

COATINGS BY CHEMICAL VAPOR DEPOSITION

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By definition, CVD is the deposition of elements or compounds formed by chemical reactions which take place at or near a substrate surface. Vapor deposited materials by the physical technique-vacuum evaporation sputtering, and CVD, sometimes called vapor plating, are making a significant impact in our economy at present and promises to be of greater importance in the future. The reason for their importance is that the deposition process is an extremely versatile and relatively inexpensive for of molecular forming by controlled deposition of matter on an atomic or molecular basis. In this respect, it is similar to electro-deposition. Chemical vapor deposition, though, has the greatest ability to deposit uniformly on relatively complex shapes. However, the substrate, must usually be heated to relatively high temperatures. This can be a severe limiting factor, though, for many substrate materials.

Despite the seeming simplicity of the vapor deposition process, its control to prepare materials of desired structure and composition at practical rates is quite involved. In fact, it is considered more of an art than true science at this time.

Although much progress has been made in the development of new materials, there exists at present no single material which can withstand all the extreme operating conditions in modern technology. Protection of metals from hostile environments has therefore become a technical and economic necessity. In many situations, protective coatings are required to minimize such effects as wear, erosion, corrosion, high temperature oxidation, and high temperature fusion. For these applications the protective coating is normally selected to complement the substrate material so that the combined properties of the composite system can satisfy a particular set of operating conditions.

CVD is one of several convenient methods used to coat surfaces. It is generally defined, once again, as a deposition of a solid material onto a usually heated substrate surface as a result of chemical reactions in the gas phase. These reactions may occur on, at, or near the substrate surface. Because of the recent development in deposition techniques, there exists several coatings methods which fall into the framework of this definition that which, until now, have been separated from CVD. It seems desirable and indeed necessary to have unified classification of these methods

The following will review the principles and techniques of various CVD processes and the applications of CVD protective coating. The unique characteristics of CVD then can be discussed in terms of advantages and disadvantages considered in the light of these unique characteristics. The unified classification of the known CVD processes are generally differentiated by the parameters:

1. Principles mode of activation of the chemical reactants.
2. Mode of transport of the chemicals.
3. The initial state of the gaseous chemical reactants.

This differentiation arises in part from the different fields of application and in part from the different fields of application and in part from recent developments in deposition technique. This separation of techniques is not really necessary, nevertheless, the different description names of the CVD processes are well established in literature.

<u>Chemical Vapor Deposition Process</u>	<u>Principle Mode of Activation of Chemical Reactants</u>	<u>Related Vapor Deposition Process</u>
Conventional		
a. Conventional CVD	Thermal	
b. Pack Cementation	Thermal	
Nonconventional		
a. Chemical Spray Deposition	Thermal	
b. Reactive evaporation	Thermal or Electron Beam	Evaporation (or vacuum metallizing)
c. Activated reactive evaporation	Plasma, Thermal or Electron Beam	Evaporation (or vacuum metallizing)
d. Plasma Activated CVD	Plasma with or without Thermal	
Reactive sputtering	Plasma	Sputtering
Reactive ion plating (hybrid CVD process)	Plasma, Thermal, or Electron Beam	Ion Plating
Chemical ion plating (hybrid CVD process)	Plasma with or without Thermal	Ion Plating

Conventional CVD

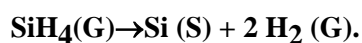
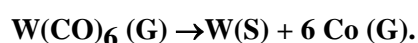
Conventional CVD is a process in which the stable gaseous chemical reactants are transported to the reaction chamber, activated thermally in the vicinity of the heated substrate, and made to react under controlled conditions to form a solid deposit on the substrate surface.

This technique is fairly well developed and has been to date referred to simply as CVD. It is also known as gas plating by analogy with electroplating.

There are several principle types of thermo-chemical reactions in CVD, and these are loosely classified as follows:

1. Thermal decomposition reactions.

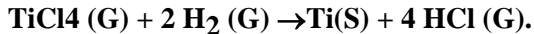
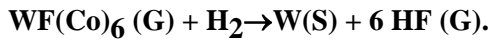
These reactions are also known as pyrolytic reactions and they mostly involve the metal carbonyls, hydrides, and halides, and organo-metallic compound. Some representative reactions are:



Other examples of these reactions are the well-known case hardening processes such as carburizing, nitriding, and carbonitriding.

2. Reduction reactions.

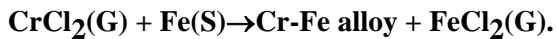
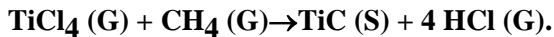
The reducing agent in these reactions is usually hydrogen. Some typical examples are:



Active metals such as potassium (K) sodium, (Na) magnesium, (mg), Zinc, (Zn), and cadmium (Cd) can also be used as a reducing agent, but in practice, the control of such reactive atoms is generally difficult.

3. Displacement or exchange reactions.

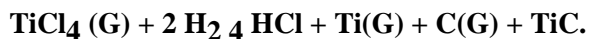
Some examples of these reactions are



4. Disproportionation

An example of this reaction is: $2 \text{TiCl}_2(\text{G}) \leftrightarrow \text{Ti}(\text{S}) + \text{TiCl}_4(\text{G})$.

Some CVD coating processes can include several types of reactions simultaneously. An example is the following:



For any given set of coating conditions, the selection of suitable CVD reactions should be made on the basis of thermodynamics. It must be noted, however, the thermodynamic criteria alone are often insufficient because of the absence of information on reaction kinetics and activation energies.

Most chemical reactions in CVD are endothermic, so that thermal energy must be supplied by heated substrate and/or by the environment in the neighborhood of the substrate. Generally, this is an advantage, since the reactions can be controlled by regulating the substrate temperature. This control is often more difficult for exothermic reactions.

