PHYSICAL VAPOR DEPOSITION WEAR RESISTANT AND DECORATIVE COATINGS

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Physical Vapor Deposition (PVD) includes vacuum evaporation, sputtering, and ion plating. PVD processes are used to apply functional hardcoatings and decorative thin films. The most widely used coating is titanium nitride (TiN). Other coatings successfully commercialized include titanium carbonitride (TiCN), chromium carbide (CrC), chromium nitride (CrN) zirconium nitride (ZrN), and titanium aluminum nitride (TiAlN). Coating applications include cutting and forming tools, and plastic molds. CrC and CrN can be a direct replacement for chromium plating for decorative applications. Coatings are applied to prostheses as well as surgical instruments. There are a wide range of decorative applications. PVD coating processes, properties of coatings, and commercialized applications are reviewed.

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Physical Vapor Deposition

Physical Vapor Deposition describes a family of coating processes. PVD produces surface layers that are the result of the deposition of individual atoms or molecules. All PVD processes are carried out under a hard vacuum. Workpieces are heated to temperatures generally less than 500°C (930°F). Heating is done to enhance coating adhesion.

PVD includes evaporative and sputtering processes. During sputtering, argon is admitted into a vacuum chamber at relatively low pressure. A DC high voltage is applied to the target which creates a gas discharge between the target and substrate holder. Argon ions that have been created during the discharge strike the target with high energy. The ions free atoms from the target which are then transported to the substrate. These atoms become deposited as a thin film.

PVD evaporative processes consists of heating a source material in a high vacuum. This produces a vapor. The vapor condenses on the substrate as a thin film. Ion plating, which is an evaporative PVD process, uses an electron beam gun to melt the source. The introduction of an inert gas at low pressure creates a plasma discharge between the source and the substrate. The ions impinge the substrate surface during deposition resulting in changes in the interface region, and improving film properties. A negative bias on the substrate enhances coating adherence. To produce compound coatings, the ions are reacted with a gas (like nitrogen or methane) to produce a nitride or carbide. This process is known as reactive ion plating.

All PVD processes are line-of-sight processes. To obtain coating uniformity, it is necessary to use specially shaped targets or multiple vaporization sources and to rotate or move the substrate uniformly to expose all areas to the coating source.[1]

Functional hardcoatings are typically deposited by evaporative type coating PVD processes. Thin films for decorative applications are applied by sputtering processes, although either process may be adapted for either category of coatings. Characteristics of PVD coating processes are shown in Table I.

In order to achieve good coating adherence it is necessary for substrate surfaces to be free from any contamination. The slightest amount of grease, dust, grinding burn, and finger prints can result in poor adherence. Parts to be PVD coated are normally first bulk cleaned in multi-station ultrasonic cleaning lines. The cleaning line includes a series of wet chemical rinses, usually detergents or solvents. Ultrasonics are used to activate the surface of the components being cleaned and assist in removal of contaminants. Drying of parts is necessary to eliminate any water spots. Hot air dryers are equipped with micropore filters to prevent dust from depositing on the cleaned surfaces. While most precoating cleaning methods are satisfactory, some parts that are to be coated cannot be adequately cleaned. If components have been treated with a plastic rust preventive or salt bath heat treated where residual salt remains on the surfaces, special cleaning methods may be required to promote good coating adherence.

Physical Vapor Deposition
1. Low temperature coating process carried out at less than 500°C (930°F).
2. No post coating heat treatment.
3. Functional coatings deposited to 2 to 5 microns thick; decorative coatings about 0.2 to 0.5.
4. Mechanical bond formed between the coating and substrate surface.
5. Coating process replicates the surface finish of component onto which it is deposited.
6. Process maintains sharp corners; no build up on corners as with electroplating processes.
7. Broad range of materials can be deposited onto a wide variety of substrates.
8. Tight tolerances can be maintained.
9. Process is suitable for coating brazed materials.

Table I: Characteristics of PVD coating processes.

