# CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition (CVD) is a distinctly different coating process than the PVD vacuum process of vacuum evaporation, ion plating, or sputtering. A heat-activated process, CVD relies on the reaction of gaseous chemical compounds with suitably heated and prepared substrates.

The primary reactive vapor can be either a metal halide (chloride, bromide, iodide, or fluoride) or a metal carbonyl, M (CO), although some hydrides and organometallic compounds are used. In general, deposition of a pure metal from the halide can occur either by hydrogen reduction at a given temperature or by direct pyrolytic decomposition at a higher temperature.

Whenever carbides, nitrides, or borides are the desired CVD products, the metal halide vapor is accompanied by an additional reactive species such as methane, nitrogen, or boron trichloride respectively. The addition of a reactive species lowers the free energy of the reaction products so that the compound is formed in preference to the pure metal. However, manipulation of reactor pressure, temperature, and/or reactant composition can also influence the deposition products.

## ADVANTAGES AND LIMITATIONS

The versatility of the CVD process has been demonstrated by the wide variety of geometrical configurations into which it forms refractory metals, alloys, and refractory compounds. Users of CVD maintain that the process compares favorably with other methods of plating and forming in its ability to produce high-density materials, high-purity materials, high-strength materials, and complex shapes. The extraordinary throwing power of the CVD technique is such that very intricate coatings may be formed on substrates of complex geometry.

Materials in excess 99.9% of theoretical density are commonly produced by this process. Thin structures made by CVD are used for applications in which vacuum tightness is required; in some cases, such structures could not be made by any other process.

Engineering materials can be deposited at considerably higher purity levels than is possible with other manufacturing means because of CVD's ability to purify the precursors. The strength of CVD materials is dependent on crystal structure and size, purity, density, and internal stress, much the same as that of materials formed by other processes. Generally the CVD materials are more ductile because of their purity and can have comparable and/or higher mechanical strength than wrought material, providing that they are dense and have a fine equiaxed grain structure.

Not all deposited materials exhibit high strength; certain materials, such as pure tantalum and pure columbium, which are weak in their fully annealed condition, have low yield strengths and high ductility in the vapor-deposited condition. However, when pure rhenium, pure columbium, tantalum alloys, and most rhenium alloys are formed by CVD, they have higher strengths.

Metals that are readily electroplated or electro-formed commercially are generally not well suited to chemical vapor deposition. In the case of the former, CVD processes are precluded due to the unsuitable or hazardous properties of potential reactants. For example, electroplated metals such as lead, tin, and copper, and alloys such as brass are available as cyanides and fluoroborates and not as CVD-compatible halide salts. With electro-forming, in general, the electroformed part is the product desired and not the coating-substrate combination. However, molds for forming plastics that are vapor formed from nickel carbonyl are available for commercial use when their longer life justifies the higher costs.

A closed system is usually required when depositing the materials because of the corrosive, toxic, or moisture-sensitive characteristics of most reactants. Within the control volume, low pressures reduce the likelihood of homogenous (gas-phase) nucleation and induce conditions favorable for heterogeneous (gas-to-solid) nucleation. Moreover, closed systems tend to normalize gas compositions while preventing

the formation of undesirable species. Material utilization can be low, and reactant cost may be high, which may increase the overall cost of the process. In addition, the high temperature of the reaction can cause distortion of the parts being coated.

## COATINGS DEPOSITED

A variety of pure metals or carbides, nitrides, borides, silicides, and oxides of metals can be deposited by CVD processes. Coating thickness is usually in the range of 0.0002 to 0.050" (5 to 1270 um). The co-deposition of titanium carbide (TiC) and titanium nitride (TiN) to form titanium carbonitride (TiCN) by Moderate Temperature Chemical Vapor Deposition (MTCVD) process is rapidly expanding in use. Chromium deposition on steel substrates, resulting in carbides of chromium and iron, $(CrFe)_7C_3$, provides exceptional resistance to corrosion and cold welding.

The selection of the base material and the coating depends on their mutual interaction and on the operating conditions in the field. Moreover, these compounds have shown very good oxidation resistance in hot forging applications.

## APPLICATIONS

The major applications of CVD take advantage of the unique characteristics of the process, such as good throwing power, the ability to deposit refractory materials at temperatures far below the normal ceramic processing temperatures, and the capability of producing materials of exceptionally high purity. Typical uses for the CVD process include the fabrication or coating of tubing, tungsten boride crucibles, decorative trim, and dinnerware.

