

Nano-grained Tungsten Carbide-Cobalt (WC/Co)

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Abstract

Cemented tungsten carbides are commercially one of the oldest and most successful powder metallurgy products. These composites are essentially aggregates of particles of tungsten carbide bonded with cobalt metal via liquid-phase sintering. The properties of these materials are derived from those of constituents – namely, the hard and brittle carbide and the softer, more ductile binder. The wide applications of cemented carbides for cutting tools and wear parts arise because of their unique combination of mechanical, physical, and chemical properties. Nano-grained WC/Co composites have potential to replace standard materials for tools and dies, and wear parts because of their increased hardness and toughness. By means of particle size reduction, the fracture toughness and wear resistance of WC/Co can be increased significantly. In this review, we describe the historical development and properties of cemented tungsten carbides. We will also review synthesis and consolidation efforts for nano-grained WC/Co. The challenges for nano-grained WC/Co to achieve engineering success are also discussed.

1. Introduction

Cutting tools must be able to resist high temperature and severe temperature gradients, thermal shock, fatigue, abrasion, attrition, and chemical induced wear [1, 2]. Thus materials for cutting tools and dies must have high hardness to combat wear, hot strength to overcome the heat involved, and sufficient toughness to withstand interrupted cuts or vibrations occurring during the machining process. Cutting tools are a two billion-dollar industry worldwide and form the backbone of manufacturing operations for metals, polymers, and advanced materials such as intermetallics and composites of all types [1, 2].

Tungsten carbide (WC) has been well known for its exceptional hardness and wear/erosion resistance. Matrices of ductile metals, such as cobalt, greatly improve its toughness so that brittle fracture can be avoided. Cemented tungsten carbides are commercially one of the oldest and most successful powder metallurgy products [3]. These composites are essentially aggregates of particles of tungsten carbide bonded with cobalt metal via liquid-phase sintering. The properties of these materials are derived from those of the constituents – namely, the hard and brittle carbide and the softer, more ductile binder. The cutting tool and wear part applications arise because of their unique combination of mechanical, physical, and chemical properties.

Although other metal carbides, such as TiC, are also used in cutting tools, around 95% of all cemented-carbide cutting tools are tungsten carbide-based [3]. In 1992, 60% of metallic tungsten produced went into WC for cutting tools, dies, etc., only 25 % went into lamp filaments, heating elements, and mill products, with most of the remainder was used in steels and super-alloys [4]. Annual production of tungsten for use in tungsten carbide worldwide was about 25,000 metric tons in 1991/92 [5].

The Discovery of Tungsten Carbide

Henri Moissan (1852-1907), a Nobel Laureate (1906), is best known as the inventor of the electric furnace and for his unsuccessful attempts to prepare artificial diamonds. It was in his laboratory at the School of Pharmacy at the University of Paris, that the two carbides of tungsten were discovered, namely W_2C (1896) by H. Moissan and WC (1898) by P. Williams [6].

Figure 1 shows the tungsten-rich part of the binary W-C equilibrium diagram [7]. Three W-C stoichiometries have been found, hexagonal W_2C crystallizing in three modifications, the PbO_2 , Fe_2N , and CdI_2 types, denoted β , β' , and β'' , respectively, the cubic sub-carbide WC_{1-x} crystallizing in the NaCl type structure denoted γ , and the hexagonal WC denoted δ . W_2C exhibits a comparatively wide homogeneity range of 25.5 to 34 at.% C at 2715 °C. This phase originates from a eutectoidal reaction between elemental W and δ -WC at 1250 °C and melts congruently with the W solid solution at 1715 ± 5 °C and with γ - WC_{1-x} at approximately 2758 °C. Phases of W_2C stoichiometry

are obtained as intermediate products during WC production. The γ -phase results from a eutectoidal reaction between β and δ at 2535 °C and melts at approximately 2785 °C. It can be obtained at room temperature by extremely rapid cooling, e.g., in plasma sprayed layers. The technically important δ -WC is the only binary phase stable at room temperature and has almost no solid solubility up to 2384 °C but may become carbon deficient between this temperature and its incongruent melting point [8].

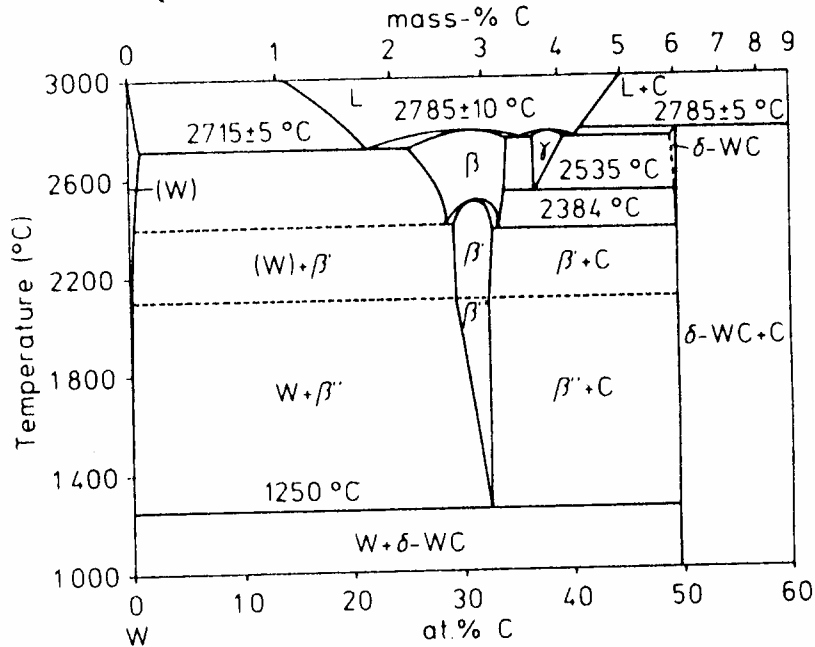


Figure 1. The W-C phase diagram [7].

The monocarbide, WC, has a simple hexagonal crystal structure with two atoms per unit cell and a c/a ratio of 0.976 [8]. The structure of WC showing interleaved trigonal prismatic cells is given in Figure 2. In the primitive hexagonal lattice, half of the six-fold coordinated carbon positions are unoccupied. The structure unit of the hexagonal phase is thus the M_6C triangular prism with carbon in the center, or the C_6M with a six-fold coordinated metal atom. The advantage enjoyed by this WC structure, relative to the NaCl-type, is a lower energy for the electrons in the dd M-M bonding states [9].

Figure 2. The structure of WC, showing interleaved trigonal prismatic cells [9].

