

**CVD Coatings: From Cutting Tools to Aerospace Applications and Its Future Potential.**

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**Abstract:**

CVD has been a prime coating technique making a significant impact in the cutting tool and aerospace fields where the technique has been used to form numerous types of protective coatings. While many of the products served by this technology are mature, it will remain in usage for decades because of its versatility and its ability to provide an inexpensive means of molecular forming. This controlled deposition of matter on an atomic or molecular basis can deposit coatings uniformly on relatively complex shapes compared with other chemically non-reactive coating processes.

Since no single material can function over the extreme operating conditions required for cutting tools and aerospace alloys, CVD has been used to enhance new material development where improved properties are needed. It provides the ability to protect metals from hostile environments. The protective coatings provide a solution to minimize the effects of wear, erosion, corrosion, and high temperature oxidation. These coatings have been selected to complement the substrate material so that the combined composite system properties can satisfy a particular set of operating conditions. The dramatic changes achieved in application of this technology in the period from 1960 - 2000 will most likely be reduced to incremental improvements. The target will change from "one coating does it all" to choosing specific coating designs to suit a particular set of conditions. The review will explore the historical development of protective coatings, and attempt to predict their future direction coatings in the cutting tool and aerospace fields.

## 1. Introduction

Why has CVD found an important role in metallurgical development? In CVD, gaseous chemical reactants are transported to the reaction chamber, activated thermally in the vicinity of the heated substrate, and then reacted under controlled conditions to form a deposit on the substrate surface. This technique has also been called vapor plating, gas phase coating and pack cementation in some of its process manifestations and has multiple process advantages.

- 1) CVD can be environmentally friendly with waste products easily neutralizable.
- 2) CVD has the ability to coat complex shapes internally and externally.
- 3) CVD is able to deposit selective elements for oxidation, wear and corrosion protection.
- 4) CVD can produce graded and/or multi-layered coatings and provide coatings of a variety of metals, alloys, and compounds not readily obtainable by other means.
- 5) Coating structure and grain size may be controlled.
- 6) CVD has a wide range of throwing power and deposition rates.
- 7) Coatings are dense and their purity may be controlled.

There are also process disadvantages, however, that need to be considered when choosing this process. Some of those are:

- 1) Up-front capital costs can be high with complex handling, safety, and automatic systems. This may be a significant factor in gaseous CVD systems but less significant in pack and gas phase process units.
- 2) High temperature requirements may limit substrate choices.
- 3) Some substrates can be attacked by the coating gases.
- 4) Gas phase depletion problems may occur with some system designs.
- 5) Poor adhesion or lack of metallurgical bonding is possible.
- 6) Masking of portions of parts not to be coated can be difficult.

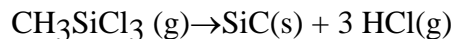
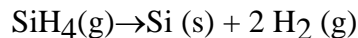
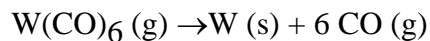
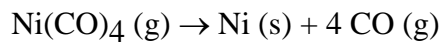
Little can be done to avoid high capital procurement costs except to keep the system as simple as possible. Substrate limitations with respect to temperature characteristics and attack by the coating gases can be particularly difficult. Gas phase depletion can often be avoided using multiple gas inlets - which may also make the gas handling systems more complex. An understanding of the causes of poor adhesion can often permit the minimization of this problem which can usually be designed around. Some of the factors affecting poor adherence are:

1. Chemical attack on substrate surface.
2. Presence of oxide films or other contaminants on substrate surface.
3. The formation of brittle and porous zones between the substrate and coating.
4. Formation of powdery or flaky deposits due to gas phase nucleation.

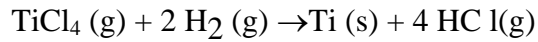
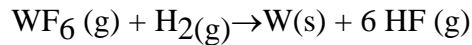
## **2. General CVD Reaction Types**

An understanding of the types of thermo-chemical reactions used in CVD for the cutting tools and aerospace fields can be very helpful [1]:

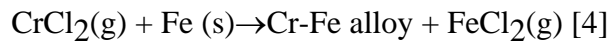
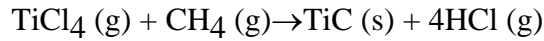
1. Thermal decomposition reactions:



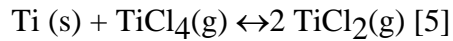
2. Reduction reactions.



