

Cambridge University Press

978-0-521-10355-8 - Mechanical Properties, Performance, and Failure Modes of Coatings

Edited by T. Robert Shives and Marshall B. Peterson

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SESSION I

NEW COATING TECHNOLOGIES

CHAIRMAN: W. WINER

GEORGIA INSTITUTE OF TECHNOLOGY

Cambridge University Press

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## A REVIEW OF COATING TECHNOLOGY

S. Ramalingam  
University of Minnesota  
Minneapolis, Minnesota 55455

**Abstract:** Friction- wear-induced mechanical failures may be controlled to extend the life of tribological components through the interposition of selected solid materials between contacting surfaces. Thin solid films of soft and hard materials are appropriate to lower friction and enhance the wear resistance of precision tribo-elements. A variety of thin film coating technologies have been developed to deposit thin solid layers to reduce friction or to extend wear life. They include chemical vapor deposition (CVD) and physical vapor deposition (PVD) processes.

A particular advantage offered by the newer coating processes is that they allow close control of coating thickness and composition not possible with many of the older and traditional processes. Moreover, they allow well-bonded thin films to be deposited at low temperatures. Hence, specific modification of friction and wear characteristics is possible as a finishing treatment requiring no further processing.

In this review, the coating technologies that have been developed and brought into commercial use in recent years are discussed. The specific advantages offered and the benefits realized are identified. Particular attention is directed at coating technologies which qualify as finishing treatments for the modification of the tribological characteristics.

**Introduction:** A number of new technologies have been developed in recent years for the modification of surface properties that offer considerable flexibility and process economies in surface property modification for tribological control. They rely on the deposition of a range of soft and hard compounds as well as metals. The real advantage offered by the new technologies is that they allow close control of coating thickness and composition not available in most standard treatments. They also permit combinations of coatings - for example, a soft overlay on a hard coat - in such a manner that no further finishing of the tribo-element is necessary. These processes include pyrolytic decomposition, chemical vapor deposition, physical vapor deposition, reactive evaporation, sputtering, arc coating, etc.

In this review, surface coating techniques particularly suited for the treatment of precision tribological elements are discussed. This review is not intended to be comprehensive. Key concepts are referred to and technical details are left out. The reader should consult the literature cited for a more complete understanding of the specific processes discussed.

**Relevant Coating Techniques:** Pyrolytic decomposition of organo-metallics, halide metallurgy, electrosynthesis in molten salt bath and a number of electrically-assisted vacuum coatings are among the principal surface coating techniques now available to improve tribological characteristics of mechanical components. Each of these possesses one or more special characteristics not readily available in another. Hence, all of the techniques will have to be considered before selecting a particular technology for a specific tribological application. CVD (halide metallurgy) and PVD (vacuum coating) techniques are presently the two widely used

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processes for surface coating to protect tribological components.

**Pyrolytic Decomposition:** In some organo-metallic compounds, the metal atom can be in a valence state which permits easy decomposition of the compound by thermal means. By heating the substrate to be coated in a flowing mixture of inert gases and appropriate organo-metallics, thin coats of chromium (1), aluminum (2), gold (3), silver (4), nickel (5), etc., are easily produced. Gold and silver coatings so produced can be useful for soft coating of tribo-elements.

Temperatures involved in metallic coating are usually low. The coating rates are also low. Thin noble metal soft coats can therefore be produced without serious thermal problems to afford tribological protection to precision engineering components.

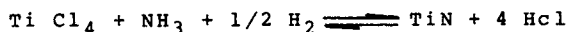
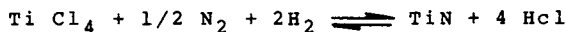
Hard coating, especially with oxides, is also possible by the use of pyrolytic decomposition. Alumina, silica, zirconia, and thoria coatings may be deposited by the thermal decomposition of metal alkoxides (6). The temperatures involved are, however, higher than those usually encountered in the deposition of metal layers. Production of alumina coating by the decomposition of aluminum isopropoxide, for example, requires (6) temperatures of 700-800° C. Hard coating by thermal decomposition may, hence, require a thermal treatment following thin film deposition.

Decomposition of nickel carbonyls (5) is now in use to construct foundry patterns to withstand abrasive wear. Soft, noble metal coats produced by thermal decomposition are also in use. Apart from this, pyrolytic decomposition has not found wider use in tribological applications.