The first commercial tungsten carbide products were melt cast wire-drawing dies. Unfortunately, the cast pure WC is quite impractical because the stoichiometric compound WC, with 6.13 weight percent carbon, does not melt congruently; it decomposes to a fragile mixture of W_2C , WC and graphite upon cooling. However, at lower carbon contents, mixtures of WC and W_2C are formed on cooling, which melt at a relatively moderate temperature, around 2750 °C, and result in a cast product which is very hard, although by nature quite brittle, but nevertheless usable for some applications, such as dies [6].

The first sintered tungsten carbide was produced in 1914 for use in drawing dies and rock drills. It was developed in an attempt to avoid the casting defects common to the molten product, and consisted of powdered tungsten carbides or molybdenum carbide or mixtures of both, which were pressed and then sintered just below the melting temperature of the pure WC. However, the sintered product was very brittle and unsuccessful in industrial use [6].

The Development of Cemented Carbides

Cemented tungsten carbide originated in the electric incandescent lamp industry in the US and in Germany. Since the invention of tungsten filaments for use in incandescent lamps at the beginning of the 20th century, the lamp manufacturers had been searching for a replacement for the expensive diamond dies used in the wire-drawing of fine tungsten filaments. Prompted by a strategic shortage of industrial diamonds at the beginning of World War I, the German lamp industry turned to the tungsten carbides as

potential substitute materials. Because of their extreme hardness, the carbides of tungsten initiated a substantial research and development effort on the part of the incandescent lamp industry and their suppliers, for more than two decades.

A major breakthrough took place with the advent of cemented tungsten carbide in the 1920's. The successful development of the cemented carbides was generally attributed to the work of Karl Schröter who was a chemist [6]. At the beginning of World War I, he began searching for substitute materials for diamond in tungsten-wire-drawing equipment, starting with cast and sintered tungsten carbides. But neither the sintering process nor the casting process for making tungsten carbide wire-drawing dies were deemed successful and the work was abandoned. It was resumed about 1920 at Osram.

Systematic experiments to bind powdered tungsten carbide with iron, nickel or cobalt were carried out from 1918 to 1923 [10]. The first sintered cemented carbide dies were prepared in 1922. The wire-drawing tests showed cobalt to be the best additive. The invention of the cemented carbide tool materials was first disclosed in 1923 in Karl Schröter's patent application [11]. The two inventions claimed by the patent were:

- a unique hard metal alloy composition, namely the combination of the very hard tungsten carbide, WC, with small amounts of a metal of the iron group: Fe, Ni and Co; and
- the manufacture of the hard metal alloys by the application of the process of powder metallurgy, namely the pressing and sintering of mixed powders of tungsten carbide and binder metal.

The manufacturing process, then and now, is one of powder metallurgy, with liquid phase sintering. Karl Schröter's "decisive step" consisted of sintering a mixture of 90 wt% tungsten carbide and 10 wt% binder metal, namely iron, nickel or cobalt, but preferably cobalt, at temperatures at which the binder is liquid and complete consolidation of the compact occurs. The resulting microstructure consists of an aggregate of fine (1-2 micrometers) WC particles embedded in the cobalt-rich binder. The properties are controlled by composition and microstructure: the hardness increases with decreasing Co content and smaller particle size of WC, but, in general, at some cost of rupture strength and fracture toughness. The result was what we now know as "cemented carbides," a class of materials having distinctive microstructure and superior physical properties. The importance of the invention is confirmed by noting that today, seventy years later, the same compositions, made by essentially the same process, are still a very significant product of the tool materials industry.

In tungsten-wire plants, the cemented carbide drawing dies quickly replaced diamond dies for reducing heated tungsten wire in the coarse range, after the swaging operation, i.e. from about 0.7 mm down to 0.3 mm in diameter. Significant as it was for wire-drawing dies, the new material represented a truly revolutionary cutting tool material for machining. The addition of cobalt to tungsten carbide not only allows the

sintering of dense compacts at reasonable temperatures, but also results in materials with adequate toughness at very high hardness levels. When the new tools, made from sintered WC-Co, were placed on the market in 1927, they caused a sensation in the machine tool industry, by allowing cutting speeds 3 to 5 times faster than the best high speed steel tools in use at that time.

Modification of Schürer's compositions by replacing either a portion or all of the tungsten carbide with other carbides (in particular those of titanium, tantalum, and molybdenum) led to the major discovery that such additions were essential for cutting steel at speeds that provide economic advantages. The discovery by Schwarzkopf that solid solutions of carbides are superior to an individual carbide was the starting point of the development of multi-carbide cutting tools for high-speed machining of steel [12].

The most important advance in cutting tool technology since the development of WC-Co was the development of coated tools in late the 60's and early 70's [13]. Coatings are diffusion barriers, and they prevent the interaction between the chip formed during machining and the cutting material. Typical coatings are Titanium Carbide (TiC), Titanium Nitride (TiN), Titanium Carbonitride (TiCN), and Alumina (Al_2O_3), which are extremely hard, thus very abrasion resistant. TiN has the added advantage of a significantly lower coefficient of friction against steels compared to WC/Co. Thus it reduces the energy needed during the cutting operation. All these compounds have extremely low solubility in iron and they enable inserts to cut at much higher speeds than is possible with uncoated cemented carbides. It was estimated that 80% of carbide tools sold today are coated [14].

Properties of Tungsten Carbides

The properties of sintered WC-Co composites are critically dependent on their final composition and structure [3]. Slight deviations from the ideal carbon content bring about the occurrence of either graphite or a ternary compound. Both of these phases are usually undesirable, and result in degradation of mechanical properties and cutting performance. Therefore, the carbon content must be maintained within narrow limits to obtain the desired composite with optimum properties. It is now well established that two types of η phase can be obtained – $M_{12}C$ (Co_6W_6C) of substantially constant composition and an M_6C in which the composition can vary within the range of $Co_{3.2}W_{2.8}C$ and Co_2W_4C . The M_6C type of η phase is in equilibrium with the liquid phase and can nucleate and grow during the sintering process. This not only embrittles the structure by replacing the binder with a brittle phase, but also reduces the effective contribution of WC to the strength of the composite. The $M_{12}C$ type is formed in the solid state (during cooling) with small grains distributed throughout the matrix and is therefore effectively less embrittling.

Figure 3 shows an isothermal section of the WC-Co phase diagram at 1425 °C [15], which provides information on phase equilibria in the sintering range of commercial

WC-Co composites. Table 1 lists properties of representative grades of cemented WC [16].

