CARBIDES, CEMENTED

1. Introduction

Cemented carbides belong to a class of hard, wear-resistant, refractory materials in which the hard carbides of Group 4–6 (IVB-VIB) metals are bound together or cemented by a soft and ductile metal binder, usually cobalt or nickel. Although the term cemented carbide is widely used in the United States, these materials are better known internationally as hard metals (see also REFRACTORIES; REFRACTORY COATINGS; REFRACTORY FIBERS).

Cemented carbides were first developed in Germany in the early 1920s. The first cemented carbide to be produced was tungsten carbide [12070-12-1], WC, having a cobalt [7440-48-4], Co, binder (1). A number of scientific and technological advances provided impetus to development (2): (*1*) discovery of the high hardness of cast WC; (*2*) production of fine particles of WC, by reaction of the elements or by carburizing with hydrocarbons (qv); (*3*) application of sintering technology to the carbides; (*4*) lowering of the high sintering temperature of pure carbides by the use of a liquid phase of eutectic alloys of the iron-group metals; and (*5*) discovery of a unique combination of properties of the WC–Co alloys, including high compressive strength, high elastic modulus, abrasion resistance, toughness, and thermal shock resistance.

Over the years, the basic WC–Co material has been modified to produce a variety of cemented carbides containing WC–TiC, WC–TiC–TaC, WC–TiC–(Ta,Nb)C, WC–Mo_2C–TiC, and other solid solution carbides, which cover a wide range of applications including metalcutting, mining, construction, rock drilling, metal-forming, structural components, and wear parts. About 50% of all cemented carbide production is used for metal-cutting applications. Efforts to replace cobalt completely by nickel or iron in WC-based compositions have not been very successful, although partial replacement with nickel has been shown to offer benefits in certain applications (3).

Attempts to produce WC-free compositions for metal-cutting applications were made in the 1930s with the development of TaC−Ni, TiC−Mo_2C−Ni, and TiC−VC−Ni−Fe−Co alloys. But these alloys could not compete with the stronger WC−Co based cutting tools. However, in the 1950s, an understanding of the role of molybdenum in improving the wettability of titanium carbide [12070-08-5], to Ni binder brought the TiC−Mo_2C−Ni alloys closer in performance to WC−Co based tools in finish machining of steels. Further improvements in tool performance were obtained by additions of other carbides such as tantalum carbide [12070-06-3], TaC, and niobium carbide [12069-94-2], NbC, to the TiC−Mo_2C−Ni Ni alloys.

The first carbonitride alloys based on Ti(C,N)−Ni−Mo were introduced in 1970 followed by (Ti, Mo) (C,N) based compositions having fine microstructures that provided a balance of wear resistance and toughness (4). Continued research on the titanium carbonitride alloys in the 1980s led to the development of complex cermets having a variety of additives such as molybdenum carbide (2:1) [12069-89-5], Mo_2C, TaC, NbC, zirconium carbide [12020-14-3], ZrC, hafnium carbide [12069-85-1], HfC, WC, vanadium carbide [12070-10-9], VC, chromium carbide (3:2) [12012-35-0], Cr_3C_2, and aluminum, Al (5). Various mixes of these additives impart different combinations of wear resistance, thermal shock resistance, and toughness and allow tools to be tailored for a wide range of machining applications.

The binder metal, cobalt or nickel, is obtained as very fine powder and is blended with the carbide powders in ball mills, vibratory mills, or attritors using carbide balls. The mills are lined with carbide, low carbon steel, or stainless-steel sleeves. Intensive milling is necessary to deagglomerate the carbide particles, break up the initial carbide crystallites, and disperse the cobalt among the carbide particles to enhance wetting by cobalt during sintering. Milling is usually performed under an organic liquid such as alcohol, hexane, heptane, or acetone to minimize heating of the powder and to prevent its oxidation. In the milling process, a solid lubricant such as paraffin wax or polyethylene glycol/is added to the powder blend to impart strength to the pressed or consolidated powder mix. The lubricant provides a protective coating to the carbide particles and greatly reduces the oxidation of the powder. After milling, the organic liquid is removed by drying. In a spray-drying process, commonly employed in the cemented carbide industry, a hot inert gas such as nitrogen impinges on a stream of carbide slurry droplets and produces free-flowing spherical powder aggregates (see Fig. 1).

The milled and dried grade powders are pressed to desired shapes in hydraulic or mechanical presses. Special shapes may require a presintering operation followed by machining or grinding to the final form. Cold isostatic pressing, followed by green forming, is also common in the manufacture of wear-resistant components and metal-forming tools. Rods and wires are formed by the extrusion process. Complex parts can be formed by injection molding.

The pressed compacts are normally set on graphite trays and sintered. The vacuum sintering process consists of lubricant removal (400−500°C), oxide reduction (500−1000°C), rapid densification (1300−1350°C), and WC grain growth (1300–1500°C). During the final sintering operation, the cobalt–carbon eutectic melts and draws the carbide particles together, shrinking the compact by 17–25% on a linear scale and producing a virtually pore-free, fully dense product. In addition, the carbide grains coarsen due to solution and reprecipitation of the finer carbide particles in the eutectic melt.

In the 1970s, the cemented carbide industry adapted hot isostatic pressing (HIP) technology to remove any residual internal porosity, pits, or flaws from the sintered product (6). The HIP process involves reheating vacuum sintered material to 25–50°C less than the sintering temperature under an inert gas pressure of 100–150 MPa (14,500–21,750 psi). The sinter-HIP process (7), developed in the early 1980s, employs low pressure HIP, up to 7 MPa (1015 psi), after vacuum sintering. The pressure is applied at the sintering temperature when the metallic binder is still molten, resulting in void-free products. After sintering, cemented carbide products that require shaping to meet surface finish, tolerance, or geometry requirements undergo grinding with metal-bonded diamond wheels or lapping with diamond-containing slurries.

Separate cemented carbide product classifications exist for metal-cutting applications and wear parts (8). Classifications that are generally accepted by producers and users are available (9).

Inhalation of extremely fine carbide, cobalt, and nickel powders should be avoided. Efficient exhaust devices, dust filters, and protective masks are essential when handling these powders.

