~~FMP 2371~~
PLATING

~~P 05636~~
27102

PHYSICAL VAPOR DEPOSITION CORROSION AND WEAR RESISTANT HARDCOATINGS

Mark Podob
Vice President
Richter Precision Incorporated
E. Petersburg, Pennsylvania

Presented at:
FINISHING '95 CONFERENCE AND EXPOSITION
September 18-21, 1995
Cincinnati, Ohio

Physical Vapor Deposition

1. Low temperature coating process carried out at less than 500°C (930°F).
2. No post coating heat treatment required.
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 1: Characteristics of PVD coating processes.

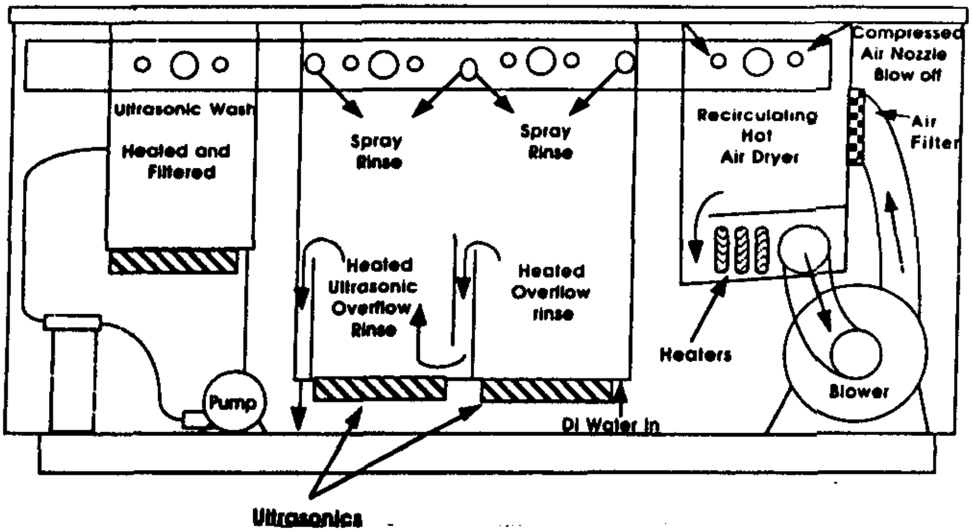

Figure 2: Schematic of an ultrasonic cleaning line used to prepare parts for PVD coatings.[2]

Results are poor when components have been treated with a plastic rust preventive, or salt bath heat treated where residual salt remains on the surfaces to be coated. These conditions can present problems for PVD coating.

PROPERTIES OF HARDCOATINGS

PVD processes, particularly sputtering, allow a variety of elements and compounds to be deposited. Compounds deposited by evaporative reactive ion plating are limited by the ability of the source metal to be conveniently vaporized.

The structure of the thin films determines their properties, including color. In general, thin films 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.

Element	Material	Color
Nitrogen	TiN	Gold (Yellow)
	ZrN	Gold (Green)
	HfN	Gold (Yellow)
	VN	Light Brown
	V_3N	Gray Brown
	WN	Brown
	TiAlN	Brown (Violet)
	Ta_2N	Gray-Black
	MN*	Gray-Black
	M_2N**	Gray-Black
Carbon	Be_2C	Red
	CeC_2	Yellow
	NbC	Light Brown
	TaC	Amber
	TiC	Gray-Black
	WC	Gray-Black
	ZrC	Gray-Black
	C	Gray-Black
Carbon + Nitrogen	TiCN	Brown
Boron	BeB_2	Brick Red
	MnB	Red Brown
	MnB_2	Red Brown
	ThB6	Red Violet
	LaB_6	Red Violet, Blue
	CaB_6	Gray-Black
	SrB_6	Gray-Black
	BaB_6	Gray-Black
	UB_6	Gray-Black
	MB_6***	Blue

* M = Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu
** M = La, Ce, Pr, Nd, Sm, Cr, Mn
*** M = Ta, W, Sr, Ba

Table 2: Common compounds reacted from metallic elements and nitrogen, carbon, and boron.[3]

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.