There are several established methods of heating the substrate, each of which has its own advantages and disadvantages. The choice of a heating method depends largely on such factors as the type of deposition process, and the shape, size, and composition of the substrate material as well as on economics. More common methods are:

1. Direct resistance heating in this method an electric current is passed through the substrate. It has the advantage that only the substrate surface. However, the substrate is necessarily limited to conductive materials. This method is particularly suitable for continuous coating of wires and filaments.
2. Radio-frequency induction heating--this method is very convenient. for coating simple components of a conducting material, although special techniques are available for heating non-conductive materials. The advantages and disadvantages are similar to those of direct resistance heating.
3. Thermal radiation heating here the coating chamber is placed inside an oven or furnace. This heating method has the advantage that both the substrate and the reactor walls become coated. On the other hand, unlike direct resistance and radio frequency induction, which generally is an advantage for endothermic deposition reactions.
4. Photo radiation heating--in this technique the substrate is heated by high intensity photons from such sources as quartz, iodine or tungsten filament lamps, concentrated solar

radiation, and high-powered lasers. Only the substrate is heated and the reactor walls generally remain cool. This method, like thermal radiation heating, is suitable for both electrically conductive and non-conductive substrates. Solar radiation and lasers generally give localized or spot heating, and rotation of a substrate may be necessary.

In any CVD process there are several inter-related deposition parameters which must be collectively optimized in order to achieve a good coating. These parameters include not only the temperature, pressure, chemical concentration, and velocity of gas flow, but also the geometry of the gas inlet, the geometry of the substrate, and the configuration of the reactor. Therefore, the deposition conditions are system-dependent so that in general they can not be completely separated from the reactor. Vertical, horizontal, and cylindrical reactors are commonly used, and choice of configuration depends largely on the deposition process.

Within the deposition chamber of the reactor, the gas flow patterns are affected by the geometry of the substrate, the geometric arrangement of the gas inlet, and the velocity of the gas flow. In such cases these gas flow conditions can induce localized temperature and concentration gradients in the vicinity of the substrate, which may lead to non-uniform coatings. In addition to these localized gradients, there are chemical concentration gradients due to the depletion of reactants and the formation of reaction products along the reactor. Under some conditions an uneven coating may be expected. The second type of CVD coating to be done is "pack cementation" and is a well established CVD technique for applying diffusion coatings to metallic substrates. Coatings formed by processes such as aluminizing, chromizing, and silicizing are commonly used to protect metals against oxidation, corrosion, and erosion. A more recently developed process of boronizing is finding applications for wear protection.

The technique of pack cementation is relatively simple. In essence, it consists of packing the part to be coated in a powder mixture contained in a retort and heating the pack to a sufficiently high temperature for a sufficient time to produce the desired coating. The process can be carried out in normal atmosphere, in vacuum, or in an inert gas environment. The powder mixture consists normally of a source of the coating element in the form of a pure metal or alloy, an activator which is usually a halide salt, and an inert filler material such as alumina. At reaction temperature, generally in the range 900-1100°C, the activator decomposes and the liberated halogen reacts with the coating element to form a volatile metal halide. This metal halide then decomposes at the substrate surface to form a coating. When ammonium halide is used as the activator, Hydrogen reduction of the metal halide on the substrate surface is another possible reaction.

In principle, the essential difference between the deposition process in Pack cementation and in conventional CVD is the generation of gaseous reactants within the powder packing. Like conventional CVD, Pack cementation has its own set of deposition parameters which must be optimized in order to achieve good coating performance. The chemical composition of the substrate material generally plays an important role in Pack cementation because of the high temperature fusion processes occurring in the substrate.

The deposition or substrate temperature in both conventional CVD and Pack cementation is generally high. At present there is a very limited number of protective coatings which can be deposited below 600°C, which places an undesirable limitation on the types of substrate material which may be coated by these processes. In the past few years there has been an increasing interest in processes whereby the chemical reactants are excited by non-thermal means such as plasma and photochemical activation.

There are several common techniques for reducing the deposition temperature, and the applicability of these techniques depend on the type of deposition process. In conventional CVD where only thermal activation is used, it is possible to minimize the deposition temperature for any coating by:

1. **Selecting suitable chemical reactants.** For example, the deposition temperature for silicon nitride from the chemical mixture $\text{SiH}_4\text{-N}_2\text{H}_4\text{-H}_2$ is lower than that from the chemical mixture of $\text{SiH}_4\text{-NH}_3\text{-H}_2$. Another example for temperature lowering is the use of the $\text{WF}_6\text{-C}_6\text{H}_6\text{-H}_2$ instead of $\text{WCl}_6\text{-C}_6\text{H}_6\text{-H}_2$ for tungsten carbide coatings. Moreover, it has been found that benzene has a lower temperature requirement for these coatings than other hydrocarbons.
2. **The use of organometallic compounds is also a possible means of lowering the deposition temperature.** Organometallic compounds are normally defined as compounds with metal-carbon bonds. However, as is the common practice in CVD literature, these compounds are considered in the more general sense to include metal-nitrogen and metal-oxygen bonds as well as organic-metal complexes. The main characteristic of this class of chemicals is the relatively weak bond between the metal and non-metal atoms, so that deposition can be carried out at relatively low temperatures. Metal carbonyls such as $\text{Ni}(\text{CO})_4$ and $\text{W}(\text{CO})_6$ are well known organometallic compounds which have been used for deposition of metals and metal carbides at low temperatures. Other examples of organometallic compounds used for depositing coatings below 600°C are documented chromium for chromium carbide, dialkylamides of titanium, zirconium, and niobium for TiN, ZrN and NbN respectively.