2. Recycling of Scrap

Recycling of cemented carbide scrap is of growing importance. The nonsintered scrap is reused in the milling of grade powders. The sintered cemented carbide scrap is recycled by several different processes. In one recycling method, the sintered scrap is heated to 1700–1800°C in a vacuum furnace to vaporize some of the cobalt and embrittle the material. After removal from the furnace the material is crushed and screened. In chemical recycling, the cobalt is removed by leaching, leaving carbide particles intact. In the zinc reclaim process, commercialized in the late 1970s, the cleaned scrap is heated with molten zinc in an electric furnace under inert gas at $\sim$800°C. The zinc reacts with the cobalt binder and the carbide pieces swell to more than twice their original volume. The zinc is distilled off in vacuum at 700–950°C and reclaimed. The treated carbide pieces are pulverized and screened to produce a fine powder. The cobalt is still present and there is no change in grain size from the original sintered scrap. The coldstream reclaim method employs a high velocity airstream to accelerate cemented carbide particles against a target surface with sufficient energy to fracture the particles. The coldstream process, so called because the air cools as it expands from the nozzles, is employed in combination with the zinc reclaim process.

3. Tool Failure Modes

Cutting tools are subjected to various failure modes during use. A primary failure mode is abrasive wear, which can be explained in terms of relative hardness

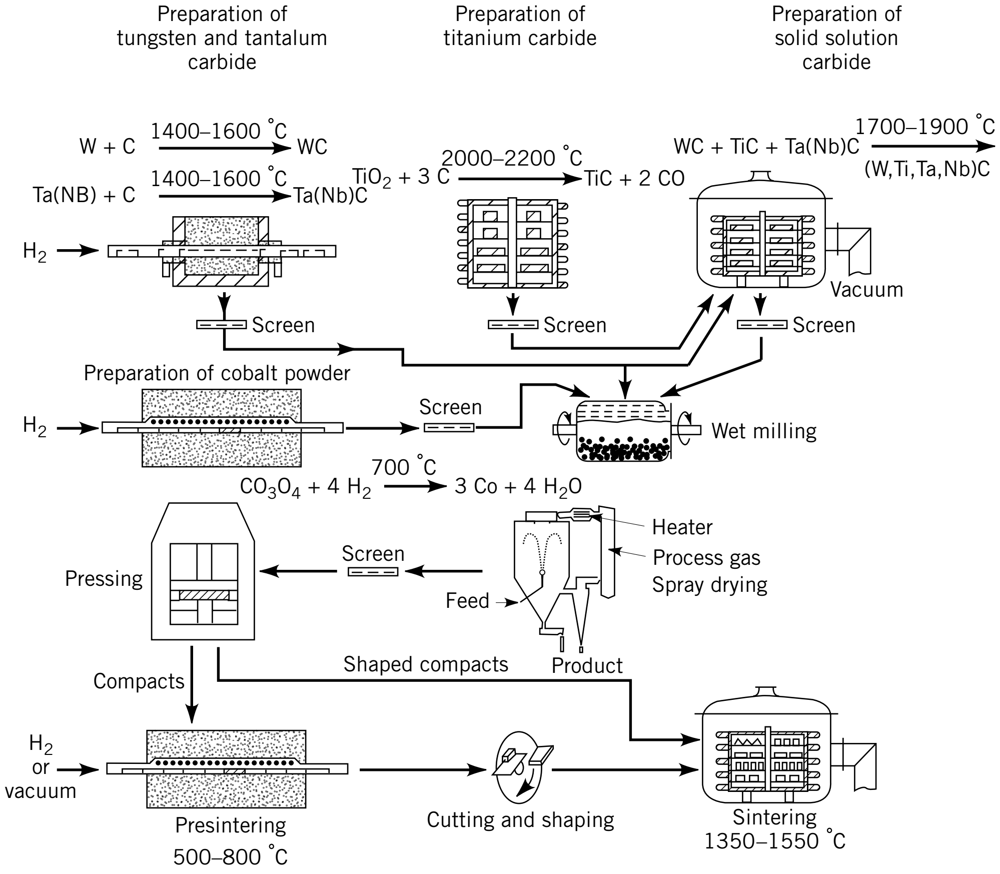

Fig. 1. Preparation of cemented carbides where cobalt serves as the binding metal.

of the cutting tool and the workpiece material that is machined. In simple terms, a cutting tool must be harder than the material being cut. In addition to abrasive wear, other failure modes can occur due to high-localized tool tip temperatures ($\sim$1000°C) and high stresses ($\sim$700 MPa or $\sim$101,500 psi). High temperatures and stresses can cause blunting of the tool tip from plastic deformation, whereas high stresses can lead to catastrophic fracture. The workpiece may chemically interact with the tool material. The tool may also experience repeated impact loads during interrupted cuts. The useful life of the tool would depend on its response to the conditions existing at the tool tip. Figure 2 presents examples of tool failures often observed in metal-cutting operations.

3.1. Crater Wear. Crater wear (Fig. 2**a**), observed on the rake or top face of cutting tools, generally occurs during machining of steels and ductile irons at high speeds. It is primarily caused by a chemical interaction between the rake face of a metal-cutting insert and the hot metal chip flowing over the tool. This interaction may involve diffusion or dissolution of the tool material into the chip.

3.2. Flank Wear. Flank or abrasive wear (Fig. 2**b**) is observed on the flank or clearance face of a metalcutting insert or at the working end of wear

