Industrial Dry Coating Technologies and Applications

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While electroplating remains the primary metal finishing technology today, recent years have seen significant growth in the use of dry coating and surface processing methods. This is driven partly by environmental concerns and, more strongly, by performance, while being frequently inhibited by cost. Major growth is occurring in the use of thermal spray for wear and corrosion protection, with vacuum coating (physical vapor and chemical vapor deposition, PVD and CVD) broadening its industrial usage outside its traditional applications for cutting tools. Various other specialized processes, such as laser and weld methods, are also finding niche applications in the marketplace, while others (such as ion implantation) have largely died out in the metal finishing industry. This paper will discuss various dry process technologies and their applications, together with the drivers and barriers for market acceptance. We will also discuss where we believe the surface finishing market is heading and where the different technologies will fit in the future.

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1. Introduction

Industrial finishing can be broadly split into two types of process

1. Aqueous processes, which include electro- and electroless plating, anodizing, chromate conversion, etc.
2. Dry processes, which include thermal spray methods, vacuum coatings, weld coatings, and heat treatments, with a huge number of variants of each general technology type.

Clean coating practitioners generally tend to think of aqueous tank processes as the outdated technology of the past and dry coating as the modern approach. But the real situation is not nearly as clear-cut. Certainly there are a growing number of applications where dry coating methods are taking over from the old standbys of hard chrome, Cd plate and electroless Ni. However, tank-based methods remain largely low-cost and there are many applications where tank plating methods have inherent distinct advantages that dry methods cannot readily overcome. The constant evolution both of electroplating, electroless plating, and other aqueous technologies and of the various dry coating technologies also changes the calculus of which approach will provide the best performance or most attractive cost-benefit for any given application.

This paper explores some of the benefits, limitations and applications of dry coating technology, comparing it with tank-based methods, and attempts to provide some guidance as to where the different approaches fit into the highly diverse applications for surface finishing.

2. Dry metal finishing processes

There are a great many dry metal finishing processes, the major categories of which are shown in Figure 1.

- Thermal spray is used for wear coatings (carbide composites for aircraft landing gear, industrial rolls and hydraulic actuators), and for corrosion protection of large structures such as concrete bridges and steel communications towers (Zn and ZnAl).
- PVD and CVD coatings are generally higher cost and tend to be used for small, high value items such as wear coatings on cutting tools and dies, erosion and thermal barrier coatings on turbine blades, as well as for abrasion-resistant decorative coatings on items such as pens, door hardware and plumbing fixtures.
- Various types of weld coatings (such as weld overlay, laser cladding and electrospark alloying) are used for different thickness of coating or repair, such as rebuilding eroded or corroded components. With its high

deposition rate, cold (or kinetic) spray is beginning to be developed for similar applications.

- In addition there are numerous heat treatments, including carburizing, nitriding, nitrocarburizing and metallization (aluminizing, boronizing, chromizing) that are widely used for surface enhancement. For example, most gears are carburized to resist wear, while many hot section turbine blades are aluminized for oxidation resistance.

