Recycling of Cemented Tungsten Carbide Cutting Tools

M.Narasimha, S. Ramesh

Abstract— 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. 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.

Index Terms— Cemented Tungsten Carbide

I. INTRODUCTION

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 oC. The zinc is subsequently distilled at 700-950 oC [1, 2]. 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 [3]. 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 [4, 5]. The scrap is normally digested by fusion or roasting with oxidizing

M.Narasimha, PhD Scholar of Sri Venkateshwara University Meerut, India

S. Ramesh, Department of Mechanical Engineering, Veltech Hightech Dr RR Dr SR Engineering College, Avadi, Chennai, India

agents such as $NaNO_3$ or $NaNO_2$ [6]. 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 [7] and HNO_3-HCl- HF [8] solutions have also been used to recover WO_3 or H_2WO_3 from tungsten carbide wastes.

II. 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 [9]. Several techniques have been used during research on the consolidation of nano WC/Co composites.

III. 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 [10]. 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 μm are extremely difficult to feed into the gas flow and can result in plugged particle feed lines because of particle agglomeration [10].

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 [10].

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 [11].

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 (1350^0C). 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 [11].

IV. 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 [12]. 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 [13]. 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 [14]. 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 oC, 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 [15-16]. 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-reprecipitation) [15]. 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,

Ln – L0n = Kt where L is the mean size at time t, L0 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 [15]. 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 oC, 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 [17]. 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 µm grains after densification by both PAS and quick HIP processes Figure 1 displays the dot map of the cobalt distribution in nano-grained WC/Co with a magnification of 2000 [17].
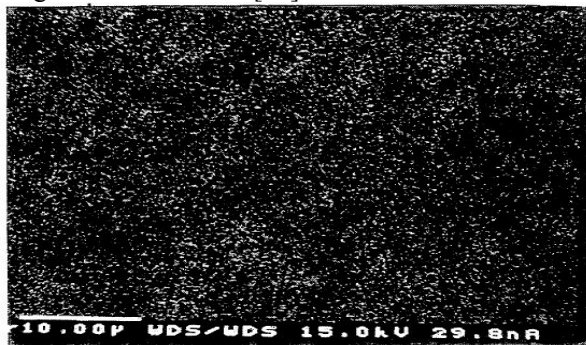

Figure 1 Cobalt dot map of MMI WC/Co @2000 X.

V. Applications

The performance of cemented carbide as a cutting tool lies between that of tool steel and "cermets" [18]. 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 [18]. 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.

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) [19]. 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 oC in the fan and from 40 to 260 oC 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 oC.

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 [14].

VI. 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.

VII. References

[1] M. G. Park, J. K.; Han, "Processing of Reclaimed Tungsten Carbide/Cobalt Powders with Virgin Properties", TaehanKumsokHakhoechi 1992, 30(8), 996- 1004 (Korean).

[2] K. Hirose and I. Aoki, "Recycling Cemented carbides without Pollution - Sorting Charging Material for Zinc Process", Int. Conf. Process.Mater.Prop., 1st 1993, 845-848 (English). Edited by Henein, Hani; Oki, Takeo. Miner.Met.Mater.Soc: Warrendale, PA.

[3] G. N. Srinivasan, and A. Varadharaj, "Electrolytic Recovery of Tungsten Carbide and Cobalt from Scraps/Rejects of Cemented Tungsten Carbide", Trans. PowderMetall. Assoc. India 1992, 19, 90-96.

[4] S. A. Vasilev and E. N. Kuznetsova, "Redox Processing of Dust Wastes from Finish Grinding of Tungsten Carbide Tools", U.S.S.R. SU 1,770,425 (Cl. C22B34/36), 23 Oct 1992, Appl. 4,849,716, 11 Jul 1990. From Izobreteniya 1992, (39), 88.

[5] N. Y.; Doroshkevich, E. A.; Shevno, A. N.; Khonyak, "Manufacture of Sintered Tungsten-containing Hard Alloys from Chip Waste, Bord", U.S.S.R. SU 1,717,283, (Cl. B22F3/12), 07 Mar 1992, Appli. 4,801,342, 29 Jan 1990. From Izobreteniya 1992, (9), 44.

[6] E. Lassner, "From Tungsten Concentrates and Scrap to Highly Pure Ammonium Paratungstate (APT)", in The Chemistry of Non-Sag Tungsten, Ed. L. Bartha, E. Lassner, W.-D. Schubert and B. Lux, Pergamon, 1995, pp.35-44.

[7] S. L. Gromov, A. N. Zolotnikov, "Recycling of Tungsten-Containing Sludges", Lhim.Prom-st (Moscow), 1993, (11), 579-80 (Russian).

[8] J-C. Lin, J-Y.Lin, S-P.Jou, "Selective Dissolution of the Cobalt Binder from Scraps of Cemented Tungsten Carbide in Acids Containing Additives", Hydrometallurgy, 43(1-3), 47-61, 1996.

[9] R. J. Dowding, J. J. Stiglich and T. S. Sudarshan, "Synthesis and Consolidation of Nanoparticles", in Advances in Powder Metallurgy & Particulate Materials, Ed. C. Lall and A. J. Neupaver, 1994, pp 45-58.

[10] S. Eidelman and X. Yang, "Three Dimensional Simulation of HVOF Spray Deposition of Nanoscale Materials", NanoStructured Materials, 9, 79-84, 1997.

[11] L. E. McCandlish, B. H. Kear, B. K. Kim, L. W. Wu, "Low-Pressure Plasma- Sprayed Coatings of Nanophase Tungsten Carbide-Cobalt", in Protective Coating: Processing and Characterization, Proc. TMS Northeast Reg. Meet. 5th 1989 (Pub. 1990), 113-119. Edited by Yazici, R. M.The Metallurgical Society, Warrendale, PA.

[12] R. Porat, S. Berger and A. Rosen, "Dilatometric Study of the Sintering Mechanism of Nanocrystalline Cemented Carbides", NanoStructured Materials, 7, 429-436, 1996.

[13] K. Mohan and P. R. Strutt, "Observation of Co Nanoparticle Dispersion in WC Nanograins in WC-Co Cermets Consolidated from Chemically Synthesized Powders", NanoStructured Materials, 7, 547-555, 1996.

[14] L. Zhang and T. E. Madey, "Initial Stages of Sintering of Nanostructured WC- 7wt.%Co", NanoStructured Materials, 2, 487-493, 1993.

[15] Z. Fang and J. W. Eason, "Study of Nanostructured WC-Co Composites", Proceedings of the 13th International Plansee Seminar, Eds. H. Bildstein and R. Eck, MetallwerkPlansee, Reutte 1993, Vol 3, 625-638.

[16] D. F. Carroll, "Processing and Properties of Ultrafine WC/Co Hard Materials", Proc. of the 14th Int. Plansee Conf. Abstract No. 89, 1997.

[17] J. J. Stiglich, C. C. Yu and T. S. Sudarshan, "Synthesis of Nano WC/Co for Tools and Dies", Tungsten Refract. Met. 3-1995, Proc. Int. Conf., 3rd 1995 (Pub. 1996), 229-236. Edited by Bose, Animesh; Dowding, R. J. Metal Powder Industries Federation: Princeton, N. J.

[18] A. T. Santhanam, P. Tierney, and J. L. Hunt, "Cemented Carbides", Metals Handbook, ASM Int., Vol. 2, 10th Ed. pp. 950-977, 1990.

[19] J. D. Schell and K. P. Taylor, "Wear of Jet Engine Components", ASM Handbook, Vol. 18, ASM Int., pp. 588-592, 1992.