A substantial field of CVD application exists for the hard coating of tools fabricated from high-speed steels, air-hardenable tool and stainless steels, and the cemented carbides. In particular, both titanium carbide (TiC) and titanium nitride (TiN) are regularly used to enhance the life of cemented carbide cutting tools and high-speed steel punches and dies. In the fastener industry, the vertical integration of high-temperature, low-pressure CVD of TiC and TiN into the tool manufacturing sequence has shown the greatest benefit. Similarly, the incorporation of TiC and TiN in the carbide cutting tool industry has proven to be of significant commercial value. Tools coated by CV D have a significantly longer life span.

More exotic depositions include the silicon and silicide coating of tungsten, and the platinum and rhenium coating of electronic hardware. Emitting surfaces and structures for cathodes as well as structural hardware for grids and anodes can be created by this process. Chemical vapor deposition is also the basis for several steps in the manufacture of integrated circuits for microelectronic applications and for solar cell fabrication.

Chemical vapor deposition is used for depositing a refractory metal on jet aircraft turbine blades and for joining tungsten to other refractories at low temperature. Many applications are found in the nuclear power field, such as the coating of nuclear fuel particles for fission product retention or for matrix compatibility. Nuclear fuel can be contained by direct deposition of refractory metals and/ or pyrolytic carbon on the surface of the fuel itself. Ceramic-to-metal seals have been made by the deposition of metals, ceramics, or both; and there are many applications for composite materials that use deposited high-density oxides and metals. Tungsten and/or carbon fibers have been encapsulated with both boron carbide and silicon carbide by CVD processes. The filaments have been subsequently used as reinforced composites in structural components.

The protection of chemical equipment is an obvious application of CVD. Steel with less than a 0.002 (50 pm) deposited coating of tantalum will frequently outperform stainless steel, or Monel or Inconel (the International Nickel Co., Inc.) at a competitive cost. Cladding for abrasion resistance also warrants serious consideration. Many hard refractory-metal compounds cannot readily be formed or finished by mechanical means. On the other hand, hard coatings such as silicon carbide, tungsten carbide, tantalum carbide, or titanium diboride are readily deposited.

## PROCESS FACTORS

Some important factors in CVD processes are the thermo-dynamic combinations of gas pressure, temperature, and velocity, and reactant composition; composition material; substrate cleanliness and temperature; the gas storage, flow, and recovery systems; scrubber systems for the by-products; and the composition and construction of the reaction vessel.

## Substrates

When the process is used for plating or coating, the substrates must be free of greases and oils for good adhesion. This surface preparation is accomplished by ultrasonic and/or vapor degreasing before loading. Substrate surfaces are also frequently vapor honed to improve adhesion. During heat-up, oxide layers may be removed by insitu scrubbing with reducing gases or mild acids. The temperature of the substrate promotes the reaction; ideally, it should be uniform and vary as little as possible because variations tend to affect the uniformity of structure, thickness, composition, and properties of the film.

Substrate materials must accept heat without deforming, since deposition temperatures may vary from 400 to 3600 F (200 to 2000 C). However, compensation for deformation during deposition is practical in many cases. Conducting heat into the substrate is simple if the workpiece is small and regular in shape, but difficult if it is large and complex. Small workpieces may have to be racked or rotated. The irregular geometry of some workpieces will call for individual designs for injecting and exhausting the gas for film uniformity; but some substrates can be tumbled, vibrated, or fluidized for uniform deposition, especially if the transport properties of the reactant species are low.

### Reaction Temperature

To decompose or reduce the metal compound, a transfer of heat energy is involved, and the substrate is usually held at a substantially higher temperature than any other part of the system. For this reason, the reaction chamber may present more of a high-temperature problem than any other part of the system. Most reactions are also conducted in an anhydrous and anaerobic environment, and frequently at sub-atmospheric pressures.

Typical deposition temperatures range from 1500 to 2200 F (800 to 1200 C). The selection of temperature and pressure is dictated by the properties desired in the deposit, the degree of thickness and compositional uniformity, and the deposition rate, which may vary from 0.000003 in./min (0.07 mm/min) at low temperatures to significantly more than 0.001 in./min (25 mm/mm) at higher temperatures. The ability to provide uniformly thick coatings with refined grain is also influenced by the deposition temperature. In both cases, low-temperature processing is frequently desirable, although a tradeoff with rate of deposition must often be made. Fewer CVD reactions are available for use at temperatures below 1500 F (800 C) than above. However, the temperature required for a given reaction can, in selected cases, be lowered by exposing the substrate to an electrical plasma in the gas phase during deposition. This procedure is referred to as plasma-assisted CVD or simply plasma CVD.