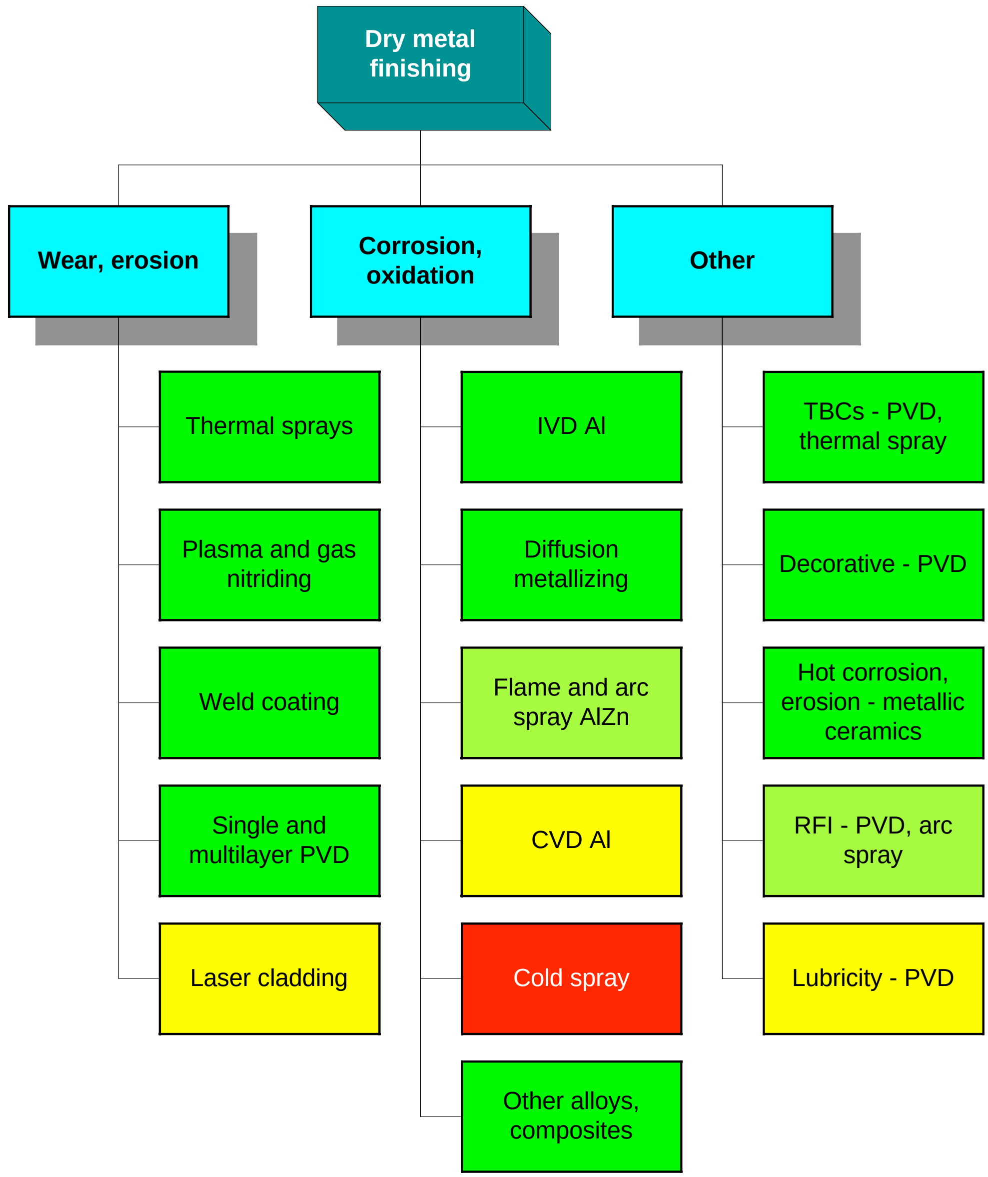

Figure 1 Dry coating technologies (commercial technologies in green, near-commercial in yellow, R&D in red).

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Dry processing has several advantages over traditional electro- and electroless plating:

1. Dry processing has great flexibility in the materials that can be deposited and the substrate materials that can be coated. A very broad range of exceptionally hard or corrosion resistant alloys, ceramics and composites can be deposited that cannot be directly electroplated by standard aqueous methods, such as WC for wear and Al for corrosion resistance (which can only be electroplated from an organic solution). Hard particles can be entrained in electro- and electroless plates, but process control is a major issue.
2. Because of its flexibility in the use of materials, dry processing permits much enhanced properties, especially wear resistance.
3. Improved material performance frequently improves system performance and significantly reduces life-cycle cost.
4. Dry coating avoids the large volumes of (usually contaminated) waste water needed to rinse electroplated parts.
5. The Environmental Safety and Occupational Health (ESOH) issues are generally much reduced with dry processing methods (avoiding worker exposure to Cr^{6+}, for example).

At the same time, dry processing has shortcomings that limit its appeal

1. The very flexibility of dry processes increases the complications of using them. The engineer who used to specify hard chrome for wear and Cd plating for corrosion must now have a much broader knowledge of the options in order to make the best decision, frequently leading to implementation problems.
2. Few dry processes can easily treat complex shapes and internals, which are much more readily treated by tank-based technologies.
3. Although they may have a higher life cycle cost (an estimated cost), tank methods usually have lower process and material cost (a clearly known cost).