**Chemical Vapor Deposition:** In CVD processes, halide compounds are reacted with hydrogen in an appropriately designed chemical reactor to deposit thin films of needed metals or compounds on hot substrates. The halide compounds needed may also be produced by reacting hot metal chips with selected halogens within suitable containers. To deposit carbides, nitrides, oxides, borides, etc., the wear-resistant coatings of interest to tribologists, the chemical potential of the needed atomic species is enriched by entraining suitable source gases in the process streams. Soft coat deposition by CVD is not common.

A schematic representation of CVD facilities presently in use is shown in Figure 1. Some of the characteristic reactions exploited for CVD coating of different materials are shown in Table 1.

The coating temperature in CVD is determined by the energetics of the reaction chosen. Free energy change accompanying the selected reaction must be negative at the desired coating temperature. To deposit TiN, for example, the following reactions may be used:



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TABLE 1: CHEMICAL VAPOR DEPOSITION

REACTION TYPE	EXAMPLES
Pyrolysis	$\text{Ni}(\text{CO})_4(\text{g}) \rightleftharpoons \text{Ni}(\text{s})^* + 4\text{CO}(\text{g})^*$
Reduction	$\text{SiCl}_4(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{Si}(\text{s}) + 4\text{HCl}(\text{g})$
Oxidation	$\text{SiH}_4(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{Si}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$
Hydrolysis	$\text{Al}_2\text{Dl}_6(\text{g}) + 3\text{CO}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons$ $\text{Al}_2\text{O}_3(\text{s}) + 6\text{HCl}(\text{g}) + 3\text{CO}(\text{g})$
Nitride formation	$3\text{SiH}_4(\text{g}) + 4\text{NH}_3(\text{g}) \rightleftharpoons \text{Si}_3\text{N}_4(\text{s}) + 12\text{H}_2$
Carbide formation	$\text{TiCl}_4(\text{g}) + \text{CH}_4(\text{g}) \rightleftharpoons \text{TiC}(\text{s}) + 4\text{HCl}(\text{g})$
Disproportionation	$2\text{GeI}_2(\text{g}) \rightleftharpoons \text{Ge}(\text{s}) + \text{GeI}_4(\text{g})$
Synthesis	$(\text{CH}_3)_2\text{Cd}(\text{g}) + \text{H}_2\text{Se}(\text{g}) \rightleftharpoons \text{CdSe}(\text{s}) +$ $2\text{CH}_4(\text{g})$

\* (g) = gas; (s) = solid

Equilibrium calculations (7) show that the first two reactions require temperatures in excess of 1000 K for TiN deposition, while the third reaction is possible at temperatures of the order of 600 K.

Since well-bonded coatings are essential for tribological applications, reaction temperature alone is not the sole criterion in the choice of preferred deposition reactions. It may be necessary to deposit an interlayer to enhance coating adhesion, to serve as a diffusion barrier, etc. Over such a layer, low temperature depositions can be made to produce dense, fine grained coats with excellent wear properties (7).

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In CVD, the deposition of a specific solid phase is usually desired. Process streams and operating conditions will have to be chosen to ensure process repeatability, to obtain desired coating rates, to maximize deposition efficiency, etc. To attain these goals, CVD phase diagrams (8) and computation packages have been developed (9) in order to identify the key process control variables. A CVD phase diagram for  $TiB_2$  deposition taken from Reference 8 is shown in Figure 2. A similar diagram for  $B_4C$  deposition, also from Reference 8, is shown in Figure 3. The CVD phase diagram for tungsten carbide deposition may be found in Reference 10. From Figures 2 and 3, it is clear that while titanium diboride deposition is possible over a range of conditions, deposition of boron carbide requires close process control. A similar situation is encountered in the deposition of tungsten monocarbide (10).

Equilibrium computations which allow these diagrams to be calculated enable the determination of specific process variables such as temperature, total pressure, ratios of chemical elements in the input gas, etc., in order to identify the condensed phase which will deposit, the equilibrium deposition rate, and the deposition efficiency of reactions. Gas phase reactions and resulting porous coatings can then be avoided to produce dense coatings with excellent tribological characteristics. It should be recognized that kinetic variables such as the total flow rate, coating system geometry, substrate chemistry, and surface finish also play a role in determining the quality of thin coats deposited. Uniform coating coverage of complex part geometry without the use of specialized coating fixtures is possible with CVD. This is not readily accomplished with most PVD processes.