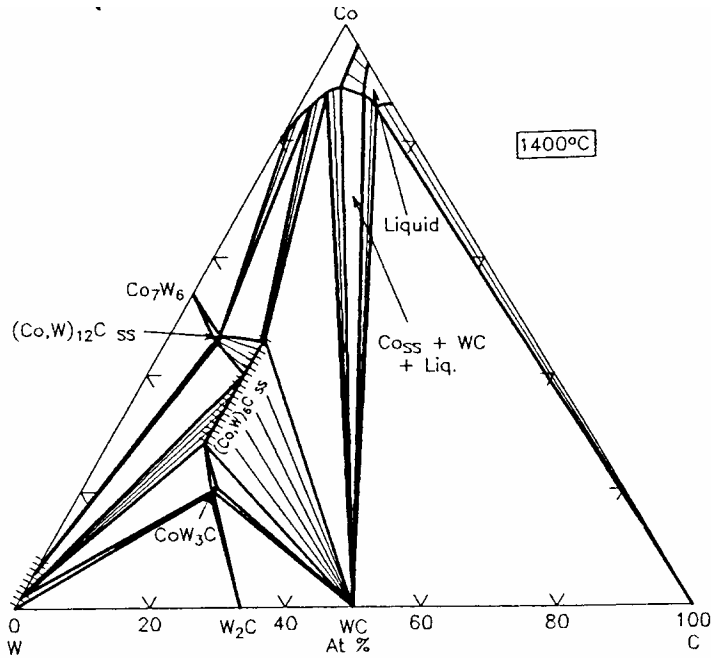


Figure 3. The isothermal section of WC-Co phase diagram at 1425 °C [15].

Table 1. Properties of representative grades of cemented carbide [16].

Cemented carbide	Room temp. hardness, HV	Modulus of elasticity, GPa	Transverse rupture strength, MPa	Coefficient of thermal expansion, $10^{-6}/K$	Thermal conductivity, W/m•K	Density, g/cm ³
WC-20 wt% Co	1050	490	2850	6.4	100	13.55
WC-10wt% Co	1625	580	2280	5.5	110	14.50
WC-3 wt% Co	1900	673	1600	5.0	110	15.25
WC-10 wt% Co-22 wt% (Ti, Ta, Nb)C	1500	510	2000	6.1	40	11.40

Compared to other refractory carbides, the thermodynamic stability of tungsten carbide is relatively low, as is its room-temperature hardness. At high temperatures, most

cubic carbides rapidly lose their hardness, whereas the hardness of the WC is quite stable. Coupled with this fact, the unique deformation characteristics of WC are the basis for its predominance as the hard refractory phase in cemented carbides. Other noteworthy properties of WC are its extremely high modulus of elasticity, second only to that of diamond, and its high thermal conductivity. The other refractory carbides have been used effectively as grain growth inhibitors in liquid phase sintering of WC-Co. It has been found that the effectiveness of a transition metal carbide as a grain growth inhibitor is related to its thermodynamic stability, and they may be ranked as follows:



It was also found that there is a maximum level above which no further grain growth inhibition occurs. This level is believed to correspond to the maximum solubility of the carbide phase in liquid cobalt. A liquid phase that is saturated with inhibitor carbide would reduce the solubility of WC, and thereby reduce its coarsening rate. Table 2 lists properties of refractory carbides and binder metals [17].

Table 2. Properties of refractory metal carbides and binder materials [17].

Material	Hardness HV (50 kg)	Crystal structure	Melting temperature (°C)	Theoretical density, g/cm ³	Modulus of elasticity, GPa	Thermal expansion, μm/m•K
WC	2200	Hexagonal	2800	15.63	696	5.2
W ₂ C	3000	Hexagonal	2777	17.3	————	————
TiC	3000	Cubic	3100	4.94	451	7.7
VC	2900	Cubic	2700	5.71	422	7.2
HfC	2600	Cubic	3900	12.76	352	6.6
ZrC	2700	Cubic	3400	6.56	348	6.7
NbC	2000	Cubic	3600	7.8	338	6.7
TaC	1800	Cubic	3800	14.50	285	6.3
Cr ₃ C ₂	1400	Orthor- hombic	1800	6.66	373	10.3
Co	<100	Cubic/hex agonal	1495	8.9	207	16.0
Ni	<100	Cubic	1455	8.9	207	15.0

The role of cobalt in cemented carbides is to provide a ductile bonding matrix for tungsten carbide particles. Cobalt is used as a bonding matrix because its wetting or capillary action during liquid phase sintering allows the achievement of high densities.

Because of the relatively high cost of cobalt, attempts have been made to design alternate materials, with iron and nickel as the predominant cobalt substitutes. However, sliding wear tests show that cobalt content is very important for cemented carbides to have good wear resistance.

Fracture in WC/Co systems with high Co contents has been found to occur mainly by the ductile rupture of Co through void nucleation and coalescence [18]. Other fracture modes such as fracture along WC/Co interface and WC/WC grain boundary decohesion as well as cleavage across WC grains were also noted. These mechanisms occur especially at low volume fractions of Co binder in the composite at which the contiguity of WC grains begin to increase. The effect of the contiguity of WC skeleton on fracture toughness has also been demonstrated. In a fracture toughness experiment, in a given crack plane, the crack propagation is easy along the relatively weak WC/Co and WC/WC boundaries and final fracture is primarily controlled by the area fraction of Co regions intact across the crack plane ahead of the tip. Since the WC/WC decohesion and WC/Co interface fracture energies are likely to be lower than the fracture energy absorbed in ductile fracture of the binder, ductile failure of Co can be considered as a primary mechanism manifesting the fracture resistance.

Several investigations attempted to correlate the microstructural parameters and mechanical properties of constituent phases to experimentally measured fracture toughness values. In particular, it has been universally found that the fracture toughness increases with volume fraction, the mean free path length of the binder and the size of WC grains. In addition, higher toughness has been suggested to result from the increased contiguity of Co binder, which minimizes the fracture along weak WC/WC boundaries. For a given volume fraction, geometrical arrangement of the ductile binder as a continuous thin matrix phase is beneficial for high toughness while retaining high strength. This arrangement could be most desirable of several possible arrangements in which the deformation of ductile Co phase is highly constrained in the microstructure [18].

Nanoparticle Materials Research and Promise

Nanoscale particle research has recently become a very important field in materials science. Nanoscale particles (1 to 100 nm) usually have physical properties different from those of large particles (10-100 μm) or the molecular/atomic species. It has been found that nanoparticles exhibit a variety of previously unavailable properties, depending on particle size, including magnetic, optical, and other physical properties as well as surface reactivity [19, 20]. Recent experiments have shown that consolidated nano-materials have improved mechanical properties, such as increased hardness of metals and increased ductility and plasticity of ceramics [21]. The unique properties of nanoscale particles and nanograin bulk materials can be attributed to two basic phenomena. The first is that the number of atoms at the surface and/or grain boundaries

in these materials is comparable to that of the atoms located in the crystal lattice, thus the chemical and physical properties are increasingly dominated by the atoms at these locations. The second phenomenon is the “quantum-size effect” or quantum confinement effect. When particles approach the nanometer size range, their electronic and photonic properties can be significantly modified as a result of the absence of a few atoms in the lattice and the resulting relaxation of the lattice structure.