3. Displacement or exchange reactions.



4. Disproportionation or Exchange Reactions



### 3. Significant Process Parameters

In the process development of the above coatings, there are several related deposition parameters that must be optimized in order to achieve a good coating [6]. Some of the variables that have been studied were:

- 1) Reaction Temperature.
- 2) Metal Halide ( $\text{SiCl}_4$ ,  $\text{TiCl}_4$ , etc.) Concentration - input rate.
  - a)  $\text{H}_2$  carrier flow.
  - b) Vapor Pressure/Temperature.
- 3) Carbon input ( $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ , etc.) - for carbide formation.
- 4)  $\text{N}_2$  /  $\text{NH}_3$  Input - for nitride formation.
- 5) System Pressure.
- 6) Gas Purity.
- 7) Metal halide Generator Temperature -  $\text{AlCl}_3$ ,  $\text{HfCl}_4$ ,  $\text{ZrCl}_4$ .
- 8)  $\text{HCl}$  or  $\text{Cl}_2$  input rate.
- 9)  $\text{H}_2\text{O}$  /  $\text{CO}_2$  flow rate - for oxide formation.

In addition to the above factors, the geometry of the gas inlet and the substrate is often system dependent and can not be separated from the vertical, horizontal, or cylindrical reactor design. Gas flow conditions can induce localized temperature and concentration gradients in the substrate vicinity and lead to non-uniform coatings and chemical concentration gradients due to the depletion of reactants and the formation of reaction products along the reactor length.

Metallurgical bonding of the coating to the substrate is one of the most important requirements for the successful application of these protective coatings. Transition from the substrate material to the coating often involves an abrupt change in such properties as hardness, coefficient of thermal expansion, and thermal conductivity. Permanent and transient stress concentrations can also lead to a reduction of the bonding strength resulting in shorter service life with cracking or splitting of the coating from the substrate. Reductions of these stresses tend to increase the adhesion between the coating and the substrate. This can be accomplished by:

1. Matching the mechanical properties of coating and surface.
2. Forming intermediate layers to reduce the large gradient of properties between the coating and the substrate.
3. Controlling the structure of the coating.
4. Reducing the coating thickness.
5. Increasing the radius of curvature of the coated surface.

The matching of coefficients of thermal expansion (CTE) is required because thermal expansion has a very large effect on stresses. Selection of coating materials with similar properties and the use of an interlayer coating can be extremely important and requires some of the following considerations:

1. Properties and nature of coating on the substrate material.
2. The properties of the interlayer coating.
3. Deposition temperature.
4. Chemistry of the deposition reaction, or the nature of chemical mixture used in the deposition process.

In the selection of an ideal coating material for application to the cutting tool and aerospace field, where the coating is required to function over a wide range of operating conditions, the following needs to be considered:

1. Good mechanical properties over a wide temperature range.
2. Resistance to thermal and mechanical cycling.
3. Fully dense.
4. Hard and resistant to wear and erosion.
5. Chemically inert and resistant to corrosion and high temperature oxidation.
6. Resistant to atomic diffusion and interdiffusion at high temperatures.

The choice of a coating for any given set of conditions depends upon the operating environment, the substrate material, the coating availability, and the economics of the coating application. Thus, the coating selection is dictated by the environment, the material properties, and the substrate system. Most known materials may be deposited by CVD, thus, a wide range of protective coatings is available for exploitation. These coatings provide the wear and corrosion resistant properties [7] needed to meet the multiple demands of the conditions where they are required to function.

#### **4. Aerospace Diffusion Coatings**

The earliest commercial development of CVD was for diffusion coatings in the 1950's. Richard Wachtell and Richard Selig, both of Chromalloy Gas Turbine Corporation, were the first to commercialize these processes on a large scale - when improved material performance was needed for jet engines. The diffusion process was defined as the intermingling of atoms of the same or different materials [8] using the techniques of Pack Cementation. This permitted components to be processed by aluminizing, boronizing, chromizing and siliciding [9] for the protection of metals against oxidation, corrosion and erosion [10].

The basic diffusion process consisted of packing components in a powder mixture of a pure metal or alloy coating source element, an activator - typically, a halide salt, and an inert filler material such as alumina. The powder mixture was placed in a retort or container with the uncoated parts requiring coating and heated to a high temperature, generally 900 - 1100°C. The reaction then occurred when the activator decomposed and the liberated halogen reacted with the coating element to form a volatile metal halide. The metal halide then subsequently decomposed at the substrate surface to form the coating. With numerous studies in adaptations and the kinetics of diffusion coatings in aerospace fields [11], this process has been used to coat turbine components internally as well as externally [12]. Many refinements in processing have been made including the addition of noble metals, prior to aluminizing, by plating components with platinum, rhodium [13] and palladium [14]. In addition, active elements such as Hafnium and Yttrium have also been used as modifiers. This complex ductile or brittle coating formation, depending on the phase formation desired, has resulted in extremely sulfidation and oxidation resistant turbine component coatings,