Properties of Hardcoatings

PVD allows for the deposition of a wide variety of elements and compounds. Refractory materials may be deposited at temperatures below their melting point. For sputtering processes, virtually any material may be deposited (provided that it is available as a target). Compounds deposited by evaporative reactive ion plating are limited by the ability of the source metal to be conveniently vaporized.

For functional applications, the coatings are deposited to a thickness of 2 to 5 microns. (Deposition to a thickness greater than 5 microns does not usually enhance coating performance.) Decorative coatings are generally 0.2 to 0.7 microns thick.

The structure of deposited thin films determines their properties, including color. Properly applied coatings deposited by physical vapor deposition replicate the surface onto which they are deposited. A coating that is deposited on a smooth, highly polished surface will have a mirror-like appearance. The same coating deposited on a matte finished surface (for example, a surface that has been vapor honed) will in turn have a matte finish.

Element	Material	Film Color
Nitrogen	TiN ZrN TiAlN CrN	Gold (Yellow) Gold (Green) Violet/Black Silver
Carbon	TiC CrC	Silver/Gray Silver
Carbon + Nitrogen	TiCN	Bronze/Gray

Table II: Common compounds reacted from metallic elements and nitrogen and carbon.

The harder a material, the better its resistance to abrasion. Table III is a comparison of the hardnesses for different functional hardcoatings and commonly used substrates.[2]

Material	Hardness (HVN)
Titanium Carbide	3400
Vanadium Carbide	2800
Titanium Nitride	2600
Niobium Carbide	2400
Chromium Carbide	2200
Cemented Carbide	1600
Chromium Nitride	1600
Tool Steel	900

Table III: Hardnesses of different functional hardcoatings.

TiN, the most common function hardcoating is shiny gold in color and has a hardness of 2600 HVN. The coating acts as a chemical and thermal barrier between the surface onto which it is deposited, and the environment. TiN has a low coefficient of friction that helps to prevent galling and metal pick-up. TiC is among the hardest of the coatings deposited by PVD. It is silver-gray in color, often resembling the metallic surface of the uncoated component onto which it is deposited. TiCN ranges in color from bronze to silver-gray. The color is determined by the amount of carbon present in the compound. The more carbon, the grater the tendency of the coating to appear gray in color. As a decorative coating, TiCN was developed for its close resemblance to bronze. For functional applications, TiCN is used for machining stainless steel, high hardness steels and high alloy materials. CrC is silver in color. When titanium or aluminum alloys are machined with tools coated with TiN, there is a tendency of the aluminum to chemically react with the nitrogen in the coating. This causes the tool to pick-up metal. CrC is effective for machining aluminum as it is difficult to form aluminum carbide. Titanium alloys, like Ti-6Al-4V contain aluminum, hence CrC is effective for machining these materials as well. CrN is also silver in color, and can be an excellent substitute for chromium plating. This is a significant benefit of PVD coatings, as there are no environmental concerns associated with these processes. ZrN ranges from yellow-gold to brass in color, depending upon its stochiometry. It has mechanical properties similar to TiN. While not commercially popular as a functional coating, its use as a decorative coating, particularly on brass hardware is extensive. TiAlN is violet/black in color. When used on cutting tools, it is believed that the aluminum in the coating oxidizes, providing high temperature protection to the tool, thereby extending tool life.

PVD Coating Applications

Cutting Tools

Among commercial applications for PVD coatings, cutting tools are among the most significant. Improvements in tool life for PVD coated tools range from two to eight times over uncoated tools

Tools that are routinely PVD coated for extending their tool life include:

Taps	Milling Inserts
Drills	Gear Cutting Hobs
Reamers	Shaper Cutters

End Mills	Broaches
Dovetail Form Tools	Circular Form Tools
Threading Tools	Routers
Counter Sinks	Counter Bores
Saws	

The coatings discussed above have in common abrasion resistance, adhesion resistance, excellent lubricity and corrosion resistance.