The worldwide cemented carbide cutting tool industry has approached the problem of higher mechanical properties for their cutting tools by altering composition primarily in the direction of increased carbide content [22]. Unfortunately, at the level of 94 to 97 weight percent carbides, fracture toughness and strain tolerance have fallen below acceptable levels and excessive brittleness results. One answer to this dilemma is to reduce the average particle size of the hard carbides, thus reducing the mean free path between carbide particles. This usually has the effect of increasing fracture toughness as well as wear resistance. The latter effect is achieved because the matrix is now exposed to the abrasive/corrosive environment over much smaller dimensions, even though the WC/Co composition has not changed.

By means of this particle size reduction process, the fracture toughness and strength can be increased significantly, as long as two other deleterious effects have not been introduced. These are (1) excessive impurities such as oxygen during the very long milling times necessary for mechanical mixing, and (2) establishment of WC-WC particle contact, especially over distances spanning many WC particles, thus creating a brittle fracture initiation site and propagation path. These two problems will negate any increase in fracture toughness in other portions of the volume of the tool. These effects limit the cost-effective mechanical milling reduction of particle size and proper WC/Co dispersion to a typical average WC size of 0.5 to 1.0 micron. Table 3 shows a comparison of properties of representative WC-Co compositions with different grain sizes [23]. The most striking is the abrasion resistance, with finer grain composites (still in micron range) having much better abrasion resistance.

2. Synthesis of Nano WC/Co Composites

The traditional method of making WC-Co cemented carbides is by crushing, grinding, blending and consolidation of the constituent powders. Taking this approach, the microstructural scale can be no smaller than the size of the milled powders, typically 1-10 microns in diameter. With great effort, the microstructural scale can be reduced to about 0.5 micron in premium WC-Co grades.

Table 3. Properties of representative cobalt-bonded cemented carbide grades [23]

Nominal Composition	Grain size (in micron size)	Hardness HRA	Density, g/cm ³	Transverse strength, MPa	Compressive strength, MPa	Modulus of elasticity GPa	Relative abrasion resistance	CTE, ppm/K	CTE, ppm/K, at 1000 °C	Thermal conductivity, W/m•K
97WC-3Co	Medium	92.5-93.2	15.3	1590	5860	641	100	4.0	————	121
94WC-6Co	Fine	92.5-93.1	15.0	1790	5930	614	100	4.3	5.9	————
94WC-6Co	Medium	91.7-92.2	15.0	2000	5450	648	58	4.3	5.4	100
94WC-6Co	Coarse	90.5-91.5	15.0	2210	5170	641	25	4.3	5.6	121
90WC-10Co	Fine	90.7-91.3	14.6	3100	5170	620	22	————	————	————
90WC-10Co	Coarse	87.4-88.2	14.5	2760	4000	552	7	5.2	————	112

Meeting the challenge of obtaining improved properties by further reduction in grain size requires new approaches. There is worldwide interest in nano-grained WC/Co materials, and many efforts have been made to synthesize nano-grained WC/Co composites [24-29].

Researchers at Rutgers University and Nanodyne have been developing new capabilities for the chemical processing of nanostructured WC/Co, starting from water-soluble precursor compounds [30-51]. The Spray Conversion Process consists of three sequential steps.

- 1). preparation and mixing of aqueous solutions of the precursor compounds to fix the composition of the starting solution
- 2). spray drying of the starting solution to form a chemically homogeneous precursor powder
- 3). thermochemical conversion of the precursor powder to the desired nanostructured end-product powder

The original lab-scale process at Rutgers University made use of a single chemical precursor compound, $\text{Co(en)}_3\text{WO}_4$ (where en = ethylenediamine), which after thermal-chemical conversion gave WC-23wt % Co. In order to extend the range of compositions available to those of commercial interest (3-30 wt% Co), homogeneous precursor powders were made by rapid spray drying of aqueous solutions of W and Co salts. In spray drying, the solvent phase is rapidly evaporated in a hot gas stream, which results in rapid precipitation of the solute mixture. At sufficiently high rates of precipitation, phase separation can be avoided. Tests on spray drying of $\text{Co(en)}_3\text{WO}_4$ - H_2WO_4 solutions showed that amorphous or microcrystalline precursor powders could be made without phase separation. Homogeneous precursor powders can be made from ammonium metatungstate (AMT, $(\text{NH}_4)_6(\text{H}_2\text{W}_{12}\text{O}_{40}) \cdot 4\text{H}_2\text{O}$) and CoCl_2 , $\text{Co}(\text{NO}_3)_2$ or $\text{Co}(\text{CH}_3\text{COO})_2$, which are readily available commercially. By spray drying solution mixtures of AMT and cobalt salts, the Co/W ratio can be adjusted.

Thermochemical conversion of the precursor powder in a fluid bed reactor is also an important step in the integrated process. This is because the local environment with respect to temperature and gas concentration in the fluid bed reactor is the same for all parts of the bed, which ensures uniform conversion of the precursor powder to the end-product powder. Carburization treatments of the reduced powders were conducted in CO/CO₂ gas mixtures with controlled carbon activity. Carbothermal reaction processing can also be carried out in CO/Ar and CO/H₂ gas mixtures. An advantage of the CO/H₂ mixture is that it permits better control of the formation of uncombined, or free carbon, while maintaining a high carburization rate.

Nanodyne is the world's only manufacturer of NANOCARBTM composite powders whose WC grain sizes are 20 to 40 nm, which are 10 to 20 times smaller than

those available in the finest conventional micrograin powders. A typical NANOCARBTM powder particle consists of a hollow, porous 75 micron sphere (typical range is 20 to 100 microns), containing hundreds of millions of WC grains in a cobalt matrix. Figure 4 shows the arrangement of WC grains within the NANOCARBTM powder particle [52]. Because the process begins with a solution, the constituents of NanocarbTM powder are mixed on the molecular level. There is no milling involved and the process is sealed to the environment from the start.

Dow Chemical Company is producing submicron tungsten carbide powders on a commercial scale with three grades, super ultrafine (0.2 μm), ultrafine (0.4 μm), and fine (0.8 μm) [53]. Through carbothermal chemistry and proprietary reactor design, the Dow process is designed to produce inherently fine carbide powders without milling or classification. The impurities of the powders (carbon, oxygen) are comparable to those of powders larger than one micron. The oxygen content remains in an acceptable range (< 0.20%).