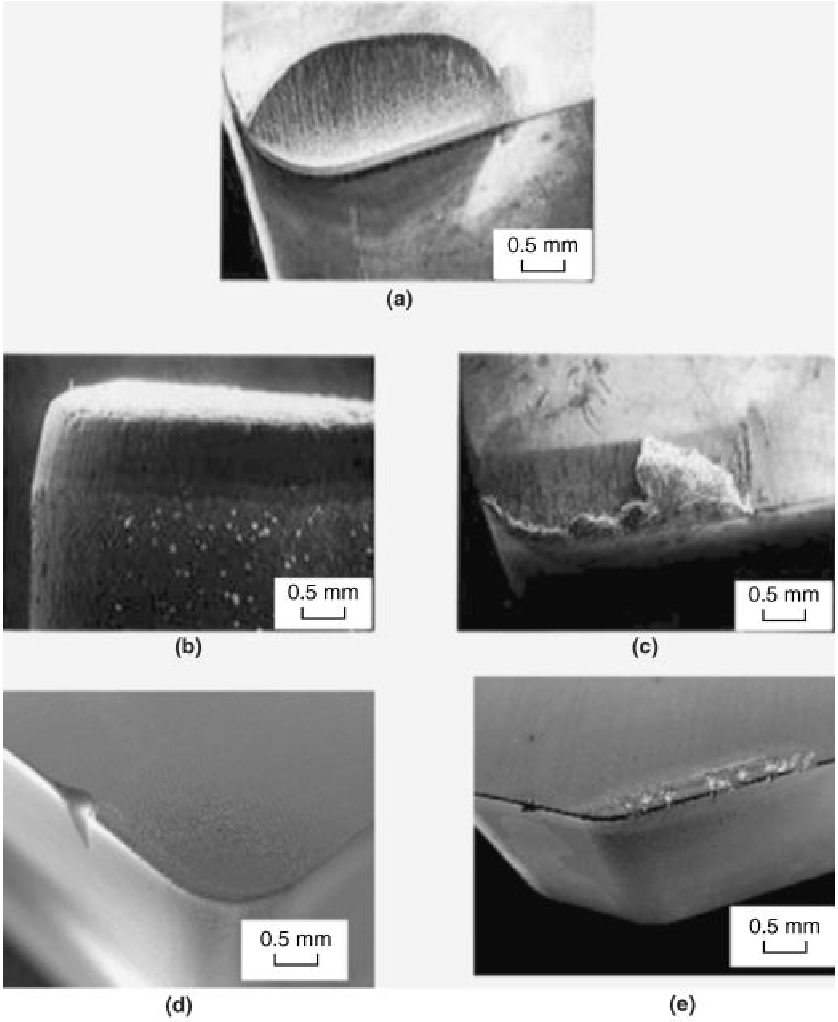

Fig. 2. Tool failure modes: (**a**) Crater wear on a cemented carbide tool produced during machining plain carbon steel. (**b**) Abrasive wear on the flank face of a cemented carbide tool produced during machining gray cast iron. (**c**) Built-up edge produced during low speed machining of a nickel-based alloy. (**d**) Depth-of-cut notching produced in nickel-based alloy machining, and (**e**) Thermal cracks on tool edge produced during face milling of alloy steel.

parts or mining tools and is related to the hard microstructural phases of the workpiece. Harder tool materials provide greater flank and abrasive wear resistance.

3.3. Built-up Edge. Under certain conditions, when ductile materials such as low carbon steels or aluminum are machined, the workpiece may weld to the tool tip as built-up edge, BUE (Fig. 2**c**). Workpiece build-up can lead to poor part finish and premature tool failure. During machining, the built-up material may also break off carrying with it small fragments of tool material. BUE formation can arise from a mechanical or chemical effect. Built-up edge from a mechanical cause refers to the adherence of the workpiece metal at relatively low speeds when the tool surface is rough. It can be suppressed by polishing the tool or increasing the tool tip temperature through higher metalcutting speed. With coated cemented carbide tools, BUE may occur when the coating layer flakes off exposing the carbide substrate. Even if the coating is intact, some coating materials such as chemical vapor deposition (CVD)−TiN show a tendency to react chemically with steel workpieces causing a built-up edge. BUE from chemical causes can be suppressed if the top TiN layer is removed to expose the more stable underlying Al_2O_3 during postcoat treatment. With rough coatings BUE can occur from a mechanical effect, which can also be suppressed by post-coat polishing treatment.

3.4. Depth-of-Cut Notching. Depth-of-cut notching (DOCN) is a localized tool wear process that occurs at the depth-of-cut line (Fig. 2**d**). Notching is a problem with workpieces that tend to work harden and generate high tool-tip temperatures, such as austenitic stainless steels or high temperature alloys. Notching is attributed to the chemical reaction of the tool material and the atmosphere, or to abrasion by the hard, sawtooth outer edge of the chip. DOCN can lead to tool fracture.

3.5. Thermal Cracks. Cemented carbide tools sometimes exhibit a series of cracks perpendicular to the tool edge when applied in interrupted cutting conditions such as milling (Fig. 2**e**). These thermal cracks are caused by the alternating expansion and contraction of the tool surface as it heats while cutting and then cools outside the cut. With prolonged intermittent cutting, lateral cracks may appear parallel to the cutting edge. The thermal and lateral cracks may join together and cause small fragments of tool material to break away.

Fracture is the least desirable mode of tool failure because it is unpredictable and catastrophic. The preferred tool failure mode is flank wear, because it progresses gradually and can be easily monitored for tool-changing protocol. Tool material development work is focused on minimizing flank wear and preventing unwanted tool failure modes such as catastrophic fracture, gross plastic deformation, BUE, DOCN, and crater wear.

4. Evaluation of Properties

In addition to chemical analysis, a number of physical and mechanical property evaluations are required to determine cemented carbide quality. Standard test methods employed by the industry for abrasive wear resistance, apparent grain size, apparent porosity, coercive force, compressive strength, density, fracture toughness, hardness, linear thermal expansion, magnetic permeability, microstructure, Poisson's ratio, transverse rupture strength, and Young's modulus are set forth by ASTM/ANSI and the ISO.

Among the physical properties, density is very sensitive to composition and porosity of the cemented carbide and is widely used as a quality control test. Magnetic properties most often measured are magnetic saturation and coercive force. Magnetic saturation provides an accurate measure of the carbon content in the cemented carbide alloy and is also used as a quality control test. The carbon content must be controlled within narrow limits to prevent the formation of a

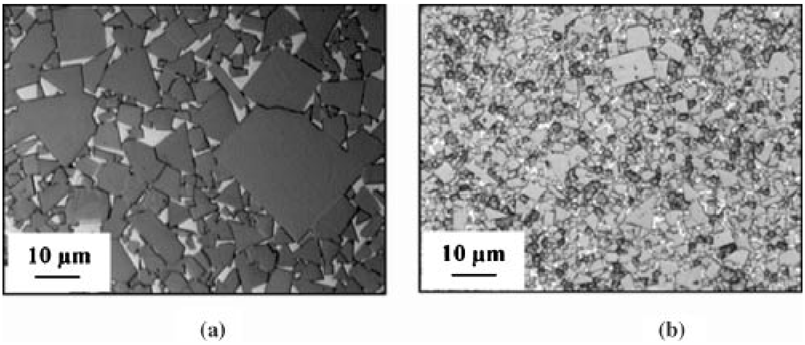

Fig. 3. Microstructures of cemented carbides: (**a**) 90% WC—10% Co alloy, coarse grain. (**b**) 86% WC—7%(Ta,Ti,Nb)C—7% Co alloy, medium grain size. The gray angular particles are WC and the dark gray rounded particles are solid solution carbides. The white areas are cobalt binder.

brittle eta-phase, of composition Co_3W_3C or Co_6W_6C, at low carbon levels, or free graphite where carbon levels are high. For a WC-6 wt% Co alloy, the preferred carbon window is 0.09 wt%. Coercive force may vary considerably as sintering temperature increases and indicates the structural changes that take place during sintering. For a given cobalt and carbon content, the coercive force provides a measure of the size and distribution of the carbide phase in the microstructure.