Taking the cited factors into consideration and recognizing that the deposited films may interact diffusively with the substrate, optimal conditions for the deposition of tribological coatings can be identified. When adverse diffusive reactions are unavoidable, a barrier coating, also deposited with CVD, may be used. Sequential or multi-layer coatings are clearly possible through the change of process streams and deposition temperatures.

Chemical vapor deposition is presently an established technology with a sound scientific base. Cobalt bonded carbide tool inserts are now routinely CVD-coated with  $TiC$ ,  $TiN$ ,  $HfN$ ,  $Al_2O_3$ , etc., singly or in combination. Major benefits in wear resistance have been demonstrated in commercial use.

Despite wide spread use in tooling applications, CVD has had a far smaller impact in general tribological applications. This is in part due to the higher temperatures encountered in current CVD practice,  $800^\circ$  to  $1000^\circ$  C, for the deposition of hard compound films. In the case of tribo-elements made of steel, the high CVD temperatures used necessarily require post processing following CVD coating. Coating internal stresses and thermal stress induced cracking of the deposited films is then common. A refinishing of the CVD-coated precision components is further necessary, as the coated parts usually do not possess satisfactory, as-coated, surface finish. Distortions due to thermal treatment following CVD will also have to be removed.

In spite of these limitations, well-bonded CVD coatings, especially the  $TiN$  coatings on steel, hold great promise in severe tribological applications. Significant scuff resistance exhibited by CVD-coated steel components (11) suggests, that in hostile environments, i.e., higher temperature applications where effective liquid lubrication is not possible, in sealed transmission systems, in solid lubricated rolling element bearings, and in high vacuum bearing applications (12), CVD-coated tribo-elements can provide superior tribological life. Systematic evaluation of coated elements including gear contacts are essential to validate the expected superior tribological characteristics of CVD coated components.

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**Electrosynthesis in Salt Baths:** High temperature salt bath surface treatments driven solely by differences in chemical potential are well known and form the basis of cyaniding, carbo-nitriding and other similar processes. Attainable surface hardnesses with these processes are low compared with those possible by the deposition of refractory metal compounds. If well bonded, continuous, single phase compounds can be deposited at low temperatures, they can be of considerable utility for friction and wear control. Deposition of such compounds at low temperatures is particularly desirable to avoid post deposition thermal treatments. Electrosynthesis offers a means of depositing the needed hard compound layers.

Early electrosynthesis work (13) demonstrated the feasibility of producing iron, tungsten, and molybdenum carbides in alkali carbonate/borate baths at temperatures which compare favorably with those used in CVD. Current interest in hard layer deposition has led to the revival of salt bath electrosynthesis and deposition research. Within the last year, investigators have demonstrated low temperature deposition of nickel boride (14), synthesis of tantalum and vanadium monocarbides (15), and the electrolytic deposition of tantalum carbide (16).

NRL investigators (16) have identified the deposition conditions for the production of well-bonded layers of Ta<sub>2</sub>C and TaC on nickel substrates at temperatures between 750 and 800° C. Preliminary friction and wear tests show promise. Other investigators have shown that nickel boride can be electrodeposited at temperatures between 500 and 670° C. Coatings as thick as 46 microns have been produced in approximately 24 hours. High temperature alloys such as Hastelloy B have been deposited with boride films 6 microns thick at low temperatures.

Since it is known empirically that thick wear resistant layers are not necessary to afford significant tribological protection, the demonstrated ability to produce well-bonded thin films at low temperatures suggests that molten salt electrosynthesis is a promising means of hard coat deposition. As in the case of CVD, uniform coating of parts of complex geometry is feasible with salt bath electrosynthesis. Reported coating of substrates with tungsten carbide (15) is further evidence of the potential held by electrosynthesis.

Although the coatings produced apparently possess good film-to-substrate bond strength, the deposited coatings require refinishing before use. Coatings produced are crystalline and are hard. They are likely to possess a columnar structure. Further tribological characterization is essential before coatings produced can be considered to be suitable for engineering applications.