An alternate approach to the gas-phase carburization has also been developed, in which a polymer precursor such as polyacrylonitrile is used as an in situ carbon source [54, 55]. The use of a polymer as an in situ carbon source can reduce the diffusion length, thus making this approach very attractive for large-scale production. The availability of a uniform distribution of carbon through the polymer precursor can potentially give better homogeneity in the final product.

Influences of processing parameters on the formation of WC-Co nanocomposite powder employing polyacrylonitrile as a carbon-source have been investigated systematically [55]. The processing parameters investigated include firing time and temperature, addition of a small quantity of cobalt acetate initially as a catalyst, and the sample quantity for a given firing scheme. The investigation provides basic information for optimizing processing parameters to obtain finer WC-Co nanocomposite powders with less impurity phase contamination.

Pure WC-Co could be obtained with a WC particle size of 50-80 nm in lab-scale experiments using polyacrylonitrile as the carbon source. However, a small amount of undecomposed polymer or free carbon was also observed in the final product. The phase purity of the products is strongly influenced by the synthesis and processing conditions such as firing temperature, time, and atmosphere.

Co-precipitation of tungsten and cobalt salts in the liquid phase, followed by carburization has also been used to produce nano WC-Co particles. Novel precipitating agents, such as guanidine salts, can be used which offer the advantages of complete pyrolysis of residues at low temperature, lower cost, and lower molecular weight than other organic amines. A co-precipitate of (W, Co) compound is formed in the presence of ammonium metatungstate, guanidine carbonate, and cobalt nitrate. A 20% methane

and 80% hydrogen mixture was used to transform the (W, Co) co-precipitate into WC/Co with average particle size of 56 nm [22].

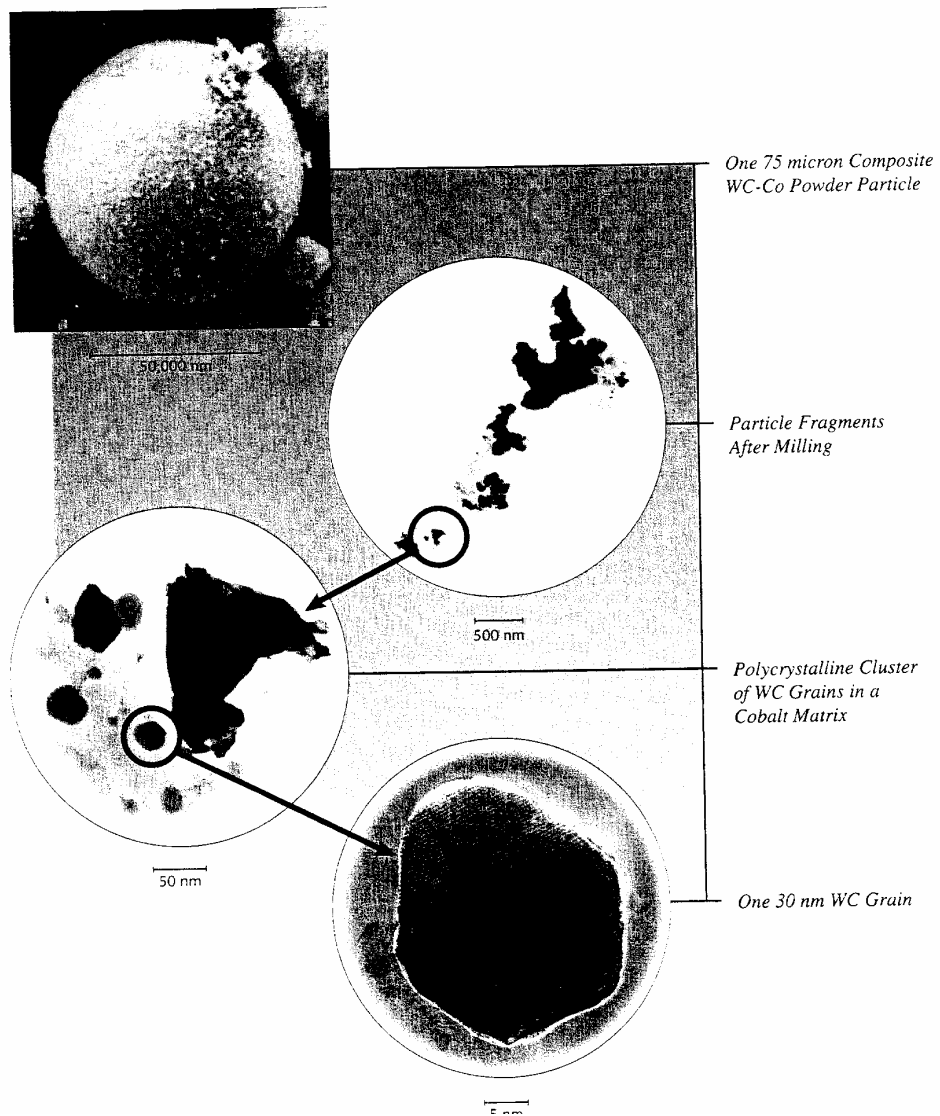


Figure 4. Hierarchical arrangement of nano WC grains within a large particle [52].

Tungsten has a very rich solution chemistry and can form both stable and, due to slow kinetics, also metastable species. Ammonium salts of the di-cobalt anion, $[\text{H}_2\text{Co}_2\text{W}_{11}\text{O}_{40}]^{8-}$, have been used as precursors for nano WC-Co materials [56]. The structure analysis on the salt, $(\text{NH}_4)_{6.8}\text{Co}_{0.6}[\text{H}_2\text{Co}_2\text{W}_{11}\text{O}_{40}] \cdot 17\text{H}_2\text{O}$ showed that cobalt ions were distributed among three different positions: one at the center of the Keggin ion ($[\text{H}_2\text{Co}_2\text{W}_{11}\text{O}_{40}]^{8-}$); a second in one of the octahedral sites of the anion; and a third as a counter ion outside of the Keggin anion. The amount of “external” cobalt can be varied by altering the synthesis conditions, thus it is possible to vary the WC/Co ratio within a desired range.

Tungsten carbide particles can be coated with cobalt by sol-gel or other chemical processes, and this has been regarded as one of the future tungsten carbide technologies [57]. This approach eliminates the need for a wax or other lubricant to enhance pressability and green strength. It also eliminates the need for dewaxing prior to sintering, which shortens the manufacturing cycle. Individually coated particles also allow solid-state sintering, reduce matrix segregation, and prevent excessive carbide matrix reaction.