The properties and performance of cemented carbide tools depend not only on the type and amount of carbide but also on carbide grain size and the amount of binder metal. Information on porosity, grain size and distribution of WC, solid solution cubic carbides, and the metallic binder phase is obtained from metallographically polished samples.

Optical microscopy and scanning and transmission electron microscopy are employed for microstructural evaluation. Figure 3 shows typical microstructures of cemented carbides.

Hardness, which determines the resistance of a material to abrasion and deformation, is affected not only by composition but also by porosity and microstructure. Higher cobalt content and larger carbide grain size reduce hardness and abrasion resistance but increase the toughness of cemented carbides. The trade-off between abrasion resistance and toughness enables the cemented carbide manufacturer to tailor these materials to a wide variety of metal-cutting and nonmetal-cutting applications.

Hardness is measured by the Rockwell A-scale diamond cone indentation test (HRA) or by the Vickers diamond pyramid indentation test (HV). Although the Rockwell scale has been used for decades in the carbide industry as a measure of hardness, a true indication of the resistance of the tool to deformation in metal-cutting operations can be obtained only by measuring hardness at elevated temperatures. Hot-hardness tests are performed using Vickers diamond pyramid indentors. The hardness of cemented carbides decreases monotonically with increasing temperatures.

Cemented carbides possess high compressive strength but low ductility at room temperature, but at temperatures associated with metal cutting these materials exhibit a small but finite amount of ductility. Measurement of yield strength is therefore more appropriate at higher temperatures. Like hardness, the compressive yield strength of cemented carbide decreases monotonically with increasing temperatures.

The most common method of determining the fracture strength of cemented carbides is the transverse rupture strength (TRS) test. A disadvantage of this test is the large scatter in the experimental data resulting from surface defects in the test specimens. Nevertheless, TRS is an excellent quality control test and it is particularly useful for large carbide components. A better measure of the intrinsic strength of the cemented carbide is the fracture toughness parameter, K_{Ic}, which indicates the resistance of a material to fracture in the presence of a sharp crack (10). The fracture toughness of carbide materials increases with cobalt content and carbide grain size but decreases with additions of cubic carbides.

Resistance to thermal shock is another important property that determines tool performance in milling. No laboratory test has yet been developed that can consistently predict the resistance to thermal shock of a tool. However, empirical parameters have been suggested that can be used to evaluate tool materials for their thermal shock resistance (11). A commonly used parameter is $\sigma k/E\alpha$, where σ is the transverse rupture strength, k is the thermal conductivity, E is the Young's modulus, and α is the coefficient of thermal expansion. In general, the higher the value of this parameter, the higher is the thermal shock resistance of the tool material.

Although hardness is a measure of abrasion resistance of cemented carbides, tool manufacturers use a wet-sand abrasion test to measure abrasion resistance directly. In this test, a sample is held against a rotating wheel for a fixed number of revolutions in a water slurry containing aluminum oxide particles. Abrasion resistance is reported as a relative ranking based on the reciprocal of volume loss of the material. Note that the abrasion resistance measured at room temperature does not correlate directly with high temperature wear resistance in metal-cutting operations.

5. Metal-Cutting Applications

5.1. Tools and Toolholding. Early carbide metal-cutting tools consisted of carbide blanks brazed to steel holders. When the brazed tool wore out, the carbides were reground and used again. Indexable inserts were introduced in the 1950s. In this configuration the so-called throwaway carbide insert is secured in the holder pocket by a clamp or some other holding device instead of a braze. When a cutting edge wears, a fresh edge is rotated or indexed into place. The main advantages of indexable inserts are ease of replacement, consistent positioning of the cutting edge relative to the workpiece, elimination of regrinding, and the ability to coat the inserts with the chemical vapor deposition (CVD) or the physical vapor deposition (PVD) processes. Indexable inserts also feature chipbreaker grooves, which not only control chip formation but also reduce the cutting forces. The edges of both brazed tools and indexable inserts are often modified, slightly rounded (honed) or chamfered, to prevent chipping and premature failure of a too sharp and therefore a weak cutting edge.

5.2. Compositions. For machining purposes, alloys having 5–12 wt% Co and carbide grain sizes from 0.5 to >5 μm are commonly used. By controlling the amount of Co and WC grain size, different combinations of wear resistance and toughness can be obtained. Powder metallurgical processing allows the manufacture of cemented carbides with any combination of raw materials to obtain the desired properties. The straight WC–Co alloys have excellent resistance to simple abrasive wear and are widely used in machining materials that produce short chips, eg, gray cast-iron, nonferrous alloys, high temperature alloys, etc and in a broad spectrum of industrial applications, including metalworking, metal and coal mining, transportation and construction industries. WC–Co alloys having submicrometer carbide grain sizes have been developed for applications requiring more toughness or tool edge strength. Such applications include indexable metal-cutting inserts and a wide variety of solid carbide drilling and milling tools. Grain refinement in these alloys is obtained by small (0.25–3.0 wt%) additions of TaC, NbC, VC, or Cr_3C_2 during carburization of tungsten or later in the powder blend.

5.3. Ultrafine-Grained WC—Co Alloys. Since the late 1980s there has been a tendency toward ultrafine-grained cemented carbides (WC grain sizes <0.5 μm) for woodworking tools, printed circuit board drills, and endmills. A number of factors have contributed to this development (12): (*1*) Observation that both hardness (abrasion resistance) and strength (transverse rupture strength) can be substantially improved with ultrafine grained carbide without seriously impacting bulk fracture toughness. (*2*) The hardness advantage over conventional cemented carbide is maintained up to 800–900°C. (*3*) Advent of sinter-HIP technology has allowed manufacture of ultrafine-grained carbides without pits and flaws. (*4*) The decrease in thermal conductivity with decreasing carbide grain size is more than compensated with increase in strength, so that the thermal shock resistance is not adversely impacted. (*5*) Advances in powder milling, granulation, and pressing technology have allowed the manufacture of ultrafine-grained cemented carbide possible. (*6*) Availability of advanced PVD and CVD coatings has enhanced tool performance and improved productivity. The use of ultrafine-grained carbides is expected to grow not only for woodworking tools, wear parts, and printed circuit board microdrills, but in metal cutting insert applications (milling of Al-Mg alloys, cast iron engine blocks, etc).

