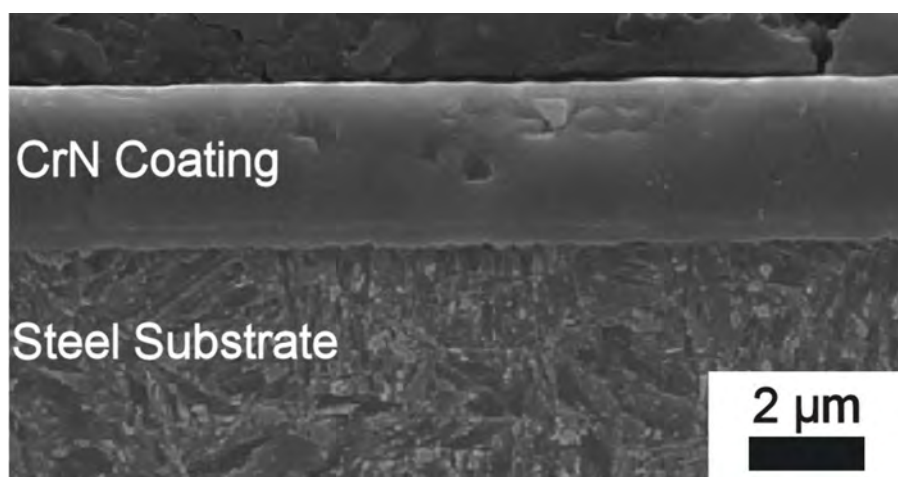


FIGURE 1 Metallographic cross section through a 3- μm thick CrN coating on a steel substrate.

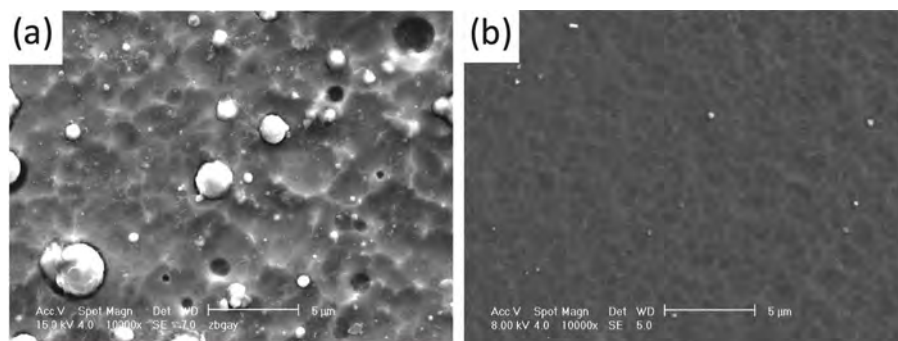


FIGURE 2 CrN coatings produced by cathodic arc evaporation. (a) Conventional CAE process, where coating contains detrimental white metallic Cr macroparticle inclusions and dark pores of various sizes. (b) Coating produced using the APA process, essentially free of macroparticles.

the cathodic source. The APA process permits control over the growth of the coating, both via the intensity of ion bombardment through the plasma density control, and the energy of arriving particles through the substrate bias potential. A key to the process is to ensure that a large number of ions are bombarding 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 results in growth of a dense and highly textured coating, having a low-defect content, and an excellent metallurgical bond to the substrate.

A recent study¹ performed in collaboration with the U.S. Army Armament Research, Development, and Engineering Center, Benét Laboratories compared the corrosion resistance of coatings produced by the APA

process with conventional SAE AMS 2460,⁸ Class 2D electroplated chromium (12 and 40 μm thick) and SAE AMS 2404F,⁹ Class 2, Grade C electroless high phosphorous nickel (40 μm thick). The PVD coatings produced by the APA process were a single layer CrN (3.5 μm thick) and a duplex CrN/SiC coating (total thickness of 3.5 μm). All coatings were deposited onto AISI 4340 steel substrates. Laboratory corrosion testing was performed in accordance with the GM9540P cyclic corrosion testing specification,¹⁰ which included 30 cycles of 16-h exposure to chloride solutions at 49 °C. The results showed that the CrN PVD and the CrN/SiC duplex PVD coatings produced using the APA process exhibited significantly better corrosion resistance than the chromium coatings, and equivalent corrosion resistance to the electroless high phosphorous nickel plate