The principle difference between the deposition process in pack cementation and in conventional CVD [15] is the means of generation of gaseous reactants within the powder

packing [16]. Pack cementation has its unique set of deposition parameters to be optimized in order to achieve good coating performance. The chemical composition of the substrate material also plays an important role in pack cementation because of the high temperature diffusion processes occurring in the substrate. Hardness and chemical composition gradients are usually present in diffusion coatings. In aluminized components, for example, the aluminum content decreases gradually from the outer coating surface to the interface. Diffusion is normally inversely proportional to the square root of time with other factors of significance being temperature as well as concentration of reactants.

## **5. Tool Coatings**

The second commercialization of the CVD process was in tool coatings development as a means to provide wear resistant coatings in the metal-cutting field. Wilhelm Rupert of Metalgesellschaft [17] was arguably the first researcher to make commercial use of coatings on tool steel substrates in the 1950's and could be termed the "father" of tool coatings. The first TiC coatings applied to tungsten carbide substrates had a film thickness of 4 $\mu$ m and were marketed in the US by Krupp Widia beginning in 1968. At Kennametal, in the US, the first tool coating was experimentally produced by John Lazar and E. N. Smith in 1968 using the simplistic TiCl<sub>4</sub> disproportionation reaction as illustrated in Figure 1.

The importance of the tool coating was based upon the need for the cutting tool to satisfy two sets of requirements. First, the surface of the tool had to be resistant to wear and chipping while the bulk had to be tough to arrest cracks generated at the surface. Second, hardness was needed to prevent plastic deformation. These bulk and surface requirements were difficult to satisfy using the same material everywhere. Therefore, the development of a composite tool consisting of a tough substrate with extreme hardness and a wear resisting coating was consistent

with the broad requirements of an ideal cutting tool. Good wear resistance was due to the chemical inertness, stability, lubricity and hardness of the coating.

The effects of tool coatings can also be highlighted by the following:

- (1) Reduction of friction (reduction of heat and cutting forces).
- (2) Reduction of diffusion between the chip and the surface of the tool.
- (3) Prevention of galling [18].

Among the coating materials that quickly came into use on WC-Co “cemented carbide” substrates were  $\text{Al}_2\text{O}_3$  [19], HfN, TiN, carbides of all group 4B and 5B metals, composite multiple layers of TiN and TiCN on TiC [20], composite double layers of aluminum oxide on TiC, TiC on WC and titanium oxy-carbides. Thus, over the 1968 - 1985 period, coatings for the WC-Co hard metal substrates found rapid acceptance and developed quickly.

One inherent problem with CVD coatings on tools was the loss of toughness when cemented carbide tools were coated with a TiC layer - due to the formation of a carbon depleted or brittle zone underneath the coating layer. Two developments helped to minimize this problem. The first development involved a cobalt enriched substrate which enhanced toughness albeit at the expense of wear resistance [21]. By special processing steps it was possible to develop an increased cobalt content at the outer zone of the tool and then overcoating that with TiC or TiC- $\text{Al}_2\text{O}_3$ . With the development of an enriched cobalt zone and a thin layer of cobalt, the TiC nucleation became more uniform. The second development involved the deposition of TiC followed by re-sintering of the carbide tool and then over-coating the component with alumina. That was found to be an acceptable method to force the bonding of the alumina coating. In addition to the application of the coatings for carbide tooling, there has been the use of very hard overlay coatings on stamping and punching dies, thread guides and protective, decorative

coatings in the watch and jewelry industry because of their hardness, chemical inertness and attractive colors [22].

## **6. Thermal barrier, Erosion Resistant, and Diffusion Barrier Coatings**

A third commercialization of CVD for the past quarter century is in the formation of high temperature oxidation resistant coatings that have been applied to Carbon/Carbon and SiC/C substrates[23]. CVD has also been used to coat the fibers from which the composite material is constructed and in a process variation called CVI or Chemical Vapor Infiltration, where the coating gases are diffused into porous substrates. Typical coatings used in both CVD and CVI include SiC, B<sub>4</sub>SiC, Si<sub>3</sub>N<sub>4</sub> as well as coating such as alumina and zirconia.