5.4. Cemented Carbides for Steel Machining. Straight WC–Co tools are not suitable for machining steels that produce long chips because they undergo crater wear from diffusion of WC into the steel chip surface. However, additions of cubic carbides such as TiC, TaC, and NbC impart chemical stability and crater wear resistance to WC–Co alloys. A disadvantage of TiC additions to WC–Co alloys is reduction in thermal shock resistance. However, TaC additions to WC–TiC–Co alloys can mitigate the deleterious effect of the TiC. Steel cutting compositions thus typically contain WC–TiC–(Ta,Nb)C–Co. It has been shown that cubic carbides are more effective in resisting crater wear and exhibit greater strength and hardness when they are added as preformed solid solutions such as WC–TiC (50:50) than when added as mixtures of WC and TiC (13). Other preformed solid solutions that are added to steel cutting compositions include TaC–NbC, WC–TiC–TaC, and WC–TaC(NbC). Tantalum carbide is often added as (Ta,Nb)C because the chemical similarity between TaC and NbC makes their separation expensive.

5.5. Coated Carbide Tools. Chemical vapor deposited TiC coatings were used in the late 1960s to combat wear on steel watch parts and cases. When applied to cutting tools, the relatively thin (~5 μm) TiC coatings extended tool life in steel and cast iron machining by a factor of two to three by suppressing the crater wear and flank wear (14). Hard coatings reduce frictional forces at the chip–tool interface, which in turn reduce the heat generated in the tool resulting in lower tool tip temperatures. Coatings also permit the use of higher cutting speeds boosting machining productivity. Currently, coated carbides account for nearly 75% of all indexable metal-cutting inserts used in the United States and CVD accounts for ~70% of coated carbides. The rest are coated with PVD process.

In the CVD coating process, tools are heated in a sealed reactor with gaseous hydrogen at atmospheric or lower pressure; volatile compounds are added to the hydrogen to supply the metallic and nonmetallic constituents of the coating. For example, TiC coatings are produced by reaction of $TiCl_4$ vapors with methane (CH_4) and hydrogen (H_2) at 970–1000°C. The reaction is

$$\mathrm{TiCl_4\ (g) + CH_4\ (g) + H_2\ (g) \longrightarrow TiC\ (s) + 4\ HCl\ (g) + H_2\ (g)}$$

During the initial stage of the TiC deposition, a secondary reaction often occurs in which carbon is taken from the cemented carbide substrate. The resulting surface decarburization leads to the formation of a brittle eta phase and associated microporosity at the coating/substrate interface. The eta phase, in turn, can produce premature tool failure resulting from excessive chipping and reduced edge strength (15). However, improvements in CVD coating technology have resulted in coatings with greater thickness uniformity, more adherence, and more consistent morphology and microstructure having minimum interfacial eta phase and associated porosity (16).

Modern CVD coatings feature multiple layers involving various combinations of titanium carbonitride [12347-09-0], TiCN, titanium carbide [25583-20-4], TiC, titanium nitride [25583-20-4], TiN, zirconium cabronitride [25583-20-4], ZrCN, and alumina [25583-20-4], Al_2O_3, with controlled crystal structures (alpha-or kappa-alumina) and grain sizes optimized for various machining applications (Fig. 4). With better control of the CVD process, tool manufacturers can now offer coatings in a wide range of thickness (5–20 μm) with consistency and reproducibility. Multilayer CVD coatings with individual layers as thin as 0.2 μm are also available for machining tough workpiece materials (17).

The high temperatures employed during CVD coating generally ensure good interdiffusion bonding between the substrate and the coating. However, during cooling, the thermal expansion mismatch between the substrate and the coating can cause stresses that adversely affect coating adhesion. In certain cases coating stresses may be relieved by cracks that form in the coating. Because the thermal expansion coefficients of the coating materials (TiC, TiCN, TiN, and Al_2O_3) are higher than those of the WC–Co based substrates, CVD coatings are in residual tension at room temperature. Residual tensile

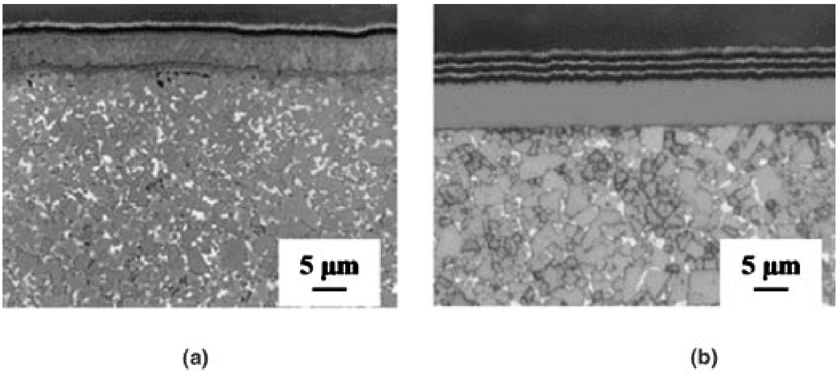

Fig. 4. Multilayer coatings on cemented carbide substrates: (**a**) 92% WC—8% Co with a TiN–TiCN–TiC–TiCN–Al_2O_3–TiN coating ~9 µm thick. (**b**) 86% WC—8%(Ta,Ti,Nb)C—6% Co with TiCN coating supporting multiple alternating coating layers of Al_2O_3 and TiN.

stresses are most severe at tool corners. To minimize stress, CVD-coated tools are honed at the cutting edge before coating.

In the mid-1980s a new CVD process for depositing TiCN was commercialized. Using a mixture of $TiCl_4$, H_2, and an organic compound such as acetonitrile, it was shown that TiCN can be deposited at moderate temperatures (800–900°C) at a faster deposition rate than the conventional CVD process (18). The reduced process temperature and faster deposition rate minimize the formation of the embrittling eta phase at the substrate-coating interface and reduce the thermally induced tensile cracks that are common to higher temperature CVD coatings (19). Tool manufacturers are currently offering TiCN and ZrCN coatings deposited by the medium temperature CVD (MTCVD) process. MTCVD TiCN coating has become an integral part of multilayer CVD coatings on carbide substrates (Fig. 5).

In another modification of the CVD technology called the plasma assisted CVD (PACVD) process, the deposition temperature is further reduced to

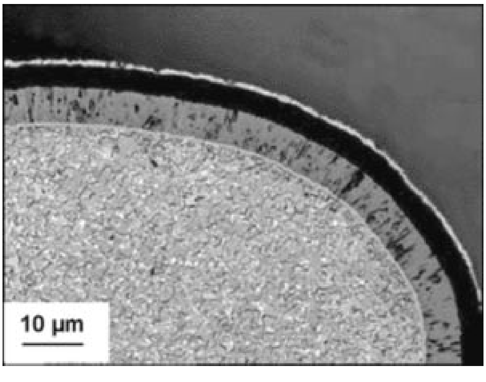

Fig. 5. Multilayer TiN–MTCVD–TiCN/Al_2O_3/TiN coating (~10 µm total thickness) >90% WC-4%Tac-6% Co substrate.