PVD Coating	Recommended Machining Applications
TiN	Free machining steels and irons, high strength steels, plastics, hard rubber.
TiCN	Tough machining steels, cast iron, abrasive materials.
CrC	Aluminum and titanium alloys.
TiAlN	Cast irons, abrasive materials, dry machining.

Table IV: Machining applications for TiN, TiCN, CrC, and TiAlN.

PVD coatings are not only applied to high speed steel cutting tools but to cemented carbide inserts as well. The use of PVD coatings to protect carbide milling and turning inserts is growing with virtually all inserts receiving a protective coating (either CVD or PVD). Features of the coatings that allow them to enhance the performance of cemented carbide tools include the following:[3]

1. The smooth surface finish of the coatings coupled with their thermal insulating properties generate less heat during machining, hence prevent the cutting edges from breaking down.

2. The low temperature of deposition preserves the transverse rupture strength of the carbide as well as prevents the formation of eta phase, a carbon-lean brittle phase. Both conditions can lead to premature tool failure.

3. PVD coatings can be applied to sharp corners, resulting in lower cutting forces.

Properly designed cutting tools fail by wear, either adhesive or abrasive. PVD coated thin films act as a chemical and thermal barrier between the tool and workpiece. The hardness of the coating provides abrasive wear protection; the chemical stability provides protection from adhesive wear. One of the more interesting applications for coatings on cutting tools are tools used in the wood working industry. The coating adds chemical resistance to the surface of the tool preventing bonding of resins and in the case of plywood, binders, from bonding to the tools.

The improvement in life generally observed for PVD coated cutting tools is a minimum two to eight times over uncoated tools. The real significance of the coatings however, is the associated increase in productivity and enhanced manufacturing economics. For the case of manufacturing automotive gears, PVD coatings on gear hobs, shapers, and broaches have reduced tooling costs significantly. Several automotive companies have installed their own PVD coating equipment to take advantage of recoating. Recoating sharpened, coated tools allows for the recapture of tool life that is lost by removing the coating from the cutting edges during the sharpening process.

An additional feature of the coatings is that they are generally applied in compression. The compressive stresses associated with the thin films serves to increase the fatigue strength of the components. It is common to apply PVD coatings as multilayered films to take advantage of the differences in compressive stresses of the individual layers. These differences allow cracks to blunt at interfaces, rather than propagate through the coating, delaying the onset of tool failure.

The benefits of PVD coatings on cutting tools can be summarized as follows:[1]

1. Extended Tool Life: Improvements in tool life as great as eight times over uncoated tools are commonly observed.

2. More Regrinds: The coating does not flake and maintains adhesion throughout the entire life of the tool, even under severe wear conditions. The coating remains secure on rake faces and wear lands that permit minimal stock removal for sharpening. Less material is removed per sharpening, at least 30%.

3. Increased Cutting Speeds and Feeds: Speeds and feeds can be significantly increased over uncoated tools, in some cases by as much as 50%.

4. Improved Surface Finish: The chemical resistance of the coatings prevents welding of the tool to the workpiece. This means that galling and tearing are effectively eliminated, producing better finishes.

5. Increased Up-time: Coated tools last longer. They stay in the machine longer than their uncoated counterparts. There is more time between sharpening and regrinds, therefore up-time is increased.

6. Part Tolerances: Coated tools do not wear as quickly as their uncoated counterparts, hence they hold tolerances longer. Tool life is not dictated by wear of the tool, hence the tolerance distribution is much tighter for the coated tools.

Metalforming (Punches and Dies)

Coatings are commonly applied to the surfaces of punches and dies to extend their life. The low coefficient of friction associated with the coatings, allows for the reduction and elimination of the use of die lubrication and draw compounds. As the cost associated with degreasing to remove residual draw compounds increases due to environmental impact, the use of coatings for these applications is becoming more important.