Although it is possible to minimize the deposition temperature by careful selection of chemicals, there still exists a lower thermodynamic temperature limit in thermochemical reactions. Moreover, the commercial availability of suitable chemical compounds is limited particularly the organometallic compounds. These compounds are generally expensive and many are not suitable for transport in the gas phase because of low vapor temperatures or thermal stability.

3. **Photochemical excitation with light and lasers.**

In photochemical excitation, the chemical reactant absorbs photons or light at wave lengths which are characteristic of this molecule. This excitation leads to an excited molecular state or to photo-decomposition. The temperature dependence of the subsequent reaction in the deposition process is decreased, resulting in a lower deposition temperature. Thus, a logical extension of the non-conventional processes is photo-activated CVD, in contrast to plasma-activated CVD. The application of photo-activated CVD is limited, however, because of selective photo absorption.

There is a close connection between photo chemical-excitation and photo-radiation heating of the substrate. Simultaneous excitation and heating can occur if the absorption spectrum of the reactant overlaps with the electromagnetic spectrum of the heating source. This is more likely in solar heating because of the broad, continuous solar emission spectrum. However, in some cases lasers can also be used for simultaneous excitation in heating. This has been demonstrated by the deposition of boron and boron nitride where the CO_2 laser is used both for exciting BC_3 and for BCl_3 heating.

In any endothermic chemical reaction, the temperature requirement is reduced if reactive atoms are used instead of stable chemical compounds. In the deposition of titanium nitride, for example, the deposition temperature of the titanium (vapor)- N_2 system is lower than that of the titanium tetrachloride- $\text{N}_2\text{-H}_2$ for the reason that the vaporized titanium atom is free of chemical bonds. The use of reactive atom is, in principle, a convenient technique for low temperature deposition processes. For some applications, however, the major inconvenience of this technique is a necessity of vaporizing the elements to atoms particularly when these elements are refractory metals.

Plasma activation

The technique of plasma activation is receiving increasing attention because of its great versatility. In any plasma-activated process, regardless of the method of plasma generation, reactive atoms and molecular fragments are produced. These chemical species are for the most part electronically excited, and some of them may even be ionized. Thus, the reaction or deposition temperature can, in principle, be easily reduced. In addition, the inherent limitations of conventional thermodynamic and of chemical availability are eliminated in plasma activation

CHEMICAL SPRAY DEPOSITION

The chemical deposition process consists, essentially, of dissolving the starting chemical in the appropriate solvent, atomizing the liquid solution, and transporting the tiny solution droplets in a spray to within a few millimeters from the heated substrate, at which point the reactant is vaporized before reacting to form a small deposit on the surface. In cases where an additional reactant is required, the second reactant may be dissolved together with the first, or it may be introduced into reaction chamber directly as a gas. Chemical spray deposition is very similar to conventional CVD. The main difference between the two techniques is the mode of transport of the chemical reactants.

Chemical spray deposition is capable of depositing coatings at relatively low temperature. Its utility depends, however, on the price and availability of chemicals, such as organometallic compounds, which can undergo pyrolysis at low temperature. On the other hand, the problems of thermal instability and low vapor pressures of organometallic compounds, which are inheriting the conventional CVD process may be eliminated by liquid solution transport in chemical spray deposition.

REACTIVE EVAPORATION

Although evaporation is a physical vapor deposition process, reactive evaporation is by definition, a CVD process. The reactive metal atoms are evaporated either by resistance heating or by an electron beam gun. These metal atoms react with the reactant gas at the heated substrate surface to form a chemical compound coating. Metal oxides and nitrides such as titanium oxide, aluminum oxide, yttrium oxide, aluminum nitride, and titanium nitride have deposited using this technique.

Reactive evaporation is effectively as activated CVD process, since the metal atoms are in activated or reactive state, in contrast with the previously described process where all the individual starting chemicals are non-reactive. In principle, this technique is therefore suitable for low temperature depositions.

ACTIVATED REACTIVE EVAPORATION

Activated reactive evaporation (ARE) is essentially a reactive evaporation process with plasma activation. The plasma can be generated by microwave, radio frequency, or electrical discharge. Excitation is not necessarily limited to the reaction zone where both the metal atoms and the reacting gas are activated by plasma. Another possible arrangement is the activation of the reacting gas before it enters the reaction zone. Various metal carbides, nitrides, and oxides have been deposited using the activated reactive evaporation technique at relatively low temperatures.

GENERAL PLASMA ACTIVATED CVD

In the ARE process, the necessity of vaporizing the metallic element into atoms is, in some cases, a limitation in technique. A more general method is plasma activated CVD in which the starting chemicals include non-reactive CVD and it is artificially limited to those processes involving stable starting chemicals. Silicon oxide, silicon nitride, and boron nitride have been deposited using this technique.

REACTIVE SPUTTERING

Reactive sputtering is a modified CVD/PVD process; while sputtering is normally classified as a physical vapor deposition process. This situation is analogous to that of evaporation and reactive evaporation. In the sputtering process the negatively biased coating material (the target) is bombarded by positively charged inert gas ions, usually argon +. The chemical species ejected from the target surface then condense on the substrate to form a coating. The target material may be an elemental metal, alloy, or compound.

Reactive sputtering is essentially sputtering with a reaction gas. The reactant gas is activated in the plasma zone before it reacts with the ejected species to form a coating on the substrate. Reactive sputtering, like activated reactive evaporation, is thus very suitable for deposition at low temperatures. Typical example of compounds deposited using these techniques are silicon nitride, titanium oxide, titanium carbide, titanium oxycarbides, and silicon carbide.

REACTIVE ION PLATING

Reactive ion plating is hybrid CVD process. More specifically, it is a combination of ion plating and activated reactive evaporation. In the pure ion plating process in which the coating material is a metal or alloy, the vaporized metal atoms are ionized in the plasma zone and accelerated toward the surface of the negatively biased substrate, resulting in a strongly adherent deposit. In most practical cases, this situation is not realized and the process actually consists of a combination of ion plating and scattered physical vapor deposition. Moreover, under normal operating conditions, only a small fraction of metal atoms are ionized although the extent of ionization may be increased with a hollow cathode discharge.