PVD includes both sputtering and evaporative processes. Sputtering is defined as the transport of a material from a source (i.e., a target) to a substrate by bombardment of the target by gas ions. These ions have been accelerated by a high voltage. Atoms from the target are dislodged by momentum transfer between the incident ions and the target. Particles that are ejected from the target move across the vacuum chamber and deposit on the surface of the substrate. PVD evaporative processes involve the transfer of material to form a coating by vaporization. The vapor is generated by the melting and evaporation of a solid metal. Generally an electron beam gun is employed to melt the source. In the case of compound coatings, the ions are reacted with a gas (like nitrogen or methane) to produce a nitride or carbide. The processes are further accelerated by activating the sputtered or evaporated ions by an electrical glow discharge plasma. With either process, coating adherence is enhanced by applying a negative bias on the workpiece. 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 of move the substrate uniformly to expose all areas.

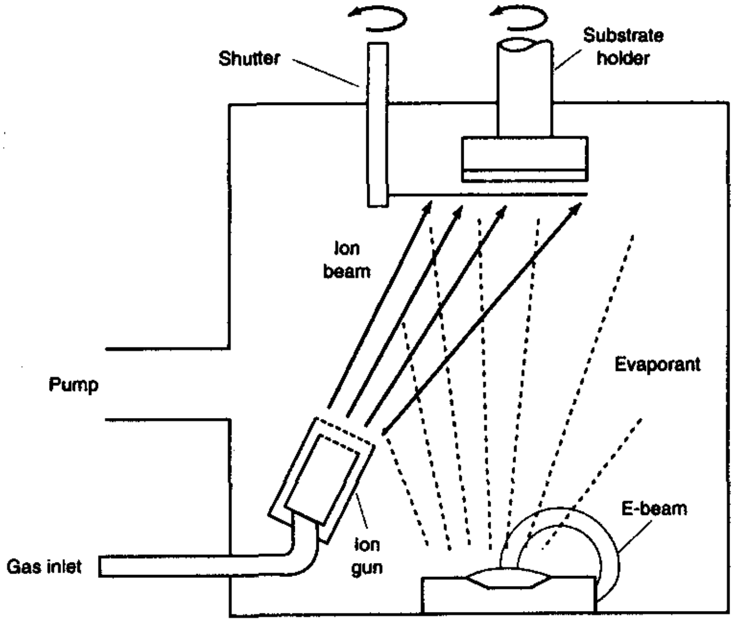

Figure 1 is a schematic of a vacuum ion plating installation. An electron beam gun is typically used to melt and vaporize the metal source.[1] An ion gun is used to ionize the reactant gases (nitrogen, methane, or hydrogen diboride). The reactant gases combine with the vaporized metal to form the coating.

Most functional hardcoatings are deposited by evaporative type coating PVD processes. Thin films for decorative applications are generally applied by sputtering processes. Characteristics of PVD coatings and processes are shown in Table 1.

Coating adherence is promoted by surfaces that are free from any contamination. This includes grease, rust, grinding burn, and even finger prints. Parts to be PVD coated are cleaned in a multi-station ultrasonic cleaning line. The cleaning line includes a series of wet chemical rinses (Figure 2). Ultrasonics activate the surface of the components being cleaned and assist in removal of contaminants. Drying of parts is used to eliminate any water spots. Dryers contain filtration to enhance cleaning, removing dust particles from recirculated hot air. While most precoating cleaning methods are satisfactory, some parts that are to be coated cannot be adequately cleaned.