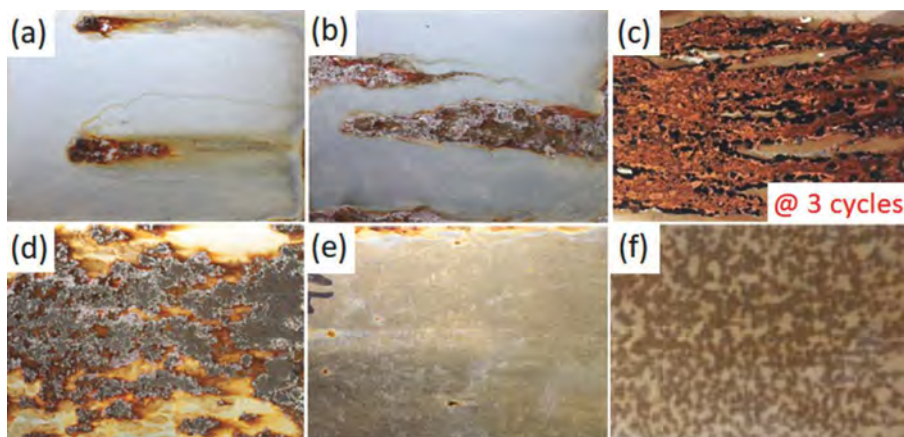


FIGURE 3 Photographs of the various coatings following 30 cycles of the GM9540P accelerated corrosion testing. (a) APA CrN coating,¹ (b) APA CrN/SiC coating,¹ (c) Conventional arc-deposited CrN (three cycles), (d) 40 μm thick electroplated Cr coating,¹ (e) 40 μm thick electroless Ni coating,¹ and (f) HIPIMS-deposited nitride.

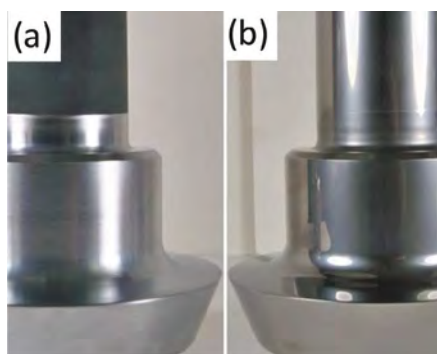


FIGURE 4 Photographs of the (a) legacy Cr plated spindle and (b) APA process CrN coated spindle.

(Figure 3). For comparison to other PVD processes, Figures 3(c) and (f) give additional images following the same corrosion testing protocol for a conventional cathodic arc deposited CrN and a high-power impulse magnetron sputtering (HIPIMS) deposited nitride, respectively. HIPIMS is a high-power density PVD process shown to produce higher density coatings and significantly enhance corrosion resistance over conventional PVD coatings.¹¹⁻¹² Note that the image in Figure 3(c) is following just three cycles as opposed to 30, illustrating the lack of corrosion protection provided with conventional cathodic arc. Significant improvement in corrosion protection is realized with the HIPIMS process vs. conventional arc but the best performance among the nitride coatings were those deposited by the APA process.

Mulligan¹ characterized the defect content of the PVD coatings produced using

the APA process, and found that the average macroparticle size was four to eight times lower than values typically reported for coatings prepared by conventional cathodic arc, with the maximum particle size in the range of 2 to 16 times smaller. They attributed the excellent corrosion protection of the APA deposited coatings, particularly when compared to conventional cathodic arc (Figure 3[c]), to the high density and this low-defect content.

Case Study of Coating Produced Using APA Process

There is a case study of the APA process used to produce corrosion protection thin-film coatings for breech spindles for howitzers.¹³ The problem being addressed by the U.S. Army was that wear and corrosion require the replacement of the spindles well before they reach their usable end-of-life. The spindle is the component that seals the breech of the howitzer. Historically, electroplated chromium coatings were applied to the spindles, but wear and corrosion cause problems, such as a loss of seal, which lead to a shortened spindle life when the howitzers are subjected to typical usage. Figures 4(a) and (b) illustrate the spindle component in the as-coated condition for the legacy Cr plated spindle and the APA process CrN. Note that the legacy Cr plated spindle also has a heavy manganese phosphate treatment on the top half due to process limitations with the Cr plate. For the case of the APA process, the entire exterior is

coated with CrN, further improving performance and producibility.

Reference 13 details the evaluation of 12 separate coating systems and it was found that PVD coatings produced by the APA process vastly outperformed chrome and the other candidates in terms of corrosion and wear. Initially, coated howitzer breech spindles were tested at a live firing on a howitzer range, and to simulate combat conditions, the spindles were weathered for 30 days in a caustic acid + acidic propellant by-product. This was followed by another round of firing plus a second weathering treatment.