Thus, the reactive ion plating process is ion plating with a reactant gas. Both the vaporized atoms and the reactant gas are activated by the plasma. Here, as in the case of straight ion plating, the extent of ionization of the various chemical species is very small. Reactive ion plating, therefore, consists of the scattered deposition of the excited neutral species and the ion plating of the small amounts of gaseous ions. It is to be expected that the more dominant process is the scattered deposition of the mixture of neutral species which may react in the gas phase and/or at the substrate surface to form a coating.

Various compound coatings have been deposited by the reactive ion plating process. Typical examples are titanium and Zirconium carbide and nitride, chromium carbide and nitride, and silicon nitride.

In the reactive ion plating process the substrate is limited to electrically conducting materials. The reactive atoms are evaporated either by resistance heating or by an electron beam gun. Heat is generated at the substrate by ion bombardment and the substrate temperature may be as high as 300-400°C, depending on operating conditions. An additional heating source may be necessary for higher deposition temperatures.

A variation of the reactive ion plating process is the use of stable, gaseous reactants instead of a combination of evaporated atoms and a reacting gas. This variation is called chemical ion plating which in principle may be considered as a generalization of reactive ion plating. The situation here is analogous to plasma assisted CVD and activated reactive evaporation. In most chemical ion plating applications, the reactants are activated before they enter the plasma zone; this additional excitation is necessary to decompose the stable compounds. An exception to this is the ion nitriding of steel using a nitrogen/hydrogen gas mixture. Another plasma activated coating process is plasma anodization or plasma oxidation. It has been used to prepare oxide films on metal substrates. However, the films are very thin, so that interest in this technique is mainly limited to electronic applications.

The above thus are general the ways of applying different kind of coatings onto numerous metallic substrates. A major application of the above techniques is to coatings onto cemented carbide tool products.

In 1929, the first patent on carbides entitled "Hard Metal Composition" was assigned to General Electric for making cemented carbide tools by powder metallurgy. This was a major advance in tool manufacturing technology since for the first time hard carbides could be shaped and used in metal processing. Many of the subsequent patents dealt with refinements and improvements of a basic concept and processes. As a consequence of this effort, the quality of cemented carbide tools has improved a great deal enabling the cutting speed to be increased by an order of magnitude and at the same time, increasing the tool life by a factor of three.

It took 40 years for a new major conceptual development to emerge, commercially in the form of coated tools. The first knowledge of TiC coatings applied to tungsten carbide tools in 1968 came from review of an insert coated by Widia, an European carbide company. This TiC coating had an approximate thickness of 0.000150 millionths of an inch or slightly less than 4 microns. At times it is difficult to foretell what the future will hold; however, the original report was far from providing an understanding of the importance of this new development. The coating itself was so thin and was envisioned to have no useful purpose since it would be immediately worn through.

To expand further on why we do coating, we must first mention that cutting tools must satisfy two sets of requirements. The surface of the tool must be resistant to wear and chipping, while the bulk must be tough by being able to arrest cracks generated at the surface. Both the surface and the bulk must be hard to prevent plastic deformation. These bulk and surface requirements are difficult to satisfy using the same material everywhere. Therefore, the development of a composite tool consisting of a tough and hard substrate and a wear resisting coating is consistent with the broad conceptual requirements of an ideal cutting tool. A major question remains as to how much more progress we are likely to make with coated tools and how long we may have to wait for the next major development to replace this currently very important item.

Among the coating materials currently being used on tungsten carbide substrates by carbide manufacturers are aluminum oxide, titanium nitride, carbides of all group 4B and 5B metals, composite double layers of TiN on TiC, 3 phase coating of TiC, TiCN, TiN, composite double layers of aluminum oxide on TiC and titanium oxy carbides. Although there is a good general misconception that these materials are good due to their hardness, their good wear resistance is due to their relative chemical inertness and stability, lubricity in addition to their being hard. Some of these materials form only mechanical bonds with the cemented carbide tool rather than chemical bonds due to their inherent chemical properties. These mechanical bonds are weak and therefore the bonding remains a problem with many coated tools. Another inherent problem is the loss of toughness when cemented carbide tools are coated with a carbide layer. An initial coating technique depended upon the disproportionation reaction between TiC_4 and titanium sponge. The chief problem relating to this coating application was the inability to control FEP/Carbon Depletion. Basically FEP (also called the Fast Etching Phase) is caused by carbon migration from the substrate into the coating. This can be controlled to a degree by adding an external carbon source such as methane, propane, toluene. This first crude coating did serve reasonably well until this procedure and the equipment required were modified to permit use of hydrogen as the reducing agent.

The CVD process includes several steps: Transport or diffusion of reactants to the substrates; absorption and diffusion of reactants at the substrate surface; chemical reactions at or near the substrate; nucleation and growth of deposit; desorption of gaseous products; and transport of gaseous products from the substrate. Numerous studies on the kinetics and mechanisms of CVD chemical reactions have been made which provide in principle useful

information such as activation energies and limiting steps of deposition reactions which are important for the understanding of deposition processes. None of these studies are wholly adequate in explaining all the data collected on this system.

The main problem CVD kinetic studies is the complexity of the deposition process. The difficulty arises not only from the various depths of the CVD process but also from the temperature and concentration gradients, geometric effects, gas flow patterns and the reaction zone, and, in some cases, temperature asymmetries and fluctuations in the reactor. Exact kinetic analysis is therefore not usually possible. Moreover, kinetic data are likely to be reactor dependent, so that disagreement in results between different laboratories is not uncommon.