**Physical Vapor Deposition Technologies:** As noted earlier, the CVD techniques presently available for hard coat deposition are high temperature processes. Electrosynthesis techniques, though promising, are not yet perfected. Since hard and soft coating of ferrous components require low coating temperatures, i.e., temperatures not exceeding those used for tempering following hardening, one will have to resort to one or more of the electrically assisted vacuum coating processes to produce the needed thin films for tribological protection.

A variety of electrically assisted, thin film deposition techniques have been developed to produce the needed coatings. They include ion plating, activated reactive evaporation, DC and RF sputtering, arc coating, coating with plasma discharge, etc. Vapor species produced by thermal evaporation or ion bombardment are used in these processes to obtain thin coats of soft and hard materials. Virtually all of the known hard materials, soft materials, and a number of nonequilibrium structures can

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be produced with one or another of the electrically assisted coating techniques. When coatings of compounds are needed, the vapor species produced may also be reacted with process gases to concurrently synthesize and deposit needed materials. The principal vacuum coating techniques suitable for tribological coating of precision mechanical components are briefly described and discussed in the following paragraphs.

A schematic of a simple vapor deposition system for thin film deposition is shown in Figure 4. It consists of a vacuum chamber, a melt power supply, a filament, boat or cooled crucible assembly to contain the melt pool, and substrate holders. When substrate heating is permissible or necessary, appropriate means are provided in the substrate holder for sample heating. Simple thermal vapor deposition may be carried out with wire filaments or resistance heated baskets. For granular or powder feedstocks, resistance heated bare metal boats of W, Mo or Ta, fabricated from sheets are satisfactory. For large scale coating, electron beam melting and induction melting may be used.

In thermal vapor deposition, the mean free path of the coating flux is large and the vapor species arrive at the sample surface without extensive gas collision. Coating is a line-of-sight process. Coating rate depends on the melt power and is inversely proportional to the square of the source-to-sample distance.

The mean energy of the coating flux produced by thermal evaporation is  $\frac{3}{2} kT^V$ , where  $k$  is the Boltzmann constant and  $T^V$  is the average vapor temperature. The mean energy of the vapor flux is insufficient to displace adsorbed species and contaminants on surfaces to be coated. Coatings produced therefore usually exhibit poor film-to-substrate adhesion. This problem can be remedied by injecting electrical charges into the vapor flux with a 'probe electrode' as shown in Figure 4. The substrate can also be biased with a positive potential. Ionized coating flux is then accelerated to impinge on the substrate with greater kinetic energy than in simple thermal vapor deposition to produce well-bonded films (17).

The structure, properties, and adhesion of the films deposited are affected by the substrate temperature permitted during film deposition. Textured films are produced at low substrate temperatures. Columnar structure is obtained at intermediate temperatures. At homologous temperatures above 0.4 to 0.5, equiaxed, but coarse, grains are produced. The original surface finish of the substrate is not duplicated by this coating technique.

By admitting reactive gases during film deposition, coatings of compounds are obtained. Control of compound stoichiometry requires coupling of gas admission rate with the evaporation rate. Dynamic pumping is the common practice. Physical vapor deposition processes with E-beam melting and probe electrodes for injecting charges into the coating flux is referred to as Activated Reactive Evaporation (17).

Ion Plating, illustrated in Figure 5, is a variant of thermal vapor deposition. Vapor flux is directed at the substrate maintained at a high negative potential. System pressure and deposition conditions are adjusted such that the substrate is enveloped by a glow discharge plasma during thin film deposition. Due to the glow discharge, material is continuously sputtered from the substrate. By continuously cleaning the substrate with sputtering as it is being coated, well-bonded films are laid. Improved film adhesion is obtained.

Use of inductively melted vapor sources allows high coating rates. In ion plating, the use of E-beam melting is not straight-forward, since ion plating pressures are

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not compatible with good E-beam operation practice. With differential pumping, this difficulty can be overcome. In the normal operating pressures for ion plating, vapor species undergo multiple collisions before they arrive at the substrate. Coating is hence not a line-of-sight process. Fairly uniform coatings and step coverage are therefore possible. Partial replacement of the inert gas used in ion plating with a reactive gas allows reactive ion plating to obtain coating of compounds.