3. Market drivers and barriers

3.1. Drivers

As with all materials technologies, the primary market drivers for changing surface finishing technology are cost and performance.

Cost:

As a general rule dry coating processing is more expensive than tank processing, but coating performance is higher, leading to lower cost of ownership. While most users pay lip service to cost of ownership, most purchasing decisions are based on processing cost. Processing cost (and hence purchase cost) is of course known when a purchasing decision is made, whereas cost of ownership is uncertain and the payback (if there is one) is usually several years. Changing the cost basis of purchasing decisions therefore requires a clear demonstration of improved life cycle cost as well as the development of credible cost models.

Performance:

In general in the aerospace industry performance has the highest priority, provided cost is reasonable, while in the automotive industry cost is the primary driver. However, performance not only encompasses lower wear and corrosion rates, but can also include other criteria important to the user. For example, one of the primary drivers for using HVOF on commercial aircraft landing gear is overhaul turnaround time, which can be reduced from days to hours because HVOF spraying of a typical landing gear cylinder takes up to an hour and requires no hydrogen bake, whereas chrome plating takes 24 hours and must be followed by a 23 hour bake.

Environmental:

For some years manufacturers have seen environmental pressures as only minor driver for changing surface finishing methods. In the last few years, however, it has become a major driver, with the advent of the End of Life Vehicles (ELV) rules in Europe, which has forced the automotive industry to eliminate Cd plate and Cr^{6+} conversion coatings from all vehicles. Even though these rules apply only to vehicles sold in Europe, they effectively cover the entire world since the automotive industry is global. The Restriction of Hazardous Substances (RoHS) rules, which became effective in July 2006, are having the same effect on electrical and electronic equipment[1]. Other ESOH drivers include the large volumes of waste rinse water required for aqueous processes and the impact of environmental regulations such as the recent OSHA PEL reducing Cr^{6+} emissions in the workplace by an order of magnitude[2].

Customer demand:

Customers are beginning to demand “green” products to meet corporate environmental responsibility mandates, or to create products that have lower cost of ownership. For example, Airbus requires that the new A380 be hard Cr- and Cd-free.

Availability:

Even those industries that are exempt from the rules, such as aerospace and medical equipment, are still affected by them since, as the rest of the industry shifts away from the use of chromates, Cd, etc. these technologies are expected to become less widely available. We are already seeing this in the area of lead-free solder; the aircraft industry can still use leaded solder, but it is effectively no longer available as most electronic components now use non-lead solder. As alternatives are demonstrated and qualified for exempt industries the exemptions will be removed, bringing them under the same restrictions.

Liability:
In addition to the environmental driver, there is also the issue of liability for health effects of some older technologies. Health liability has bankrupted many companies that manufactured asbestos or used it in products, and today we have a similar potential unfolding with the use of chromates, Cd and other surface finishes that are known to have deleterious health effects. Although these materials are widely used and perfectly legal, their use exposes manufacturers, maintainers and equipment owners to potential liability for adverse health effects many years into the future. Since the costs and probabilities are impossible to calculate they tend to be ignored, but at some point insurers and legal staffs are likely to recognize the danger and insist that their client companies minimize their risks by changing to clean technologies. This driver is weakened by the fact that there is almost no such thing as a risk-free material, and all that can be done is to limit, not eliminate, potential liabilities. For example, Cd is known to be a heavy metal poison, but its most common alternative, Zn, is a material of concern in Europe, while Ni (used in ZnNi alternatives to Cd) is also a health issue, and Al, the other alternative to Cd, has been linked to Alzheimer's disease.