Although the bulk properties of many potential coating materials are known, the properties of the corresponding material prepared by CVD are less well characterized. This is done, in part, to the wide range of CVD coating properties obtained from the different deposition conditions. In the case of titanium carbide, for example, the microhardness value of the CVD material is higher than that reported for the bulk material.

The relationship between coating properties and deposition conditions is generally complex. Most of the investigation into this relationship are, therefore, necessarily qualitative in nature. Raghuram and Bunshah have studied the effect of substrate temperature on the deposition rate, microhardness, structure, preferred orientation, and lattice parameter of titanium carbide deposited by the activated reactive evaporation process. The dependence of the deposition rate and of the microhardness of TiC on the substrate temperature is clearly exothermic in the deposition temperature range 520-1450° C, in contrast to the conventional CVD where most chemical reactors are endothermic. It has been suggested that this is due to exothermic chemical reactions involving transit species, whose formation of TiC on the substrate surface is adversely affected by high temperatures. In the 520-1450° C temperature range, there is also a variation in both orientation and structure of TiC deposits with the substrate temperature. The precise effect of the temperature on the microhardness of TiC is not known. It may be possible that the combination of high temperature and low deposition rate give a more uniform and more cohesive deposit, resulting in higher hardness. On the other hand, at very high temperatures the hardness may decrease owing to less cohesion as a result of grain effect and gas phase nucleation.

There is a complex set of interrelationship between, among other, temperature, deposition rate, structure, deposit grain size, and cohesion. The dependence of coating properties such as micro-hardness, ductility, and tensile strength on these interrelationships is not fully understood. More investigations in this area are still necessary. The investigation of temperature effect is particularly important for low temperature plasma activated CVD processes, for although coatings can, in principle, be produced at relatively low temperatures with aid of plasma activation, it is properties such as hardness and the cohesion adhesion of the deposit which ultimately determines the success of many protective coatings.

The chemical composition of the vapor phase has a direct influence on the coating properties. Particularly affected are those of the transition metal carbides and nitrides which are well known for their non-stoichiometry. For example, the effect of stoichiometry on the micro hardness of the carbides of titanium, zirconium, and hafnium produced by the ARE process has recently been investigated. It was found that carbon/metal ratio increases with the increase in the supply of the reactant gas, or with decrease in supply of metal vapor. The highest microhardness values of the deposit correspond with the highest carbon to metal values. The dependence on the hardness on the partial pressure of the reactant gas has also been observed for the carbides and nitrides of titanium and zirconium produced by the reactive ion plating process. Thus, by varying the reacting gas pressures during the deposition, a hardness gradient within the coating was obtained. Several investigations of the effect of chemical compositions on the properties of titanium

carbonitrides have also been reported. Keefer, Fisherschuff, and Myer from Metalwerke Plansee have measured the microhardness of the titanium carbonitride system produced at 1100°C. The hardness, hardness gradient, and color of the deposit are only a few examples of the properties which can be altered by varying the chemical composition. It is possible to alter other properties by doping or by depositing mixed compounds. In the deposition of silicon nitride by the reactive ion plating process, for example, aluminum was added to silicon to give a better match in a thermal expansion coefficient. This ability to specify the properties of deposit is one of the main attraction of CVD.

Strong adhesion or bonding of the coating to the substrate is one of the most important requirements for the successful application of protective coatings. Any of the potentially interesting coating substrate systems, a transition from the substrate material to the coating usually involves an abrupt change in such properties as hardness, coefficient of thermal expansion, and thermal conductivity. This is inevitably produced at the coating/substrate interface during the cool-down period after deposition and during service because of the differences in thermal properties. In addition, higher internal stresses tend to build up in thick coatings. Concentration of these permanent and transit stresses lead to a reduction of the bonding strength, which in turn may lead to cracking or splitting of the coating from the substrate. The end result is a shorter service life. Various ways and means have been used to reduce these stresses and to increase the adhesion between the coating and the substrate.

Reduce these stresses and to increase the adhesion between the coating and the substrate.

The more common methods for reducing stresses are:

1. Matching the properties of coating and surface.
2. Forming intermediary 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.

In principle, all of these methods are feasible. However, the last two methods are generally too restrictive, since relatively thick coatings are required in many applications, and the shape of the component to be coated is often dictated by design and engineering requirements.

The matching of coefficients of thermal expansion is often required in protective coatings because thermal expansion has a very large effect on the stresses. It is well know that many interesting coatings have failed because of the thermal expansion mismatch between the coating and substrate. Some applications is necessary to have matching thermal expansion curves for the whole range of operating temperatures. This is particularly important for operations involving thermal cycling. In cases where large temperature gradients exist across the coating/substrate interface, the differences in the thermal expansion conductivity as well as the coefficient of thermal expansion need to be considered. The selection of normal coating materials whose properties match closely with those of the substrate is generally limited. In most case the properties of the coating must be modified to suit the substrate. The matching of thermal expansion may be achieved, for example, by forming mixed deposits, or by forming graded coatings which generally consist of many thin interlayers.

In the case of wear resistant hard coatings there is necessarily a large difference of hardness between the coating and the relatively soft substrate. The hardness matching is clearly incompatible with the coating requirement, and the hardness discontinuity is normally present at the interface. For thick coatings, however, this discontinuity may be reduced or eliminated by inducing a gradual hardness transition from the interface to the outer surface of the coating. Since the hardness

increase gradually towards the outer surface, the stresses induced during service are distributed over the coating instead of being localized at the interface.

Gradients in such properties as hardness and chemical composition are usually present in diffusion coatings formed by pack cementation. In aluminized components, for example, the aluminum content decreases gradually from the outer coating surface to the interface. Although graded coatings and diffusion coatings generally yield smaller inter-facial stresses, the use of a single interlayer may be sufficient for some applications. In some cases, a single interlayer is used not only to reduce the stresses but also to promote adhesion.