Operation	Uncoated	TiN - PVD Coated
Forming AISI 8620 steel sockets using CPM T-15 hex head punches.	20,000	40,000
Punching low carbon steel sheet with M-4 piercing pins.	150,000	750,000
Pierce and Shave 1/4" thick 1095 steel with M-4 tools.	25,000	125,000
Manufacturing spark plug bodies, using solid carbide punches.	4,000	12,000
Forming seat belt latches, M-2 fine blanking punches.	25,000	65,000

Table V: Typical production results for TiN - PVD coated stamping tools.

Table V shows is a summary of selected applications showing tool life improvement for TiN coated tools used in the metal stamping industry.[5]

As is the case with metal cutting, the improvements in tool life and productivity are significant. The chemical resistance of the coatings provides protection from galling and metal pick-up, which can lead to premature tool failure. PVD coatings are applied at low temperatures, normally below the tempering temperature of steels used to make punches and dies. This means that tool dimensions do not change as a result of the PVD coating process. Fine blanking tools and other tightly toleranced stamping tools are excellent candidates to benefit from PVD coatings.

Plastic Molds

TiN and TiCN are used in the plastic mold industry, protecting molds, gates, screws, tips, core rods, and other associated mold components. Many plastics are abrasive, particularly those using glass-filled resins. The hardness of the coating provides abrasion resistance to mold surfaces, enhancing performance. Polycarbonate plastics, such as those used for optical applications, are particularly corrosive. The use of TiN and TiCN for the production of clear plastic lenses has provided a tool life performance of up to eight times. When the TiN coating has worn away, it is evident to the operator. This is not the case with chromium plating. TiN and TiCN may be nondestructively removed, allowing the tool to be repolished, and then recoated to provide additional life improvements. The coating perfectly replicates the high polish required for the optical finish associated with the molded products.

An additional plastic mold application is the protection of compact disc mold (mirror block) surfaces. The coatings replicate the surface onto which they are deposited. Compact discs require an extremely high surface finish particularly for retention of data on molded surfaces. The molds must have excellent release properties. Careful polishing is carried out to produce a surface that is flat and parallel with a 0 RMS finish. Visual inspection utilizing low powered microscopes ensures that all surface imperfections have been removed. Compact disc mirrors and other associated mold components are normally coated using reactive ion plating. This process ensures that the coating produced is free of porosity and defects. The use of TiCN in place of TiN for this application is growing. The higher hardness of TiCN is providing significant mirror life improvements over components that were formerly TiN coated.

Aluminum Die Casting Molds

CrC has demonstrated to be an effective coating for protecting aluminum die casting molds. The corrosion resistance of this coating serves to delay the onset of soldering that is a common failure mode for die casting molds. Reported improvements in tool life for CrC coated molds, core pins, and related hardware is on the order of three times that of uncoated components. The high oxidation temperature of the coating coupled with its hardness also aids in improving mold component life.

Wear Components

There are numerous applications for thin film PVD coatings as wear coatings. These include coating gears and bearing surfaces. Additional applications exist in the automotive industry, such as antilock brake system (ABS) and fuel (gasoline and diesel) injector components. Coatings have improved properties over traditional steel surface treatments like carburizing and nitriding. The large quantity of components available for coating has also served to reduce the price per piece for the coating making economics attractive. Additional uses for the coatings are chemical ball valves and seats to provide corrosion and abrasion resistance, and jet engine compressor blades where the coatings provide enhanced erosion resistance.

Medical Applications

The combination of mechanical properties of TiN, particularly wear and corrosion protection has led medical researchers to apply TiN and other coatings onto prosthetic implants. An additional benefit of the PVD coating process is that the coatings are applied in compression. Increasing the compressive strength of components results in a corresponding improvement in low cycle fatigue life. When coated, prosthetic implants, like hips, knees, and other joints have shown a three times improvement in life. This is significant when considering the age of patients who undergo joint replacement surgery.

Other applications in the medical industry include surgical tools where the combination of high hardness and corrosion protection play a key role in extending the life of these tools. Due to glare present in the operating theater, significant to the success of coatings is the requirement that they be non-reflective.