The erosion of mechanical components caused by impacting abrasive particles has been another well known problem for aircraft and industrial gas turbine compressor blades and vanes. The erosions of the thin metal tips and leading edge of the blades and vanes result in a deterioration of engine performance. Gene Wakefield of Texas Instruments [24] had developed a coating process for depositing titanium carbo-nitride on stainless steel compressor blades at 600-700°C using titanium tetrachloride and an amino compound to supply carbon and nitrogen, which dissociates at a relatively low temperature. A significant improvement in erosion resistance was achieved with the titanium carbonitride coating, however, with a debit on fatigue strength, it has yet to be successfully commercialized. The thermal decomposition of dicumene chromium at 450-650°C also provided another relatively low temperature process for deposition of chrome carbide (Cr<sub>7</sub>C<sub>3</sub>) as an erosion resistant coating.

Other erosion resistant coatings have involved the deposition of rhenium, tungsten, tantalum and boron carbide on the internal bore of gun barrels [25]. Because of material removal within the bore of a barrel induced by high temperature, pressure, and chemical reactions during propellant combustion, crack formation problems have occurred. The effect of this hot gas

erosion was loss of muzzle velocity and accuracy. The CVD coatings provided a significant improvement over uncoated and chrome plated gun barrels.

Diffusion barrier coatings have been needed in some applications where the fabrication requirements or high operating temperatures demand protection. Barrier coatings have been used to prevent interdiffusion between two solid layers in a composite system. Examples of such coatings are TiC, used as a carbon diffusion barrier in the deposition of tantalum on steels, and TiN used as a nitrogen diffusion barrier in the doped silicon carbide heating elements. In other cases, barrier coatings on metals have been needed to prevent the inward and/or outward diffusion of carbon in a gaseous operating environment. This problem of carburizing or decarburization is also important for high temperature gas cooled nuclear reactors and thus has found an application in that area. The application of TiN to depleted uranium core bits, used as anti-tank penetrating shells, has also been studied as a diffusion barrier coating.

## **7. Conclusion**

There is at present extensive industrial applications of CVD coatings for the protection of metals against wear, erosion, corrosion, and high temperature oxidation. Further improvements in many areas, notably tool coatings where it is estimated that 70% of all current tungsten carbide “hard metal” tooling is coated and in aerospace diffusion and overlay coatings will be incremental. Advances will be made in the continued application of coatings in specialty niche areas - such as diamond and “diamond like” coatings where machining of specific substrates will require modifications to the cutting tool surface. More protective coating applications will likely be made to many of the ceramic tool substrates. It is extremely unlikely, however, that new coatings will find the mass applications that were made earlier when the revolutionary concepts of coatings were first applied en-masse to tooling.

Diffusion aerospace coatings relying on pack, gas phase and traditional CVD will continue to provide protective coatings - with and without precious metal modified aluminides. In terms of processing costs, it is expected that traditional CVD will continue to find usage where more than one element is diffused into the substrate - particularly when several elements are required to be sequentially or simultaneously diffused into a super alloy substrate. In terms of a simple aluminide or chromide coating, when only a single element is diffused into the substrate, the pack and gas phase variants will continue to find wide usage and acceptance because of its cost effectiveness relating to simplicity of process equipment.

High temperature diffusion barrier coatings are likely to find future applications in fiber reinforced metals and alloys. This application is likely to find a specialty niche in the aerospace field. CVI is a necessary addition for substrate development while the need for "overlay" type coatings will depend upon the degree of oxidation resistance built into the substrate. Currently, this application depends on future government utilization and commercial acceptance in the aerospace field.

Low temperature WC and TiCN coatings suitable for protection against low load abrasion wear and deposited at temperatures between 300-700°C still show promise in extending the application of coatings to materials which need low deposition temperatures because of substrate limitations. However, it would appear that PVD processes, such as sputter ion plating and cathodic arc PVD, have a better chance to succeed even though these processes are line of sight. This is because masking of surfaces is easier and coatings can also be more readily applied to titanium/aluminum alloys.

In conclusion, there exist many coating materials with good protective properties. A significant number of these materials have found massive commercial acceptance. This is due in part to the compatible properties of the coating and substrate and enhancement of many positive

improvement factors. Some of the coating/substrate limitations caused by the problems of incompatibility can be overcome with the use of graded coatings and intermediate layers. Where coating temperatures pose problems, the reduction of deposition temperatures may be realized with the use of suitable chemicals such as organometallic compounds, reactive atoms, or with the aid of additional excitation such as plasma activation. Only minimal usage has been made to date in the commercial application of plasma activated CVD - so room for new growth is a distinct possibility. In addition, if the cost of procurement of specialty chemicals declines, wider use is possible of some of the moderate temperature coatings which depend on these feed materials.

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