The stresses at the interface and in the coating are not the only factors affecting the adhesion of CVD coatings. Other commonly cited causes of poor adhesion include:

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

Poor adhesion due to chemical attack on the substrate surface is particularly common for deposition processes involving hydrogen reduction of metal halides. The gaseous reaction products such as HF and HCl react readily with many metal substrates and cause non-adherence by the formation of stable compounds at the surface. Thin oxide films or other contaminants are undoubtedly present at the surface in many metal substrates. The effect of the contaminated substrate surface on the coating adherence is not well known. Although such a surface is generally expected to give poor adhesion, The level of contaminants can generally be reduced by careful handling, and the oxide film may in some cases be eliminated by hydrogen reduction in the reaction chamber. Decarburization of the carbon containing substrate material is likely to occur in deposition process carried out at high temperatures if the coating material is a strong carbide such as tantalum or titanium, the diffusion zone. The net result is reduced bonding strength. Fred Geliski of V.R. Wesson has found that in the deposition of tantalum on carbon steel at 1000°C. The adhesion between the tantalum coating and various steel substrates is generally poor, and it decreases with increasing carbon content in the steel. Good bonding of tantalum coating is achieved, however, with a thin interlayer which acts as a carbon diffusion barrier, since it is thermodynamically more stable than TaC.

Powdery or flaky deposits are produced when nucleation takes place in the gas phase and not at the substrate surface. Under such a condition, the deposition no longer involves individual atoms and molecules but aggregates of atoms and molecules. Such a coating is usually porous and the bonding strength is reduced, since the effective bonding surface area is less than that of the normal atomic and molecular process. Coatings deposited high temperature generally have better adhesion than those produced at low temperatures because of diffusion bonding. A notable exception to this observation is the adverse deposition of tantalum on carbon steels. For any coatings/substrate system the complete elimination of all the causes of poor adhesion is very difficult because of the coating requirements.

In some cases, it is necessary to minimize the stress and/or maximize the adhesion with the use of a single interlayer. This is particularly important for coating deposited at low temperatures because of the absence of fusion bonding.

The selection of a suitable interlayer is usually not straightforward. Various factors have to be considered, these include:

1. Properties and nature of coating in the substrate material.
2. The properties for the interlayer.
3. Deposition temperature.

4. Chemistry of the deposition reaction, or nature of chemical mixture used in the deposition process.

An example of the use of an interlayer to improve adhesion is found in the deposition of titanium carbide coatings on cemented carbide cutting tools. It was shown that by coating the cemented carbide surface with a thin layer of cobalt, the TiC nucleation becomes vary uniform and good TiC coverage of the surface is achieved. The cobalt interlayer improved considerably the adherence of the TiC coating, and this may provide a means of eliminating the TiC flaking problem encountered in certain cutting operations.

Another example of the use of interlayers is found in the deposition of aluminum oxide on copper or copper alloys where it has been observed that the adherence of aluminum oxide coatings in copper substrate was generally poor. The adhesion can be greatly enhanced by using a thin interlayer of aluminum, magnesium, or zirconium. These metals are strong oxide formers, and it has been suggested that the increased adhesions of aluminum oxide coatings may be due to the thin oxide transition layers formed between the coating and the copper substrate.

APPLICATION OF CVD PROTECTIVE COATING

CVD processes for depositing metals and alloys are well known. In principle, there is no limitation to the type of metal which may be deposited; the only requirement is the availability of suitable metal compounds which are capable of being transported to the substrate surface.

The required deposition temperature depends generally on the CVD technique, the selection of chemicals, and the type of chemical reaction.

An ideal material suited for application of a wide range of operating conditions would have at least the following properties:

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

Such an ideal material does not exist. In many applications, therefore, it is necessary to use protective coating such that the combined properties of the coating/substrate system can satisfy the operating conditions.

The choice of a coating for any given set of conditions depend upon the operating environment, the substrate material, the coating availability, and economics. Thus, economics aside, the choice is dictated by the environment/coating/substrate system, where the operating environment is contact with the coating may be gas, liquid, or solid, and may be permanent or transient as in the case of cyclic loading.

Most of the known materials may be deposited by CVD so that, in principle, a wide range of protective coatings is available to meet the demands of various conditions. the availability of feasibility of many protective coatings is limited by the compatibility of the coating/substrate system as well as by economics. Nevertheless, there exists, at present, extensive commercial applications of CVD protective coatings.

Wear resistant coatings produced by CVD have wide industrial applications. The use of diffusion coatings produced by the case hardening processes of carburizing, nitriding,

carbonitriding, siliconizing, and chromizing for wear protection is well known in many industries. There are also commercial applications of coatings formed by boriding, and ion nitriding, which is gas nitriding by chemical ion plating. In the past few years there has been an increasing interest in the use of very hard overlay coatings such as titanium carbide coatings on stamping and punching dies, thread guides, and cemented carbide tools are well known. The use of TiC to coat cemented carbide cutting tool inserts is perhaps one of the best examples of industrial applications of wear resistant coating. Hard metal throwaway tool inserts with TiC coatings have been on the market since 1968. These coated inserts are used in large quantities for turning the milling steel, and they now account for some 20% of the tool inserts used in the automobile industry. Although cemented carbides are relatively hard, the binder material, usually cobalt, can react with the work material during cutting at elevated temperatures. This reaction between the tool and work material results in a high wear rate and short tool life. By coating the insert with a 4 to 8 micron thick TiC layer, the wear resistance is considerably increased in comparison with that of the uncoated insert. The TiC coating, in addition to being wear resistant, acts as a heat and material transfer barrier, resulting in a lower insert temperature and higher chip temperature. The success of the TiC coated tool insert is due, however, not only to the excellent properties of TiC but also to the compatibility in the properties of the coating/substrate system.