Recycling of Cemented Tungsten Carbide Cutting Tools

The \$2 billion worldwide tungsten carbide industry generates large quantities of scrap due to the rejected parts at various stages of production and the worn out cutting tools. The greater environmental concerns have led Sandvik Coromant to offer a service to recycle used carbide inserts [*]. The most basic recycling approach would be to break down the scrap pieces into powders and then fabricate more WC base cutting tools. This approach would cause severe equipment wear due to the abrasive nature of the cutting tool materials and therefore it is not feasible. As a result, the recycling is done by chemical means, such as the zinc recovery process, electrolytic recovery, and extraction by oxidation.

In a zinc recovery process, cemented carbide scraps are immersed in molten zinc in an electrical furnace at 1 atmosphere of inert gas at 650-800 °C. The zinc is subsequently distilled at 700-950 °C [58, 59]. Optimum conditions depend on Co content and zinc to cobalt ratio. The properties of the reclaimed powders are the same as the virgin powders. Scrap cemented carbides can be sorted into medium (1.2-2 μm), coarse (~4 μm), and mixed grain sizes by optical microscopy and by composition with x-ray fluorescence spectroscopy before the zinc recovery process.

Scraps of cemented tungsten carbide can be electrolyzed to dissolve their cobalt binder and thus recover tungsten carbide [60]. Anodic passivation has been found to retard the acid dissolution of cobalt. However, in the presence of additives (e.g. 0.1 M citric acid in 1 M HCl), anodic passivation can be minimized. Under optimum conditions, the efficiency for cobalt dissolution has been found to be greater than 90%.

No contamination was found in the recovered tungsten carbide with x-ray diffraction analysis.

In an oxidative extraction process, the first step of the recycling process is scrap digestion [61, 62]. The scrap is normally digested by fusion or roasting with oxidizing agents such as NaNO_3 or NaNO_2 [63]. The charge of the digestion process is then treated with water to dissolve sodium tungstate. Filtration and precipitation processes are then carried out to remove impurities. Tungsten species are first extracted from the purified sodium tungstate solution by a reagent (such as amines) dissolved in an organic solvent (such as kerosene and alkyl benzenes) to separate from sodium ions. Re-extraction is then carried out by aqueous ammonia solution to yield ammonium polytungstate solution. Simply by evaporation, ammonium paratungstate can be crystallized from the solution. The ammonium paratungstate thus obtained is first calcined then reduced by hydrogen to tungsten metal, which is further carburized to tungsten carbide and followed by cobalt addition and sintering to produce new cutting tools. Sulfuric acid [64] and $\text{HNO}_3\text{-HCl-HF}$ [65] solutions have also been used to recover WO_3 or H_2WO_3 from tungsten carbide wastes.

3. Consolidation of Nano WC/Co Composites

Consolidation of nanomaterials is a significant and challenging requirement for the engineering application of nanomaterials. The consolidation methods must preserve the nanometer grain sizes of the starting materials in order to preserve their expected advantages in physical properties through scale up to engineering application. There has been limited effort to consolidate nanoparticles to specimen volumes useful for physical property measurements [66]. Several techniques have been used during research on the consolidation of nano WC/Co composites.

Plasma Spray

Using thermal spray processing to deposit a coating of nano powders offers a high rate deposition method that can provide the effective pressure and temperature required to sinter high density nanostructured materials [67]. However, most “as is” nano scale powders cannot be deposited, as they will closely follow the stream lines of the carrier gas. Thus, when the thermal spray gas jet is impinging on a substrate surface, very small particles will be slowed down and diverted by the flow in the stagnation region. Another practical difficulty is feeding the small particles into the gas stream. Particles smaller than $10\ \mu\text{m}$ are extremely difficult to feed into the gas flow and can result in plugged particle feed lines because of particle agglomeration [67].

However, nano WC/Co particles can be processed to form controlled size agglomerates by spray drying of nano WC/Co powder and a binder suspension. The nano WC/Co particles in the agglomerates are retained by the van der Waals force as well

as by the binder. During the coating process in the high temperature jet, the binder evaporates and agglomerated WC/Co particles can be deposited [67].

An oxidative decomposition, which involves decarburization of the WC phase to form W, occurs in thermal spraying of conventional WC-Co powders, and is exacerbated by the high surface area of the as-synthesized nano WC-Co powders. The severity of this problem can be diminished to some degree by densification of the powder particles prior to thermal spraying. A practical solution to this generic problem has been to conduct the thermal spraying operation in vacuum, as in vacuum plasma spraying (VPS) or low-pressure plasma spraying (LPPS). This technique has been used successfully for depositing WC-Co coatings on various substrates, using both conventional and nanostructured powders as feed stock [68].

An important distinction between thermal sprayed conventional and nanostructured powders is their inherently different melting and solidification characteristics. Conventional powder particles experience surface melting only, accomplished by slow and limited dissolution of the WC particles in the liquid Co, as the temperature is increased above the pseudo-binary eutectic (1350 °C). The resulting spray deposited coating layer, therefore, tends to be somewhat porous, since the presence of the relatively large WC grains in the partially melted particles impedes fluid flow on the substrate surface. Nanostructured powder particles, due to the high surface area of contact between the Co and WC phases, undergo homogeneous or “bulk” melting, accompanied by rapid and extensive dissolution of the WC nanograins with superheat above the eutectic. In this case, the resulting coating is much denser, owing to the facility with which the nanodispersed semisolid or “mushy” particles can spread out over the substrate surface [68].

Liquid Phase and Solid State Sintering

Liquid phase sintering is widely used for consolidation of conventional WC-Co powder. After cold compaction of WC/Co containing a lubricant - binder such as paraffin in a high-pressure hydraulic press, the powder compact is heated in vacuum or hydrogen to a temperature above the pseudo-binary WC-Co eutectic where liquid phase sintering occurs. Theoretically dense structures are routinely produced by this method. However, sintering usually causes grains to grow larger. One of the challenges in the quest for nanostructured materials, including WC-Co, has been controlling the grain growth during sintering.

Dilatometry has been used to study the sintering behavior of nano grain WC/Co as well as larger WC/Co powders [69]. The results of the dilatometric experiments indicate that the shrinkage characteristics of the nanoparticle-sized powder are different from those of the regular, micron particle sized powder. Sintering of nano particle sized WC is usually attempted in the solid state, while most densification of micron particle sized WC particles is done by liquid phase sintering. The smaller the particle size the

lower the temperature at which full density is attained in both liquid phase and solid state sintering.