INTRODUCTION

Physical Vapor Deposition (PVD) is a group of coating processes used to apply functional hardcoatings and decorative thin films. These coatings include titanium nitride (TiN), titanium carbonitride (TiCN), zirconium nitride (ZrN), and chromium carbide (CrC). The coatings are very hard, have a low coefficient of friction, and are chemically resistant. When applied to different components they act as chemical and thermal barriers.

For functional applications, the coatings are deposited to a thickness of 2 to 5 microns. For decorative applications, the coatings are generally 0.2 to 0.5 microns thick. TiN is shiny gold in color and has a hardness of 2400 - 2800 HVN. TiCN is bronze in color, harder than TiN, and is used for more abrasive applications. ZrN resembles brass and is used extensively on brass to provide a corrosion resistant, decorative finish. CrC is silver in color, and has an additional advantage of high temperature oxidation resistance. The coatings are applied as either discrete single or multiple layers to provide different benefits depending upon the application.

PVD coatings have found applications in a variety of industries. In the metalworking industry, TiN is commonly used to extend the life of cutting and forming tools. TiN is a replacement for chromium and electroless nickel plating commonly used on plastic molds, gates, and other components. Due to its shiny silver color, CrC can be a direct replacement for chromium plating for decorative applications. In the medical industry, the coatings are applied to prostheses as well as surgical tools. There is a wide range of decorative applications including watch components, eyeglass frames, pen components, door and window hardware and plumbing fixtures.

PHYSICAL VAPOR DEPOSITION

Physical Vapor Deposition is a term used to describe a family of coating processes. These processes are characterized by the production of a surface layer that is the result of the deposition of individual atoms or molecules. All PVD processes are carried out under a hard vacuum, with workpieces heated to temperatures generally less than 500°C (930°F). Heating the substrate enhances the adhesion of the coatings.

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. The ability to provide a broad range of colors, and
3. Obtain corrosion resistance equivalent to or better than that of the coating process 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. The 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.

SUMMARY

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. Mattox, Donald M., 'Ion Plating", *ASM Handbook, Volume 5, Surface Engineering*, 1994, p. 582-591.
2. Crest Ultrasonics *Product Bulletin #550*.
3. Daido Steel Co., Ltd., Machinery Division, 'Technical Trends in Color Coatings", *Leybold AG Decorative Hard Coatings Symposium,* April, 1989.
4. Santhanam, A.T. and Quinto, D.T., 'Surface Engineering of Carbide, Cermet and Ceramic Cutting Tools", *ASM Handbook, Volume 5, Surface Engineering*, 1994, p. 582-591.
5. Badger, R. and Podob, M., 'PVD Hardcoatings for Improving the Performance of Broaches," *Broaching Technology SME Technical Seminar*, April, 1995.
6. Richter, J.H., and Podob, M., 'CVD and PVD Hardcoatings for Extending the Life of Tools Used in the Stamping Industry", *Manufacturing Solutions, Volume 2, Metalform'92 Technical Symposium Proceedings*, Feb. 1992, p. 337-349.

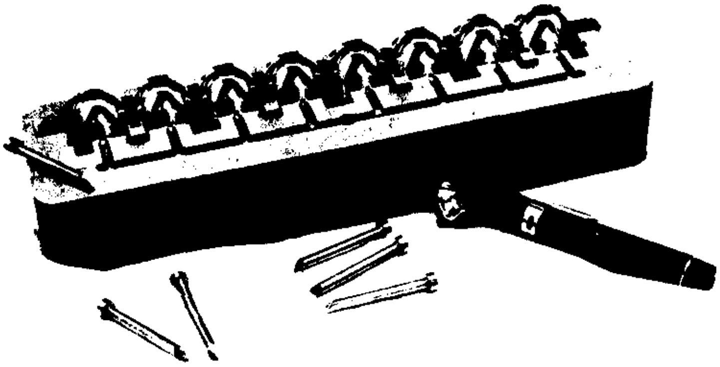

Figure 3: Photograph of mold component used for production of optical quality plastic components.

mirrors are normally coated using reactive ion plating. This process ensures that the coating produced is free of porosity and defects.