Cemented carbide tool with TiN coatings and composite coatings consisting of TiC and titanium carbonitrides are examples of other coatings produced commercially. These coatings, although less hard than TiC, have other advantage in some machining operations. The use of reactive sputtered titanium oxycarbides as wear resistant coatings for tool inserts has also been investigated.

In addition to carbide and nitride coatings, tool inserts coated with several microns of alpha aluminum oxide have also been commercialized. The wear properties of aluminum oxide are superior to those of the previous coatings, especially in high speed cutting operations where the temperature of the insert tip may be as high as 1000-1500°C. At these temperatures the titanium carbide, nitride, and carbonitride coatings unlike aluminum oxide, are no longer resistant to oxidation. It has been shown that typical cutting operations the lifetime of the alumina coated tool insert is more than twice that for the TiC coated insert, which in turn, is about 5 times that of the uncoated insert. The aluminum oxide is normally deposited on a thin intermediate layer of TiC which is used to improve the adhesion of the aluminum coating.

Titanium nitride and carbonitrides have also found application as protective and decorative coatings in the watch and jewelry industry because of their hardness, chemical inertness, and attractive colors. For example, cemented carbide watch cases coated with these materials are now in the market.

Although titanium carbides, nitrides, and carbonitrides, alpha alumina, and other materials have excellent wear properties, the deposition of these materials in the commercial CVD process requires relatively high temperatures, generally above 800°C. These high temperatures are not suitable for materials such as normal steels, copper, and copper alloys because of the degradation of the substrate properties. Many hard coatings have been deposited at lower temperatures using compounds that decompose at lower temperatures but the selection of wear resistant hard coatings deposited at low temperatures by CVD is limited – hence the reason for the development of PVD coatings which lack the bonding strength of CVD but still enhance the wear resistance considerably.

A more suitable wear resistant coating for normal steels, copper and copper alloys is tungsten carbide. Coatings of W_2C on Steels have been deposited from the chemical mixture tungsten hexafluoride, benzene, hydrogen in the temperature range 400-700°C. The relatively low deposition temperature together with the hardness and good wear performance, should be very

suitable for normal steels and non-ferrous metals such as copper, and copper alloys, particularly for applications in low load abrasion wear environment.

Another example of the industrial applications of CVD protective coatings is the use of thin films to protect metals in the electronic industries. Films of 1/2 to 2 microns thick silicon oxide and other glassy materials are used to protect, for example, silicon and aluminum metals in micro circuits against the ambient environment and mechanical scratches to ensure stable electrical properties.

EROSION RESISTANT COATINGS

Material erosion of mechanical components caused by impacting abrasive particles is a well known industrial problem, particularly in the compressor turbine blades and vanes of aircraft turbine and industrial gas turbines. The erosion of the thin metal tips and leading edge of the blades and vanes result in a deterioration of engine performance. At present, the Pack cementation method is widely used for the production of oxidation resistant coatings. Sacrificial alumina coatings formed as an outer “skin” on a pack diffusion coated item (typically aluminized) when the component is subjected to use temperatures for example, are commonly used to extend the life of super alloys and the oxidation/corrosion environment encountered in gas turbines.

There is, however, an increasing interest in the development of hard overlay coatings protection against erosion – this includes depositing titanium carbonitride on stainless steel compressor blades at 600-700°C using the chemical mixture titanium tetrachloride and an amino compound. A thin nickel interlayer is used to improve adhesion. The deposit temperature of this process is significantly lower than that of the process used for coating tool inserts. Laboratory tests have shown that, compared with uncoated stainless steels and other materials, a highly significant improvement in erosion resistance is achieved with the titanium carbonitride coating. Another relatively low temperature process for depositing erosion resistant coatings on turbine blades has been recently developed. In this process, coatings of chrome carbide Cr_7C_3 are produced by thermal decomposition of dicumene chromium at 450-650°C. A thin interlayer of ductile nickel is used to improve the adhesion of the carbide coating and to improve the mechanical properties of the composite coating. It has been claimed that the carbide nickel two layer coating is highly resistant to thermal shock, mechanical chock and erosion. This is an improvement over more brittle titanium carbonitride coating, which, although more erosion resistant, showed a 30 to 50% loss in air foil fatigue strength.

Another erosive environment is the bore of a gun barrel where crack formation and material removal are induced by the high temperature, high pressure, and chemical reactions during propellant combustion. The effect of this hot gas erosion are loss of muzzle velocity and accuracy. A significant improvement over uncoated and chrome plated gun barrels was achieved by depositing coatings of rhenium, tungsten, and boron carbide which are shown to be suitable for protection against this type of erosive environment.

CORROSION RESISTANT COATING

CVD corrosion resistant coatings have extensive application in various industries. Coatings produced by such processes as chomizing, aluminizing, and siliconizing and widely used commercially, particularly for applications against high temperature oxidation, which, in essence is a special case of corrosion.

CVD coatings of tantalum, niobium, chromium, molybdenum, aluminum, and nickel among others are also used for protection against corrosion. Titanium fasteners coated with aluminum for example are used in aerospace applications. This CVD aluminum coating process avoids hydrogen embrittlement that may result from conventional electroplating. Tantalum is well known for its corrosion resistance. Coating of this metal are used commercially in chemical processing

equipment. Steel pipes as large as several meters in length and up to half a meter in diameter have been coated with tantalum.

Several investigations of protective coatings for applications in various corrosive environment have also been reported. Silicon oxide coatings have been used to protect chrome steels against corrosion in high pressure carbon dioxide atmosphere typical of advanced gas cooled reactors. Considerable improvement in corrosion resistance has also been achieved with the silica coatings. However, these coatings developed cracks during corrosion tests, presumably formed by thermal stresses.