Decorative Applications

The use of PVD for decorative applications is increasing and is driven by a number of factors. These include:

1. The ability to compete favorably on an economic basis with decorative electroplating processes, particularly in light of environmental considerations.
2. Production of a broad range of colors.
3. Corrosion resistance equivalent to or better than that of the coating processes being replaced.
4. Use of less expensive substrates.

The list of decorative applications for PVD coatings is extensive. These include watch components including bands, jewelry, eyeglass frames, cigarette lighter cases, pen parts (barrels, clips), knives, and other accessories. Also included in this list are brackets used for orthodontic braces, where gold is a desired alternative to the silver colored stainless steel typically used for these components.

Among the driving forces for PVD coating over traditional electroplating processes are environmental considerations. PVD processes are environmentally safe, with virtually no pollution produced by the process.

One of the more interesting and widespread applications is brass hardware, particularly door and window hardware and faucet parts. While brass hardware is attractive, the corrosion resistance of brass is somewhat limited. Unlike copper, which develops an attractive and uniform green patina on weathering, brass turns a dull dark brown. In order to maintain the attractive finish of highly polished brass hardware, it requires continual polishing. The recent introduction of zirconium nitride PVD coating onto brass hardware has allowed suppliers of these components to offer "lifetime" guarantees on surface finish. When deposited to the appropriate stochiometry, ZrN has a finish that perfectly matches that of brass. It has excellent corrosion resistance, and therefore performs well in the application.

Another interesting decorative application for PVD coatings is the coating of jewelry. TiN has an appearance that resembles gold. It has the further advantage of abrasion resistance. Substituting stainless steel for gold offers a significant cost saving.

Stainless steel has high hardness, and excellent corrosion resistance. TiN coating the stainless steel jewelry provides the desired color and durability needed for the application.

PVD coatings based on chromium, particularly CrC and CrN to replace chromium plating, is being explored. The PVD coatings provide corrosion protection and resistance to wear, and when deposited on polished surfaces have a high luster. CrC and CrN coatings are replacing chromium coatings in metalcutting, predominantly driven by the expense of dealing with plating solution disposal. It is anticipated that these applications will continue to grow as environmental concerns become more critical.

Conclusion

Physical Vapor Deposition (PVD) is being used to deposit functional and decorative thin films. A wide variety of coatings can be deposited. These include titanium nitride (TiN) titanium carbonitride (TiCN), zirconium nitride (ZrN) and chromium carbide (CrC). Important mechanical properties of the coatings include high hardness, low coefficient of friction, and chemical resistance. This makes them suitable for a wide range of applications.

Applications for PVD coatings range from the those in the metalworking industry for cutting and stamping tools, to the medical industry, for implants and surgical tools, to decorative applications. Decorative applications include watch components, door and window hardware, plumbing fixtures, eyeglass frames, and pen components. As environmental concerns regarding plating processes become greater, the use of PVD coating will grow, finding new applications for the coatings and processes.

References

1. D. M. Mattox, "Ion Plating", *ASM Handbook, Vol. 5, Surface Engineering*, 1994, p. 582-591.
2. Daido Steel Co., Ltd., Machinery Division, "Technical Trends in Color Coatings", *Leybold AG Decorative Hard Coatings Symposium*, April, 1989.
3. A.T. Santhanam, and D.T. Quinto, "Surface Engineering of Carbide, Cermet and Ceramic Cutting Tools", *ASM Handbook*, Vol. 5, Surface Engineering, 1994, p. 900-908.
4. R. Badger, and M. Podob, "PVD Hardcoatings for Improving the Performance of Broaches," *Broaching Technology SME Technical Seminar*, April, 1995.
5. J. H. Richter, and M. Podob, "CVD and PVD Hardcoatings for Extending the Life of Tools Used in the Stamping Industry", *Manufacturing Solutions*, Vol.2, Metalform'92 Technical Symposium Proceedings, Feb. 1992, p. 337-349.