3.2. Barriers

Adoption cost:
Cost of adoption is always a barrier to changing technology. This is especially true in industries such as aerospace that require extensive testing and qualification. Adoption cost includes extensive testing (sometimes including expensive engine tests and flight tests), configuration control, drawing changes, changes to contracts and maintenance procedures, retraining, etc. In addition there is the capital cost of installing equipment for the new process. The major barriers to the adoption of vacuum processes are capital and process cost, as well as the perception of them as high-cost options. Additionally, the requirement for a vacuum chamber limits the size of item that can be coated and imposes strict requirements on cleanliness.

Flexibility:
A further technical barrier to the use of dry coatings is that, unlike tank plating, most cannot easily coat internals and complex shapes. For example HVOF coatings have begun to replace hard chrome on external surfaces of aircraft landing gear, large hydraulic rods and industrial rolls. However, standard HVOF guns cannot be used for internal surfaces, which can comprise 30% of the use of hard chrome in aircraft overhaul. Recently new ID HVOF guns have come onto

the market, while a number of ID plasma spray guns are now available.

Availability:
Many new dry coating technologies are not readily available or are available only from a sole source. In addition, many companies, who are comfortable with in-house tank processes, are unwilling or unable to bring more complex processes in-house. Having to send items out to be processed increases cost and manufacturing time, and can pose serious quality control issues.

Specs and standards:
Another major barrier to the use of vacuum coatings is the lack of industry standards for them. All of the older platings are deposited according to specific industry and military standards, such as QQ-C-320, the military specification for hard chrome plating, because of the recognition that the coating is (or should be) essentially the same, regardless of the supplier. However, this is not the case in the vacuum coating industry. Although coatings such as TiN and ZrN have been used industrially for many years, each supplier prides himself on having a “better” coating than his competitors. For carbon coatings the spread in properties and performance is even wider. The result is that there is no AMS or other universally-recognized industry standard that can be called out on drawings, making it impossible for most design engineers to specify these coatings.

4. Future directions

4.1. Successes and failures

Why are some changes to dry processing so successful, while others, which seem just a good, gain no headway? The answer usually lies in a complex interplay of cost, performance, and fit with each market and the way each industry does business.

For example, HVOF WC-Co and WC-CoCr have replaced hard chrome plate on many new aircraft components, including landing gear and hydraulic actuators, while their market penetration for heavy machinery actuators is small. PVD coatings are far harder and more wear resistant – why have they not gained acceptance? There are a host of reasons, including

- **Cost –** While HVOF coatings are somewhat more expensive than hard chrome (up to about 50% more), their wear performance is much better, reducing cost of ownership.
- **Wide availability –** HVOF coatings are available from a great many suppliers. Most users do not coat in-house but do need a local (or reasonably accessible) supply chain. They are also wary of any coating that has only one or two suppliers.

- **Flexibility –** Because HVOF uses a room-size booth it can accommodate large sizes and fixturing is relatives straightforward. This is not the case with most vacuum processes.
- **Temperature –** HVOF coating is carried out below the 190°C (375°F) limit permitted for high strength aerospace steels. Many PVD and most CVD coatings exceed this temperature.
- **Specifications –** Initially aerospace engineers resorted to the Boeing specification BAC 5851 as the *de facto* industry standard[3]. SAE AMS (Aerospace Material Specifications)[4] have now been developed (AMS 2447 and AMS 2448 for spraying, and AMS 7881 and AMS 7882 for powder). This allows engineers to simply call out the process on drawings. There are no industry-wide process specifications for most vacuum processes.
- **Fit –** The HVOF process is similar to other thermal spray processes long used in the aircraft industry and therefore familiar to many engineers. Unlike the thin PVD coatings, HVOF coatings can be used to rebuild worn components. Also, very importantly, they can be stripped for inspection or replacement.

However, HVOF coatings have only recently begun to penetrate the general market for large hydraulic actuators. Partly this is due to the industry's lack of familiarity with thermal spray processes and lack of availability of the process from companies specializing in that industry. Furthermore, the process is proportionally more expensive than typical industrial hard chrome, which requires less quality control and paperwork than aerospace chrome.

There are, however, some very successful applications for PVD coatings. For example, most diesel engine fuel injectors are coated with a tungsten-stabilized form of diamond-like carbon (often referred to as WC-C). The coating provides the right combination of wear and lubricity, it has a very smooth finish, and it is used on a component that is relatively small and never needs to be serviced or rebuilt. The application therefore exploits the properties of the coating process very well.