DIFFUSION BARRIER COATINGS.

Diffusion barrier coatings are required in some applications where the fabrication or the operating temperature is high. In some cases barriers are used to prevent interdiffusion between two solid layer in a composite system. Examples of such coatings are TiC, which is used as a carbon diffusion barrier in the deposition of tantalum on steels, and TiN, which is used as a nitrogen diffusion barrier in the doped silicon carbide heating elements. In other cases, barrier coatings on metals are necessary to prevent, for example, the inward and/or outward diffusion of carbon in a gaseous operating environment. This problem of carburizing or decarburization is most likely to be important for high temperature gas cooled nuclear reactors.

HEAT RESISTANT COATINGS

A basic requirement of heat resistant coating materials is thermal stability. Characteristically, these materials have very low vapor pressures and do not decompose at elevated temperatures. Thus, many high temperature materials such as refractory metals and ceramics are suitable as heat resistant coatings for applications in vacuum or inert environments. In many applications protective coatings are required to operate in air, so that these coatings must also be oxidation resistant. In these cases, the distinction between heat resistance and oxidation resistance generally disappears. This is particularly so in aerospace industries where diffusion coatings produced by aluminizing, chromizing, and siliconizing are used extensively for oxidation resistance.

CVD is a gas phase molecular forming process in which the coating is built up by individual atoms or molecules. Other commonly used molecular forming processes are electroplating, evaporation, sputtering, ion plating. Although all these methods are capable of producing dense coatings, only CVD is versatile enough to provide a wide range of coatings of metals, alloys, compounds such as carbide, nitrides, oxides, and borides.

Electroplated materials are difficult to produce in high purity because of inclusions from the electrolyte trapped in the deposits. CVD materials on the other hand, can be produced in high purity and density, so that coatings may be free of undesirable pin holes. This is particularly important for applications in corrosion environments. Electroplating is, in principle, not a line of sight process such as evaporation and sputtering, but because of the diffusion in the liquid phase, the cavities and holes are not coated as efficiently as in the CVD gas phase process. Further, hydrogen embrittlement of the substrate material may occur during electroplating. Certain advantages of CVD over other coatings methods may be listed.

1. It is a versatile process which provides coatings of a variety of metals, alloys, and compounds not readily obtainable by other means.
2. The chemical composition of the deposit may be controlled so that the graded coatings and mixed coatings can be produced.
3. The coatings structure and grain size may be controlled.
4. There is a choice of chemical systems and chemical reactions so that for example, hydrogen embrittlement can be avoided.
5. There is a wide range of throwing power or deposition rates.
6. Coatings are dense and their purity may be controlled.

7. Uniform coatings on objects of complex shape is possible, particularly when using CVD process.
8. Particles can be coated using gas fluidized bed.
9. Relatively simple equipment is required if deposition can be carried out at atmospheric pressures.

CVD has also some advantages. At present, many of the commercially interesting processes require relatively high deposition temperatures. This places a limitation on the types of substrate materials which can be coated by these processes. Another disadvantage, with the exception of Pack cementation, is the need for the careful gas handling and gas containment. The containment of the reactant gases in the reactor is a limitation on the size of the components which can be coated. However, relatively large components have been coated using special techniques: An example is a coating of large steel pipes with tantalum. Also it has been shown that in some cases the chemical spray deposition technique does not require cumbersome protection against error, especially for deposition of oxides and metals that do not form oxides.

It should be noted that the various advantages and disadvantages do not apply equally to all different techniques. The reactive sputtering process for example, generally has lower deposition rates than CVD. Moreover, unless special care is taken, reactive evaporation and reactive sputtering are expected to give less uniform coatings on objects of complex shape than conventional CVD. Thus, the unique deposition characteristics must be considered when using a particular CVD technique. For any given application, the choice between a CVD and a non-CVD coating generally depends on such factors such as economics, performance, and availability of coating.

PRESENT SITUATION AND FUTURE POSSIBILITIES

There are at present extensive industrial applications of CVD coatings for the protection of metals against wear, erosion, corrosion, and high temperature oxidation. Some examples of the more recently developed overlay coatings which have found commercial applications are TiC, TiN, titanium carbonitride, aluminum oxide, tantalum, and aluminum metal. The use of these and other coatings is expected to increase as their properties become more widely known. High temperature diffusion barrier coatings are likely to find future applications in fiber reinforced metals and alloys. Most of the present commercial CVD protective coatings are produced in relatively high temperatures by pack -cementation and conventional CVD. These coatings are generally not suited for substrate materials such as normal steels, copper, and copper alloys. However recently developed process for deposition of tungsten carbide at temperatures between 300-700°C shows considerable promise in extending the application of CVD protective coatings to these materials. The tungsten carbide coatings are particularly suitable for protection against low load abrasion wear.

Although there exist many coatings materials with good protective properties, relatively few of these materials are now in use commercially. This is due, in part, to the high deposition temperatures and to the incompatible properties of the substrate in coating materials. Some of these limitations may overcome with the use of graded coatings and intermediate layers. Progress is expected in the near future in the development of low temperature CVD processes. The reduction of deposition temperatures and these processes may be realized with the use of suitable chemicals such as organo-metallic compounds and reactive atoms, or with the aid of additional excitation such as plasma activation. All these improvements will undoubtedly result in wider application of CVD protective coatings, particularly for substrate materials such as nickel and cobalt based superalloys, steels, copper, and copper alloys. Some low temperature coating processes involving the newer CVD techniques have already been developed, but the effects of the low deposition temperatures on the structure and quality of the coating needs more investigation.

CVD has been used for the past 40 years successfully in the commercial world and improvements will continue to make it an important tool for substrate property enhancement.