High resolution analytical electron microscopy has been used to analyze morphological features in consolidated specimens of nanostructured WC/Co powder [70]. Electron microscope examination reveals a dispersion of nano-precipitates within the WC nano-grains of the WC/Co cermet. Micro-diffraction and analytical studies show that these nano-precipitates are face-centered-cubic cobalt. This is consistent with the concept that the nano-precipitates nucleate from cobalt retained within the WC nanograins, which is a consequence of the intimate intermixing of tungsten and cobalt in the original chemical synthesis process.

A highly surface sensitive technique, X-ray Photoelectron Spectroscopy (XPS), has also been used to study the sintering process of nano WC/Co composite [71]. The XPS studies in ultrahigh vacuum provide an atomic view of the sintering process. The data are consistent with a model in which WC and Co nanoparticles are distributed randomly in the as-prepared sample. Upon annealing at 1250 °C, a fraction of the Co spreads to form a thin, uniform layer of Co with about 1 monatomic thickness on the WC particles, via surface diffusion and/or vapor transport of Co. Formation of this Co film is proposed to be an initial step in the sintering process.

The challenge in sintering nanostructured WC-Co materials is to retain the ultrafine structure. Nanostructured WC-Co composites are extraordinarily susceptible to WC particle coarsening during liquid phase sintering, due to the high interface area between the WC particles and the liquid cobalt phase. The high interface area in these materials also promotes rapid liquid phase sintering. Densification of nanostructured WC-Co powder could be completed in 5 to 15 minutes if grain growth inhibitors are added [72-75]. Grains grow extremely rapidly, very likely via coalescence, during the first few minutes at the sintering temperature. After the initial rapid stage, grain growth followed the linear relationship of coarsening.

During liquid phase sintering, grains grow by coalescence or coarsening (solution-precipitation) [72]. Coalescence usually occurs in the very early stages of sintering (within 10 minutes). The most striking result is that at the first data point (t= 5 min), the grain sizes of the samples were already dramatically increased from their nominal initial sizes. It is believed that the mechanism responsible for this “explosive fashion” of grain growth is mainly coalescence. Coalescence occurs before and after partial liquid formation when heating to the sintering temperature. During coalescence, grains adjust relative orientations by rotating or shifting. Two or more grains become one when their orientations match and the grain boundary migrates through one of the coalescing grains. This process is favored by finer initial grain size.

Grains grow by coarsening after coalescence; although, these mechanisms overlap to a certain extent. During coarsening, grain growth can be described by the well known linear relationship,

$$L^n - L_0^n = Kt$$

where L is the mean size at time t , L_0 is the initial mean size, K is a rate constant, t is time, $n=3$ for diffusion controlled coarsening and $n=2$ for interface controlled coarsening [72]. The addition of VC drastically reduces the coarsening rate. For example, at 1670 K, the rate constant K of nano-VC samples is only 1.7% that of the same material without VC. The presence of VC affects grain growth throughout the sintering process. It has been reported that coarsening during liquid phase sintering is influenced by particle size distribution. The wider the particle size distribution, the faster the coarsening.

Palmquist crack resistance was used as a toughness parameter. The superior crack resistance of NANOCARBTM has been found. It may be attributed to 1) the very uniform microstructure; no abnormally large grains were observed in the microstructure of nano or nano-VC samples as was the case with standard submicron products, and 2) the homogeneous distribution of the cobalt phase among the carbide grains.

It is clearly essential to minimize the time spent at the sintering temperature in order to minimize particle coarsening, which can be quite rapid in the presence of liquid Co. Tests have shown that dense structures in WC-10 wt% Co can be achieved in 30 seconds at 1400 °C, which results in WC grain size of 200 nm. An additional 30 seconds sintering time increases the WC grain size to 2.0 microns. Such rapid grain growth is characteristic of ultra-pure WC-Co. A small amount of uncombined C, or an addition of Cr₂C₃, markedly inhibits grain growth during liquid phase sintering. On the other hand, ultra-pure WC-Co powders can be consolidated by solid state sintering, where grain growth is much slower.

New consolidation techniques suitable for nano materials have also been used to consolidate nano WC/Co, including Plasma Activated Sintering (PAS) and Quick HIP. Plasma Activated Sintering (PAS) achieved densification by a combination of resistance heating with pressure application and plasma generation among the powder particles [22]. The loose powders are loaded in a graphite mold and die unit followed by application of a modest uniaxial pressure and a pulsed electrical discharge. Typically, the uniaxial pressure is of the order 10-15 MPa and the electrical discharge of 750 A and 25 V with 80 ms pulse width is applied for 30 seconds. In the next step, a high DC current (600-2000 A) promotes Joule heating of the powder particle interfaces while the pressure is maintained or increased to 50 to 100 MPa. The time for high temperature and pressure application is short, usually on the order of minutes, to reach full densification. Specimens of 25 mm diameter X 6 to 12 mm thick have been produced.

In the Quick HIP process, very rapid increases in pressure within the chamber containing the preform can be achieved. The use of hot gases as pressure media ensures

the truly isostatic nature of the process for shapes that do not require a “can”. Significant grain growth was observed even in these “fast” consolidation processes. However, microstructures showed nano-grained WC/Co grains to be ~0.2 to 0.5 μm compared to commercial material, which contained mostly $> 1 \mu\text{m}$ grains after densification by both PAS and quick HIP processes. Figure 5 displays the dot map of the cobalt distribution in nano-grained WC/Co with a magnification of 2000 [22].

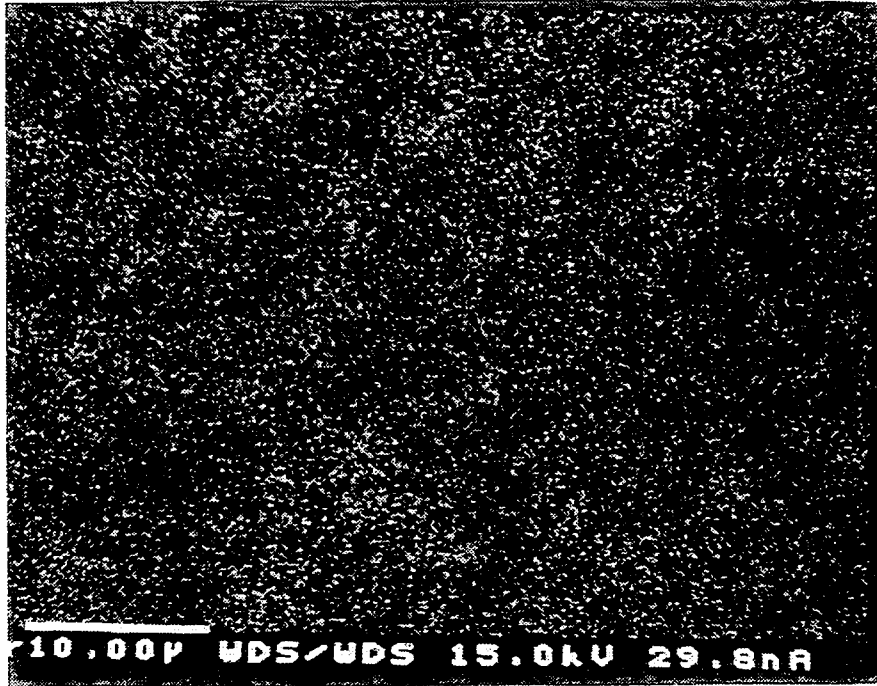


Figure 5. Cobalt dot map of MMI WC/Co @2000 X.