When a high DC voltage is applied to a cathode within a chamber maintained at low pressures, electrons emitted from the cathode ionize the gaseous atoms in the environment. Self sustaining glow discharge can be obtained in such an arrangement by adjusting the chamber pressure and the applied voltage. The positive ions produced in the glow discharge impinge on the cathode and displace the cathode atoms. The sputtered atoms diffuse through the gaseous environment and are deposited on the substrate to be coated. Over a period of time, thin films are produced. When insulating material coatings are to be produced, as the cathode is not an electrical conductor, radio frequency power supplies are essential. Common arrangements for DC and RF Sputtering are shown in Figures 6 and 7.

In sputtering, the coating rates obtained depend on (a) mass and energy of ions impinging on the cathode, (b) target to substrate distance, (c) sputtering pressure, (d) gas temperature, (e) cathode surface condition, (f) cathode geometry and dimensions, (g) shielding, and (h) target materials. Under commonly used coating conditions, the coating rates obtained are a few nanometers per minute.

Sputter coating depends on a momentum transfer process. Sputtered species have velocities nearly an order of magnitude larger than those produced by thermal evaporation. Good film-to-substrate adhesion is hence obtained on well cleaned substrates despite system operation at pressures greater than those in thermal evaporation. At common operating pressures, since multiple collision in the ambient occurs, coating is not a line-of-sight process. Good step coverage and coating uniformity are obtained without much difficulty. Suitable fixturing and drive assemblies permit a wide range of complex component surfaces to be coated with adequate uniformity. Multi-cathode coating systems allow sequential coating of several layers without breaking the vacuum. This is advantageous to obtain well bonded, multi-layer coatings.

To obtain higher coating rates than those possible with conventional DC and RF sputtering, and to coat at lower system pressures in order to obtain well bonded coatings, Magnetron Sputtering has been developed. In magnetron sputtering, crossed electric and magnetic fields are used to greatly increase the ionization efficiency of the sputtering system without raising the system pressure. The magnetic field superimposed on the electric field generates an efficient electron trap which results in the formation of intense glow discharge plasmas confined to the vicinity of the cathode. It allows the plasma to be supported at low voltages and low pressures. "Cold sputtering" at high rates in a good vacuum is facilitated. Apart from the magnetron head, the magnetron sputtering system is identical to the conventional DC sputtering system.

At the operating pressures normally used, magnetron sputtering is a line-of-sight coating process. Coating rates obtained increase linearly with the power dissipation at the cathode. Deposition rates of several hundred nanometers per minute are easily obtained when the cathode power dissipation is several kilowatts.

With the use of appropriately designed anodes and floated substrates, thermal loading on the substrate can be minimized (18) during magnetron sputtering. Experimental



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studies of temperature rise during high rate sputtering show that nearly half of the thermal loading during coating is due to condensation of the coating flux on the substrate coated. The remainder can only be accounted for by the kinetic energy of ionized species arriving at the substrate. In the case of aluminum sputtering, the mean energy of the coating species has been estimated and found to be several times the binding energy (18). Similar values apparently hold for magnetron sputtering of other materials. The high energy of the coating flux and the use of good vacuum are believed to be responsible for the well bonded films produced with magnetron sputtering.

Partial replacement of the sputtering gas with a reactive gas enables reactive sputtering to produce coatings of compounds. With commercial purity titanium targets, thin TiN films suitable for tribological applications have been successfully deposited (19-21). Coating rates obtained are lower than those for the sputtering of metals. Magnetron heads can be supported by DC as well as RF power supplies. Both DC and RF sputtered TiN coats have been produced for tribological applications.

**Arc Coating Technology:** Metallic and non-metallic coatings suitable for tribological applications may also be produced with Arc Coating techniques. This technology differs fundamentally from the electrically-assisted coating processes discussed so far. A 'hot', i.e., a thermal plasma, is used with high ion temperatures. Estimates of ion temperatures range up to  $10^5$  K. In arc coating, a vacuum arc is used for film deposition. A vacuum arc is a low voltage, high current arc sustained with a metal plasma. A feed gas, as in sputtering, is not essential, but may be used to concurrently synthesize and deposit coatings of metal compounds.

An arc coating system consists of a main cathode of target material, an anode and an igniting electrode all maintained in a vacuum of  $10^{-6}$  to  $10^{-3}$  torr. The system is equipped with a low voltage, high current DC power supply both to ignite the arc and to maintain the primary arc between the cathode and the anode (22). A variety of techniques may be used to ignite the arc, and once the arc is ignited, the igniter is deactivated. The primary arc is then sustained between the main cathode and the anode.