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 chemical stability 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. These include antilock brake system (ABS) and fuel injector components. The 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 include the coating of 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 normally 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

PUNCHES AND DIES

Coatings are commonly applied to the surfaces of punches and dies to extend their life. In the metal stamping industry, the low coefficient of friction associated with the coatings, a result of their corrosion and oxidation resistance, 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. Table 4 shows is a listing of tool life improvement for TiN coated tools used in the metal stamping industry.

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 4: Typical production results for TiN - PVD coated stamping tools.[6]

MOLDS (PLASTIC AND DIE CASTING)

TiN is used extensively 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, like 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. Unlike chromium plating which is silver in color, when the TiN coating has worn away, it is evident to the operator. The coating can be nondestructively removed, the tool repolished, and then recoated to provide additional life improvements. Figure 3 is a photograph of a plastic mold cavity and core pins coated with TiN. The coating perfectly replicates the high polish required for the optical finish associated with the molded products.

An additional significant plastic mold application is the protection of compact disc mold surfaces. The coatings completely replicate the surface onto which they are deposited. The molding of compact discs requires an extremely high surface finish. Careful polishing is carried out to produce a surface that is flat and parallel with a finish better than 0 RMS. Visual inspection utilizing low powered microscopes ensures that all surface imperfections have been removed. Compact disc 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:[5]

1. Extended Tool Life: It is not uncommon for the improvement in tool life to be up to eight times that of uncoated tools.
2. More Regrinds: The coating does not flake and maintains adhesion throughout the tool life, 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.
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.

Table 3 is a listing of the three most common functional hardcoatings used for metalworking and their recommended machining applications.

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

Table 3: Machining applications for the TiN, TiCN, and CrC, the three most common functional hardcoatings applied to cutting tools.

Metallic compounds have an inherent color based upon their metallic structure. Table 2 lists the structure of common metallic compounds as found in powder form. When these same compounds are deposited by PVD, they have similar, although slightly different coloration.

Among the compounds deposited for functional applications, TiN is the most popular. It is a hard, chemically inert compound. The coating is shiny gold in color and has a hardness greater than 2400 HVN (about 80 HRC). 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.

In general, the harder a material, the better its resistance to abrasion. TiC is among the hardest of the coatings deposited by PVD. It is characteristically 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 of this coating is influenced by the amount of carbon present in the compound. 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 that causes the tool to pick-up metal. This is especially the case when heat is generated by the machining operation. CrC is effective for machining these materials as chromium carbide is more chemically stable than aluminum carbide. ZrN ranges from yellow-gold to brass in color, depending upon its stochiometry. It has mechanical properties that lie between those of TiN and TiCN. It is not commercially popular for functional coating, however its use as a decorative coating, particularly on brass hardware is extensive.

APPLICATIONS

Cutting tools are among the most common applications for PVD coatings. Typical cutting tool applications are shown below:

Taps
Drills
Reamers
End Mills
Dovetail Form Tools
Threading Tools
Counter Sinks
Saws
Carbide Milling Inserts
Gear Cutting Hobs
Shaper Cutters
Broaches
Circular Form Tools
Routers
Counter Bores

The coatings discussed above have in common abrasion resistance, adhesion resistance, excellent lubricity and corrosion resistance. Features of the coatings that allow them to enhance the performance of cemented carbide tools include the following:

1. The smooth surface finish of the coatings coupled with their thermal insulating properties generate less heat during machining, hence protect the cobalt binder.
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.[4]

The primary failure mode of most cutting tools is either adhesive wear or abrasive wear. When deposited on cutting tools, PVD coated thin films serve as a chemical and thermal barrier between the tool and workpiece. The improvement in life generally observed for PVD coated cutting tools is on the order of a minimum two to eight times over uncoated tools. The real significance of the