4. Applications

Cemented carbides, best known for their superior wear resistance, have a range of industrial uses which are diverse compared to other powder metallurgy product applications. Common uses include metalworking tools, mining tools, and wear-resistant components. All of these applications have one physical property requirement in common: the ability to resist wear.

The performance of cemented carbide as a cutting tool lies between that of tool steel and “cermets” [76]. Compared to tool steels, cemented carbides are harder and more wear resistant, but also exhibit lower fracture resistance and thermal conductivities than tool steel. Cermets, which are composed of carbonitride based materials such as

TiCN, on the other hand are more wear resistant than cemented carbides, but may not be as tough. Advances in cemented carbides have produced a wide selection of tool materials. They are suitable to cut a variety of materials such as gray cast iron, ductile nodular iron, austenitic stainless steel, nickel-base alloys, titanium alloys, aluminum, free-machining steels, plain carbon steels, alloy steels, and martensitic and ferrite stainless steels.

Almost 50% of the total production of cemented carbides is now used for nonmetal cutting applications such as drill bits and components for mining, oil and gas drilling, transportation and construction, metalforming, structural and fluid-handling components, and forestry tools [76]. New applications are constantly being identified for carbides, largely because of their excellent combinations of abrasion resistance, mechanical impact strength, compressive strength, high elastic modulus, thermal shock resistance, and corrosion resistance.

Erosion resistance of carbides is important in applications such as sand blast/spray nozzles, seals in slurry pumps, and component parts in the oil industry. Cemented carbide is an excellent choice for the nozzles because it can outwear steel 100 to 1 and will thereby maintain the spray pattern and quantity of flow for a longer period of time, extending the service life of the nozzles. Many applications can use a small carbide nozzle insert held to other base materials by epoxy, braze, shrink fit or taper fit. This permits the use of carbide without a major redesign of a nozzle assembly or the need to manufacture a complex shape from solid carbides.

In the mining and mineral industries, the components exposed to severe mechanical interaction among very abrasive nonmetallic and metallic materials. The abrasive nature of most ores can cause significant wear to both handling and processing equipment. A variety of WC/Co materials have been used for hardfacing to meet an extremely wide range of severe abrasive conditions, especially oil well drill bits, tool joints, rock drill bits.

The physical and mechanical properties of cemented tungsten carbides make them appropriate materials for a wide range of structural components, including plungers, boring bars, powder compacting dies and punches, high pressure dies and punches, pulverizing hammers, carbide feed rolls and chuck jaws, and many others. The predominant wear factors in most applications are high abrasion, attrition, and erosion. The rigidity, hardness, and dimensional stability of cemented carbide, coupled with its resistance to abrasion, corrosion, and extreme temperature, provide superior performance in fluid-handling application, such as seal rings, bearings, valve stems, and valve seats.

Among the diverse applications of cemented carbides is a wide range of tools and components for the transportation and construction industries. Examples include tools for road planing, soil stabilization, asphalt reclamation, vertical and horizontal drilling, trenching, dredging, tunnel boring, and forestry, as well as snow-plow blades, tire studs, and street sweeper skids. Erosion resistance of carbides is important in applications such

as sand blast/spray nozzles, seals in slurry pumps, and component parts in the oil industry. The success of cemented carbides in erosion-resistant application is again due to their unique composite structure of wear-resistant WC particles in a ductile cobalt matrix.

WC-Co has also been used as coatings in jet engine parts such as fans and high-pressure compressors (HPC) [77]. The materials used for fan and HPC blade interlocks in a jet engine are usually titanium alloys, which have poor wear properties. Most fan and HPC interlocks use thermal sprayed WC-Co coatings or brazed-on WC-Co powder metallurgy wear pads to prevent excessive wear. The WC-Co coatings are successful in the titanium alloy interlock applications because of the following reasons.

- high wear resistance of the tungsten carbide,
- adequate fracture toughness because of the cobalt matrix,
- high adherence on the titanium alloy substrates, and
- good match in coefficient of thermal expansion with the titanium alloy substrate materials.

The typical range of temperatures for fan and high pressure compressor (HPC) interlocks is from subzero to 95 °C in the fan and from 40 to 260 °C in the HPC. Fortunately, WC-Co coatings appear to retain sufficient low-temperature ductility and high temperature oxidation resistance over these temperature ranges. The formation of a wear glaze at the contact zones contributes to the good wear resistance of the WC-Co in the interlock applications. The WC-Co coatings have also been used in other engine components such as nozzle assemblies. The titanium components in the exhaust nozzle generally have poor wear resistance and almost always require coatings on mating parts in relative motion. Oxidation of the carbide limits use of this coating to temperatures below 480 °C.

Nano grained WC/Co composites are expected to enter the above mentioned areas. With both high hardness and high toughness, new applications for nano grained WC/Co composites are also expected to be found. At Rogers Tool Works, printed circuit board drills made from NANOCARBTM powder were tested against standard products, and significant improvement has been found [71].

5. Summary

The development and improvement of cemented carbide cutting tools have supported the exponential increases in metal cutting productivity (measured by cutting speeds) in this century. Materials of the future will have to satisfy the requirements imposed by high-speed machining, such as high-temperature strength, chemical stability, and oxidation resistance. Currently, research is aimed at developing grades having improved wear, corrosion, and oxidation resistance.

Nano-grained WC/Co composites have the potential to become the new materials for tools and dies, and wear parts. Benefits of nano-grained WC/Co approach include shorter sintering time, high purity, and precise control of composition. These materials have superior properties and more homogeneous microstructure than those of conventional WC/Co composites do. Nano-grained WC/Co also allow optimization of specific properties without comprising others. Higher toughness and ductility can be achieved without reducing hardness and wear resistance. However, there are technical challenges to be overcome before such materials reach a commercial scale. The most important task is consolidation of nano WC/Co powders with limited grain growth utilizing a minimum amount of grain growth inhibitors. The costs of producing nano WC/Co powders will have to be demonstrated to be cost-effective.

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