$\sim$600°C but the chemical reaction that produces the hard coating compounds is activated by the use of a plasma, comprising argon and reactive gases (20). Use of plasma assisted CVD coatings (TiN, TiCN, and Al_2O_3) on carbide substrates is still not widespread.

The metal-cutting performance of coated carbide tools is dependent not only on the properties of the substrate and the coating but on the interfacial bonding between the substrate and the coating. In recent years, significant advances have been made in this area. These include chemical as well as abrasive treatment of the substrate prior to the coating process. These precoat treatments improve the surface integrity and smoothness and enhance the adhesion of the coating. Significant advances have also been made in improving the interlayer adhesion through the use of special bonding layers. These new technologies have allowed tool manufacturers to offer thicker coatings with more functional layers.

A recent development in the area of hard coatings for cemented carbide tools is the low pressure synthesis of pure diamond by carbonaceous gas decomposition in presence of hydrogen atoms (21). This process is an alternative to the high pressure synthesis of bulk diamond, which is used to fabricate PCD (polycrystalline diamond) tips that are brazed on to cemented carbide tool inserts. The CVD diamond products are available either as thin films (<30 μm) deposited on carbide substrates or as thick sheets (typically >350 μm) brazed on to carbide substrates. Both products are used in machining abrasive, non-ferrous and nonmetallic workpiece materials and in particular, aluminum silicon alloys and aluminum metal matrix composites (low silicon aluminum alloys reinforced with SiC or Al_2O_3 particles), which are used primarily in automotive (brake rotors, drive shafts, etc) and aerospace (landing gear components) industries. Special pretreatments of the carbide substrate are required to ensure good adhesion of the diamond film. While the earlier diamond films featured coarser, faceted diamond surface, process advances now enable the tools to be produced with smoother diamond morphology with improved workpiece surface finish capabilities.

5.6. Coated Carbides with Functionally Gradient Substrate Microstructures.

A breakthrough in coated carbide cutting tools occurred in the late 1970s when a peripherally cobalt-enriched substrate (2–3 times higher cobalt at the tool insert periphery than in the bulk) was developed for a TiC–TiCN–TiN coated tool (Fig. 6**a**). The cobalt-enriched periphery was also slightly depleted in cubic carbides. The bulk of the tool insert had lower cobalt and higher level of cubic carbides. The combination provided superior edge strength while maintaining the edge and crater wear resistance of the coating layers (22). The high edge strength of this tool was attributed not only to the higher level of cobalt at the tool periphery but also to the striated morphology of the cobalt binder that prevented crack propagation and catastrophic fracture. This development permitted users to make heavy interrupted machining cuts such as those encountered in scaled forgings and castings at lower speeds. Further refinements to the cobalt-enrichment concept (1.5–2 times higher cobalt and complete depletion of cubic carbides in the tool periphery compared to the bulk and non-striated distribution of cobalt), in combination with Al_2O_3 coating (Fig. 6**b**), expanded the application range of this type of tool to higher speeds (23,24). Multilayer CVD coated tools with cobalt-enriched substrates can handle

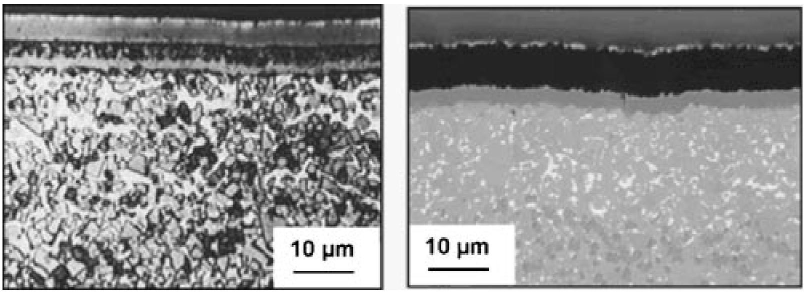

Fig. 6. Microstructure of a cemented carbide alloy: (**a**) 86% WC–8%(Ti,Ta,Nb)C–6% Co, with a cobalt-enriched periphery (first generation) and TiC–TiCN–TiN coating, and (**b**) 86% WC—8%(Ta,Ti,Nb)C—6% Co, with a second generation cobalt-enriched and solid solution carbide depleted periphery and TiCN–Al_2O_3–TiN coating.

medium to heavy roughing to semifinishing and even finishing operations on a wide range of workpiece materials such as cast irons, carbon, alloy, and stainless steels. The broad application range of cobalt-enriched tools enables them to cover a large percentage of the metalcutting operations of a plant giving the user an added level of tool edge security and performance consistency.

5.7. Postcoat Surface Treatments. One of the major problems in the performance of coated carbide tools is the susceptibility of coatings to flake in certain machining applications. This results in microchipping of the cutting edge and accumulation of workpiece build-up leading to poor part finish and premature tool failure. This problem can be largely suppressed by postcoat polishing treatments that either polish the insert edge or the entire tool surface. The top TiN coating layer is removed exposing the alumina layer underneath at the cutting edge (Fig. 7) or over the entire insert surface.

5.8. Physical Vapor Deposited Coatings. In the mid-1980s (PVD) emerged as a commercially viable process for applying hard TiN coatings onto cemented carbide tools. The coating is deposited in a vacuum, sustaining an

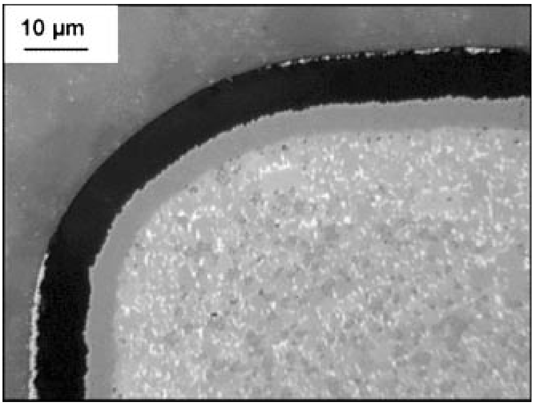

Fig. 7. Microstructure of an 87% WC—6%(Ta,Ti,Nb)C—7% Co cemented carbide substrate with a TiCN–Al_2O_3–TiN coating and postcoat treatment.