Another very successful recent application of PVD coatings is the erosion-control coating of gas turbine engine compressor blades for military helicopters using a multilayer PVD technology developed in Russia and now used on T64 and T58 helicopter engines[5]. When used in desert areas helicopters create huge amounts of sandy dust that is ingested by their engines and erodes their compressor blades. Metals resist erosion quite well when the particles impact near normal incidence, but erode quickly at oblique incidence, while hard ceramics tend to crack and spall under normal incidence impact. However, turbine blades are a very complex shape, with different areas experiencing different types of erosion. The PVD coating approach alternates Ti and TiN layers to create multilayer structure that resists erosion much better than any single material. This approach exploits the ability of the method to create finely-tuned layers of different materials.

One of the more spectacular market failures of dry processing in recent years is ion implantation. Following its wide adoption by the semiconductor industry and early encouraging data for wear and corrosion protection, it was hailed as a major improvement in clean surface processing and numerous companies grew up to offer it. Now it is available from only a few companies worldwide. Despite its proven capabilities it gained little traction in the market. It offered no better performance than established PVD coatings that were similarly priced, performance was highly dependent on the chemistry and heat treat of the underlying material, and (very importantly in the marketplace) a treated component looked no different from an untreated one.

Another spectacular failure has been diamond and coatings. Given the cachet of diamond, these materials appeared to have a major market advantage (one science fiction book even predicted diamond-coated buildings[6]). They were proposed for all manner of abrasion, wear and corrosion applications, from tools to eye glasses. Today their use is limited primarily to crash protection layers for hard drives and wear coatings for diesel engine fuel injector rods. These coatings are highly stressed and brittle, and, except in very limited situations system performance has proved no better than with other PVD and CVD coatings. Because they were made with such a wide variety of methods, they had variable chemistry and performance. This lack of consistency no doubt contributed to disillusionment with the technology – another example of the need for industry-wide specifications and standards.

4.2. Short term changes

As environmental legislation increases the cost and risk of traditional tank-based finishing processes, there is a clear shift from chrome and nickel plating toward thermal spray (especially HVOF carbides). This technology, which is now replacing chrome plate in the aerospace industry for landing gear and hydraulics, is also beginning to penetrate the general hydraulic industry, including hydraulic actuator repair. All new aircraft landing gear programs, commercial and military, now specify HVOF WC-CoCr in place of hard chrome on most parts. Most users still apply the carbides (WC-CoCr and Cr_3C_2-NiCr), but these are too expensive and have far higher wear resistance than is really needed (or even desirable) for many industrial applications. They are more difficult to grind than hard chrome and require superfinishing[7]. We expect customer demand to drive the development of cheaper powders that may provide less wear resistance but be easier and cheaper to finish.

Even for aircraft landing gear and hydraulics, where performance is a key issue, we expect that more strain-tolerant HVOF coatings will be developed to meet user demand[8]. If this is not done, landing gear may once again move back to electroplating as more sophisticated electroplating technologies enter the marketplace. For many years electroplating has been a simple coating method that is relatively inexpensive to set up and easy to use, but traditional electroplating forgoes the higher level of process control and product performance that is possible through modern techniques such as pulse plating and confomal anodes. It is quite possible that, should new tank coatings such as pulse electroplated nCo-P show adequate performance[9], they will again replace HVOF on items such as landing gear and hydraulics, since they would allow OD and ID strain-tolerant coating using a single process.

For major structures such as bridges and communication towers, it has long been predicted that thermal spray coatings of Zn, AlZn and polymers will supplant standard paints, because of their much longer time between overhaul and consequent lower life cycle cost. However, this has failed to occur, partly because paint can so easily be applied and partly because the higher up-front process cost is a political issue for governments, who own most of the transportation infrastructure. We do expect some increase in the use of these newer technologies for structures that are privately owned, such as cell phone towers and ships. However, for large structures it is relatively easy to overcome the shortcomings of current paint schemes through the development of better surface preparation and paint chemistries, and we would expect the paint industry to fight any loss of market share through improvements in corrosion inhibitor chemistry and paint fillers for abrasion resistance (e.g. nanophase clay fillers).