Following this testing, conventional chromium-coated spindles exhibited severe corrosion, but the PVD-coated spindles' performance was significantly better. Following down-select of the APA-processed CrN, more extensive testing involved firing the most aggressive rounds along with intermittent GM9540P-accelerated cyclical corrosion testing in an environmental chamber. Figures 5(a) and (b) are photographs of the APA process CrN-coated spindles, and (c) and (d) are photographs of legacy Cr-plated spindles at the completion of accelerated corrosion testing, showing the superior performance of the PVD coated spindles. The U.S. Army is now using spindles coated with CrN using the APA process, and officials at the Picatinny Arsenal have estimated a \$5 million saving over the life of the M777A2 howitzer, with even greater potential savings possible if this PVD coating technology is applied to other artillery systems.¹³

Other Factors Affecting Corrosion Protection

Reports from technical literature indicate that other process parameters may further improve the degree of corrosion protection offered by coatings produced using PVD processes. These include optimization of surface roughness and the use of a nitriding pre-layer. These are briefly discussed in the following paragraphs.

A number of authors⁴⁻⁶ have noted that substrate surface roughness affects the ability of a PVD coating to provide adequate corrosion protection. For example, Durst, et al.,⁶ summarized research results that demonstrated that, as a substrate surface became rougher, the number of visible coating

defects increased, and therefore, the corrosion protection of the coating decreased. Liu, et al.,⁴ reported that a CrN PVD coating placed onto a steel substrate polished with 6- μm diamond paste provided significantly better corrosion protection than similar coatings deposited onto rougher substrates, while Phygen recommends that the substrate surface be as smooth as practical to optimize corrosion resistance using the APA process, with a super-fine finish of <0.2 μm being optimum.

Several authors have reported that nitriding of a substrate prior to the application of a PVD coating, which is referred to as a duplex treatment, increases substrate hardness and corrosion resistance.^{2,6} Nitriding involves the diffusion of atomic nitrogen into the surface of the steel to create a hard surface layer. Nitriding can be performed in several ways—using a gaseous or liquid source of nitrogen or via plasma ion nitriding.

Fenker, et al.,⁵ confirmed that duplex treatments of nitriding plus PVD coating can provide enhanced corrosion protection, but they suggested that conventional nitriding treatments, such as gas or liquid nitriding, might provide better corrosion protection than a nitride layer produced by plasma nitriding.

Summary

In summary, laboratory studies and commercial applications have demonstrated that PVD thin-film coatings can provide excellent corrosion protection to metal substrates, as long as the defect content in the coating is kept low. The APA process is one PVD technique that is capable of producing coatings with extremely low levels of defects, and testing by the U.S. Army has demonstrated that it can outperform conventional chromium treatments.

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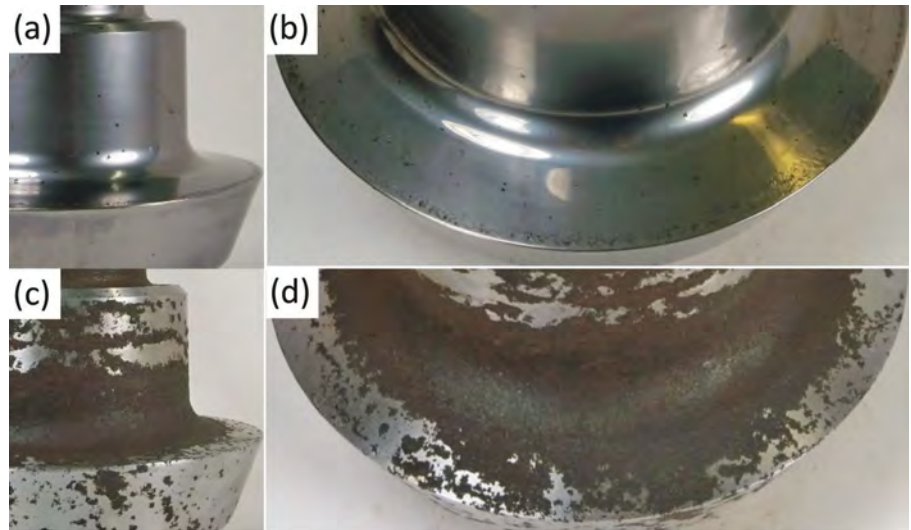


FIGURE 5 Photographs of the APA process CrN-coated spindle, (a) and (b), and the legacy Cr-plated spindle, (c) and (d), following extensive live fire and accelerated corrosion testing.

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