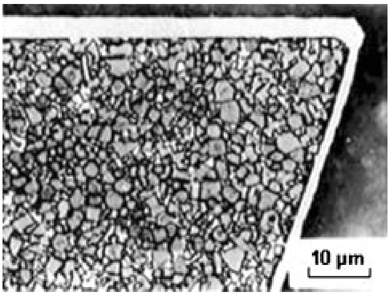

Fig. 8. An example of PVD TiN coating on a sharp cemented carbide tool.

argon gas plasma, by condensation from a flux of neutral or ionized atoms where the metal species are derived from a variety of sources, including electron-beam evaporation, magnetron sputtering, and arc evaporation (25,26). The evaporated or sputtered metal or cation species (titanium, aluminum, chromium, etc) are made to react with the anions from gaseous species (N_2, CH_4, etc) introduced into the vacuum chamber. Since PVD coatings are deposited at low pressures (10^{-3}–10^{-2} torr), the atoms and molecules have long mean free paths and undergo fewer collisions, making PVD a line-of-sight deposition technique. This requires tool fixture rotation during the deposition process to ensure coating thickness uniformity on the faces of tool inserts. A number of factors make PVD process attractive for use with cemented carbide tools: (*1*) lower deposition temperature (<550°C) prevents eta-phase formation and produces finer grain sizes in the coating layer; (*2*) PVD coatings are usually crack-free; (*3*) depending on the deposition technique, compressive residual stresses, which are beneficial in resisting crack propagation, may be introduced in the coating (27); (*4*) PVD coating preserves the transverse rupture strength of the carbide substrate, whereas the CVD process generally reduces the TRS by as much as 30% (28); and (*5*) PVD coatings can be applied uniformly over sharp cutting edges (Fig. 8). This is desirable because it leads to lower cutting forces, reduced tool tip temperatures, and finer workpiece finishes. PVD coated tools are thus successfully employed in operations where sharp edges are most beneficial, including milling, turning, boring, drilling, threading, and grooving. Typical workpieces include carbon, alloy, and stainless steels, hardened steels, cast irons, nonferrous materials, and high temperature nickel-base alloys and titanium alloys. Newer PVD coatings are rapidly becoming commercially available (Fig. 9). These include TiCN, titanium aluminum nitride, which ranges in composition from Ti_2AlN [60317-94-4] to TiAlN, chromium carbide [12011-60-8], Cr_3C_2, chromium nitride [24094-93-7], CrN, titanium diboride, TiB_2, multiple alternating layers of TiN−TiAlN, and aluminum-rich AlTiN. Crystalline PVD Al_2O_3 coatings are subject to extensive R&D effort, but are not yet commercially available. Nano-layered PVD coatings (alternating very thin layers ~20 nm each, eg, TiN/AlN) have been recently introduced into the market. The properties of these coatings are dependent on the choice of the individual layers, including the thickness and crystallinity of each layer. It is possible to increase the hardness of the composite by a factor of 2 or more at the optimum nanolayer spacing compared to the hardness of either consituent alone

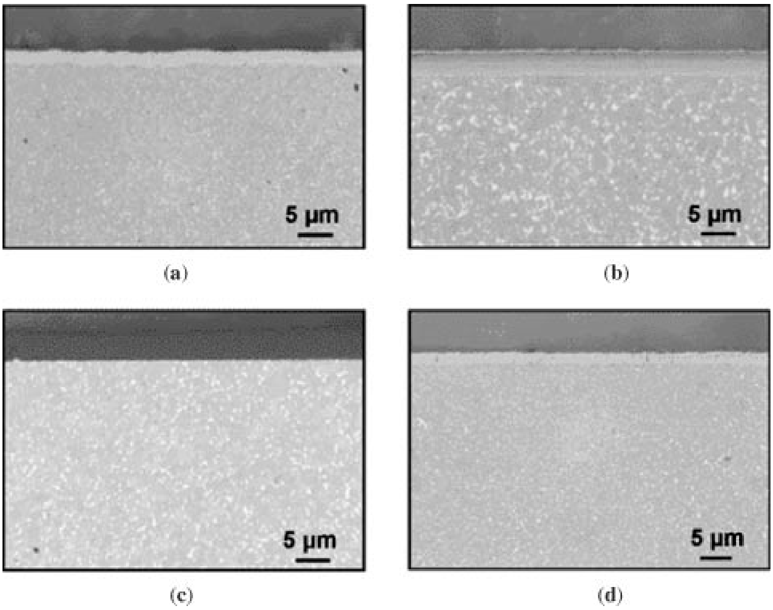

Fig. 9. Four generations of PVD coatings on cemented carbide substrates: (**a**) TiN, (**b**) TiN/TiCN/TiN, (**c**) TiAIN, and (**d**) TiB_2.

(29). Nano-composite thin films comprising two or more materials [eg, TiN or TiAlN nano-crystals, typically <4 nm, embedded in a matrix of amorphous Si_3N_4] with microhardness exceeding 40 GPa are also being developed (30).

As noted earlier, the wear behavior of coated tools and their metalcutting performance can be improved by precoat treatments. For PVD coatings, it has been demonstrated by indentation test that microblasting the tool surface with fine grit alumina or water peening can significantly improve the bonding of PVD coating to the substrate (31).

5.9. Solid Lubricant Coatings. More recent developments in hard coatings for cemented carbide cutting tools include solid lubricant coatings (hard coatings with a low coefficient of friction), eg, amorphous metal–carbon, Me–C:H and soft coatings (eg, MoS_2, pure graphite, or WC/C) deposited on a hard coating layer such as PVD TiAlN (31) (see Fig. 10). These coatings provide enhanced metalcutting performance, notably in drilling and tapping of steels and aluminum alloys by resisting chip adhesion to the tool and aiding chip evacuation.

5.10. CVD–PVD Combination Coatings. The late 1980s saw the development of a coating technology, in which an outer layer of PVD TiN was combined with CVD TiN/TiCN inner layers. The development of this technology was based on the observation that the inner CVD layers provide wear resistance and excellent adhesion to the substrate, and the outer PVD layer offers a hard, fine-grained, crack-free, smooth surface endowed with compressive residual stresses. When combined with a cobalt-enriched substrate with good bulk

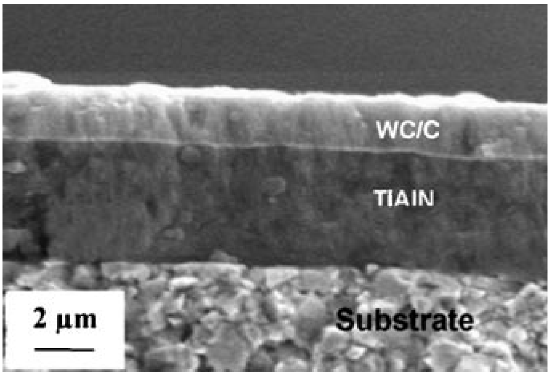

Fig. 10. TiAIN–WC/C coating on carbide substrate (Courtesy: Balzers Inc.)

deformation resistance, the CVD–PVD combination coating has been found to provide improved tool performance in milling of steel workpieces at relatively high speeds (32). Other CVD–PVD combinations involving PVD TiAlN are now commercially available.