With the proliferation of small electronic devices, there is increasing use of PVD coatings for radio frequency interference (RFI) coatings. These are usually applied by evaporation onto the internals of plastic and composite cases – a simple and inexpensive process.

Various kinds of PVD coatings are frequently put forward as ideal answers for applications where wear is the predominant failure mechanism, since these coatings are among the hardest attainable (e.g. diamond-like and B_4C coatings). In addition, both PVD and CVD coatings can be created in nanolayer form to create superhard materials[10]. In order for them to gain wide currency, however, it will be necessary to develop much larger scale and cheaper processes that are simple and highly reliable. These processes must encompass, not just the coating, but efficient and effective large scale cleaning and heating as well. Companies capable of doing this will have a strong market advantage. In order to achieve wider usage in the aerospace industry, where these coatings could have their highest potential, it will be necessary to develop industry standards, without which their market penetration will be very limited.

As the need for improved fuel efficiency drives changes in the transportation industries, we expect to see two primary changes

1. Improved methods for providing wear and corrosion protection to Al and Mg alloys.
2. Increased use of thermal barrier coatings (TBCs) to improve engine efficiency (for aircraft and industrial turbine blades as well as for internal combustion engines). These thermal barrier coatings will become increasingly complex in turbine engines, but it will also be necessary to develop inexpensive TBCs for automotive engines (piston heads, liners, valves).

There is increasing use of composites to reduced weight, especially in aircraft. However, they require coatings for RFI and to prevent galvanic corrosion between exposed carbon fibers and metallic airframe components.

4.3. Long term changes

In recent years much has been made of the move toward using nanophase technology for bulk materials and coatings. Their use is expected to grow wherever their properties provide a market advantage or offer a unique capability not available with other materials. While these technologies can offer greatly improved performance, their use is likely to be tempered by ESOH concerns over the health effects of nanoparticles. Although this is a concern for technologies that rely on the use of nanopowders (such as thermal sprays), it is not generally a concern for materials that are created in nanophase form (such as nanolayered PVD coatings).

In the long term, we expect to see increased integration of surface finishing and bulk component manufacturing. Coatings are usually the last item to be applied to the completed component (the metal finish). However, as net and near-net shape manufacturing become more widely used, it is natural to expect that the finish will become an integral part of the component, both to reduce cost and to make the finish more effective.

Partly, this will occur due to the increased use of what are generally thought of as coating technologies for net and near-net fabrication. For example,

- Some X-ray mirrors are currently fabricated by electroplating onto a mandrel that creates the outer surface shape and finish, thus manufacturing the item back-to-front – outside first, then building the bulk behind it. This eliminates the need for surface profiling or polishing.
- Similar mandrel-coating methods have been used to fabricate helmets by thermal spray.
- Metal stamping dies, plastics molds and superalloy turbine engine casings are made by spray forming.

- Turbine blades and other 3-D components can be near-net formed by laser cladding.

In an obvious extension of this approach one could create the surface finish first, by building the component back-to-front from a mold, or one could create the surface last, using precision deposition methods, such as highly controlled laser cladding, so as to manufacture near enough to net shape that the final finishing would not erase the outer surface.

5. Conclusions

The marketplace will continue to have room for both dry and wet coatings, depending on the application. While dry coatings will continue to gain market share in applications that exploit their ability to provide improved performance or reduce ESOH impacts, tank plating technologies will remain the best choice for applications such as internals and complex shapes. As plating technologies are improved by such modifications as pulse plating, composite plating and conformal anode plating, we expect to see them maintain their hold on many applications, and in some cases replace dry coating technologies where process simplicity gives them a clear advantage.

In the future we expect the industry to continue to move toward dry coating in those areas where it offers a clear advantage, but it will be inhibited by the lack of specifications and standards as well as capital and process costs and the large installed base of plating capability. As industry moves increasingly toward net and near-net fabrication we expect that surface coatings will become integrated into the total fabrication process.

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