In the cited reference (22), an electro-mechanical assembly consisting of a solenoid and an armature, where the armature carries the igniter electrode, is used. Initially the igniter electrode is in contact with the main cathode. With the current passing through the cathode-igniter circuit, the igniter is withdrawn. As the igniter electrode is withdrawn, the arc gap and length increase until arcing is initiated between the main cathode and the anode.

In arcs, the cathode temperature is high since the cathode spot is of a small size and very large current densities,  $10^5$  to  $10^7$  amp/cm<sup>2</sup>, occur. Severe localized ohmic heating and evaporation ensues resulting in the erosion of cathodic material. Vapor pressure of the cathodic material rises and conduction through the metal plasma results in arc discharge.

Arcs can be sustained over a range of pressures. At the upper end of the pressure range, multiple collisions occur within the coating flux. Coating uniformity and step coverage is hence facilitated. Since coating is not line-of-sight, use of complex fixturing is not necessary.

It is known from arc physics that arcs are of millisecond duration with current levels of several hundred to several thousand amperes. The arc appearance is charac-

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terized by a multitude of cathode spots and a diffuse interelectrode plasma. Loss of material from the cathode takes the form of ions and finite particles. The ion current leaving the electrode has a value of about 10% of the arc current with mean ion energies (in eV) exceeding the interelectrode voltage. It is the high energy ions exiting from the electrode at high speeds (of the order of  $10^5 \text{ msec}^{-1}$ ) that are responsible for the formation of well-bonded coatings.

Poorly coated substrates show evidence of arc strike-back in the form of small pits. The finite particles ejected from the cathode spots often result in the presence of 'macro particles' on the coated surface. The coated components produced hence frequently yield surface finishes poorer than those of the uncoated components. In instances where coated parts do not mate, as for example in cutting tools, surface finish deterioration accompanying arc coating is not a significant problem. In cases where precision components have to be protected against wear, as in the case of ball and roller bearings, further work is necessary to improve the surface finish obtained with arc coating.

High current and low voltage discharges may also be obtained with Hollow Cathode devices. By heating a target with hollow cathode discharge and evaporating the target material, large coating fluxes may be obtained. By requiring the coating flux to pass through the low voltage discharge, well ionized coating fluxes are obtained. Since the ionization cross section of metallic vapors is large at low voltages, with suitably configured hollow cathode discharges, well-bonded coatings are readily produced especially when the substrate to be coated is biased. Coating systems based on hollow cathode discharge have been shown to be useful for low temperature coating of substrates with hard material compounds (23).

Electrons required to heat and evaporate a target material can also be obtained from hot hollow cathode devices operated with high currents at low voltages. In the Hot Hollow Cathode discharge coating system (24), a grounded filament within a specially designed cathode structure is heated and the electrons extracted by applying a positive potential to a collinear anode. A coaxial magnetic field is employed to extract the heating beam through a narrow opening communicating between the cathode chamber and the evaporation chamber. A low voltage arc is then ignited between the filament and an insulated portion of the hollow cathode to produce a large current flow through the hot cathode.

In the hot hollow cathode discharge system, current densities of several kW per  $\text{cm}^2$  are obtained at anode surfaces to efficiently melt and evaporate the anode material. The vapor flux is effectively ionized by the low voltage electron discharge traversing across the evaporation chamber. Well-bonded coatings are readily produced. Use of reactive gases within the coating chamber enables the synthesis and deposition of hard metal compounds (24).

A Cathodic Arc Plasma deposition system may also be used to deposit thin films for tribological protection. In such a system, the CAP source is the cathode of a diode discharge operating in the arc regime (25). The arc is not sustained by the background gas in the chamber but by a metal plasma generated from the source. In the CAP-based coating system, an arc is ignited on the cathode surface over which it moves randomly. Depending on the discharge current, one or more cathode spots are produced. Each cathode spot is a source of electrons and ions.

The high energy density of the cathodic arc is believed to yield 60 to 80% of the ejected material in the form of ions with energies in the 40 to 80 eV range (25). The highly ionized and energetic coating flux produced yields well-bonded coatings