5.11. Metalcutting Tool Design. Modern metalcutting tool insert development requires a systems approach that involves (*1*) substrate design for optimum deformation resistance, fracture resistance, and thermal shock resistance, (*2*) coating design for wear resistance, lubricity, reduced frictional heat, and workpiece surface finish requirements, (*3*) macro-geometry or chip-groove design for chip control, and (*4*) micro-geometry or edge sharpness to control cutting force and surface finish, and to minimize edge chipping.

6. Nonmetal-Cutting Applications

Today almost one half of the total production of cemented carbides is used for nonmetal-cutting applications such as mining, oil and gas drilling, transportation and construction, metalforming, structural and fluid-handling components, and forestry tools. The majority of compositions used in these applications comprise straight WC–Co grades. In general, cobalt contents vary from 5 to 30 wt% and WC grain sizes range from <1 to <8 μm and sometimes up to 30 μm. Extensive discussion of hard metals employed in nonmachining applications is available (33–36).

Metal-forming applications include drawing dies, rolls for hot and cold forming of strips and bars, cold heading dies, forward and back extrusion punches, swaging hammers and mandrels, and can body punches and dies. Applications requiring high impact strength employ grades with 11–25 wt% Co. When wear resistance is of paramount importance, grades having lower cobalt content and finer grain size are suitable choices. When gall resistance, ie, resistance to metal pickup on the tool, is needed, alloy carbides such as (W,Ti)C and (Ta,Nb)C are used. Corrosion resistance applications typically employ grades having finer WC grain sizes and lower cobalt contents or combinations of nickel, cobalt, and chromium. In metal-forming applications, hard coatings, particularly by PVD, can enhance the wear resistance of carbide tools further although the use of coatings is not as widespread as in metal-cutting applications.

The impetus for the synthesis of WC and subsequent development of cemented carbides came from the wire drawing industry where the hard metals are still used. The most commonly used grade is WC—6 wt% Co with medium grain size (1–2 μm). Compositions having higher cobalt content are used in drawing tubes, rods, and bars.

Alloys having 15–30 wt% Co and very coarse WC grain sizes (up to 20 μm) have replaced steel rolls in the production of hot-rolled steel rods. Carbide rolls are also well suited for the cold reduction and finishing of strip products in Sendzimir mills where rigidity and dimensional stability are particularly important. The compositions used in these applications have a 5.5 wt% Co and medium WC grain size (1–2 μm).

The high abrasion resistance and edge strength of carbides make them ideal for use as slitter knives for trimming steel cans and stainless and carbon steel strips, cutting abrasive materials in the paper, cellophane and plastic industries, and for slitting magnetic tapes for audio, video, and computer applications. Carbides having submicrometer grain sizes and 6–10 wt% Co offer sharp cutting edges, good surface finish, and high edge strength in these applications.

Cold-forming equipment such as extrusion or heading punches and dies are made from cemented carbides to produce a variety of parts such as wrist pins, spark plug shells, bearing retainer cups, and propeller shaft ends. Generally, WC—12 wt% Co alloy is used for back extrusion punches and a WC—16 wt% Co grade is recommended for extrusion dies. Submicrometer carbides may also be used for punches. In cold-heading applications involving the manufacture of nuts, bolts, and screws the dies have to withstand considerable stress and repeated impacts and must therefore possess good fatigue strength. Alloys with 20–30 wt% Co or Co–Ni–Fe are required.

The high elastic modulus, compressive strength, and wear resistance of cemented carbides make them ideal candidates for use in boring bars, long shafts, and plungers, where reduction in deflection, chatter, and vibration are concerns. Metal, ceramic, and carbide powder-compacting dies and punches are generally made of 6 and 11 wt% Co alloys, respectively. Another application area for carbides is the synthetic diamond industry where carbides are used for dies and pistons.

The rigidity, hardness, and dimensional stability of cemented carbides, coupled with their resistance to abrasion, corrosion, and extreme temperatures, provide superior performance in fluid-handling components such as seal rings, bearings, valve stems and seats, and nozzles. In the transportation and construction industry, steel tools having cemented carbide cutting tips are used for road planing, soil stabilization, asphalt reclamation, vertical and horizontal drilling, trenching, dredging, tunnel boring, forestry, and for snowplow blades, tire studs, and street sweeper skids.

Cemented carbides play a crucial role in the recovery of metallic ores and nonmetals by underground or open-pit mining practices, recovery of minerals such as coal, potash, and trona, and drilling for oil and gas. The methods of excavation can be broadly classified into three types: rotary drilling, roto-percussive drilling, and flat-seam underground mining. In the oil and gas drilling industry tungsten carbide buttons, having 10–15 wt% Co, are used in steel drill bodies for deep penetration of metamorphic, igneous, and sedimentary rocks.

Cemented tungsten carbides also find use as a support for PCD cutting tips, or as a matrix alloy with cobalt, nickel, copper, and iron, in which diamond particles are embedded. These tools are employed in a variety of industries including mineral exploration and development; oil and gas exploration and production; and concrete, asphalt, and dimension stone cutting.

7. Economic Aspects

Cemented carbide inserts and tools for metal cutting and metal working have traditionally accounted for the largest percentage of carbide industry sales. However, carbide tool consumption in nonmetal-working fields, notably in the construction and transportation industries, has grown rapidly. On the other hand, the demand for primary materials has been somewhat reduced by use of recycled cemented carbide scrap.

There are >200 cemented carbide producers in the world. A majority of hard metal production can be attributed to Cerametal Sarl, Iscar Ltd., Kennametal Inc., Mitsubishi Materials Corporation, Plansee Tizit GmbH, Sandvik AB, Sumitomo Electric Industries Ltd., Allegheny Technologies Inc., Toshiba Tungaloy Co. Ltd., and Zhuzhou Cemented Carbide Industry Company. Many of the smaller producers have narrow manufacturing capabilities and a limited range of product offerings.

Developments in materials, coatings, and insert geometries have claimed an increasing share of research and development budgets in the cemented carbide industry. Important economic benefits of these effects have been an increase in tool performance and significant increase in metal-cutting productivity. Continuing developments in computer numerically controlled machining systems have placed a heavy emphasis on tool reliability and consistency, which in turn puts pressure on the industry to invest increasing amounts of capital in developing new materials and processes.

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