Study of Current Developments and Research Concern of Conventional Cemented Tungsten Carbides: A Review

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Abstract— Tungsten carbide- (WC-CO) based hardmetals or cemented carbides represent an important class of materials used in a wide range of industrial applications which primarily include cutting/drilling tools and wear resistant components. Tungsten carbide is applied to improve the wear resistance of moving parts in machines like rolls and balls, of bearings, and nozzles, cutting and drilling tools, and mining equipment. Tungsten carbide cemented with copper or silver is used for electrical contacts and in fuel cells. Since most cemented carbides contain tungsten carbide, which gives them their extreme hardness and their high specific gravity, these alloys are referred to as hard metals and are often also termed “tungsten carbide” This report reviews the status of research and development in conventional Cemented Tungsten Carbides.

Key words: Tungsten Carbides, WC-CO

I. INTRODUCTION

A. Development of Conventional Cemented Tungsten Carbides with binder (WC-CO):

Present trends in machining operations foresee a quest for ever-higher cutting speeds to increase the productivity. Another trend is dry cutting, i.e., without the use of cooling/lubricants in order to save on the recycling costs of the cutting fluids with their associated environmental problems. Hence there has been a continued need for new cutting tool materials, which can withstand the very severe operating conditions at and near the cutting edge of the tool. Because of their high resistance to wear and to high temperatures, ceramics and ceramic composites remain attractive candidate materials for cutting tool applications[1] With the ever-growing need for cutting productivity (measured by cutting speeds) improvement, and the increasing utilization of novel, but in many cases nearly unmachinable materials, requirements for cutting tool materials have become higher and higher, i.e. cutting tools are required to withstand the very severe operating conditions at and near the cutting edge of the tool. Tungsten carbide (WC)–based cemented carbides have played a significant role as metal cutting tools since the 1930s. Many methods to improve mechanical performance of cemented carbides have been attempted since then, including modification of composition and refinement of carbide size. However, in some industrial fields, it is difficult to apply cemented carbides containing metal binders. In particular, in corrosive environments, cemented carbides are weak due to their Metal binders. Although it is more than 80 years since the first cemented tungsten carbide cutting tool was used the pace of development in the field remains rapid. WC based cemented carbides are widely used in engineering applications for their excellent mechanical properties and outstanding wear resistance in combination with high toughness. The cutting tool industry has already seen the benefits of fine grained tungsten carbide–cobalt (WC-Co) cermets, or hard metals as they are alternatively called, and significant improvements over the existing performance are expected from their nanostructured [2]

B. Identification of the Material:

1) Identification of the Material:

- For tungsten carbide of the grade HC the following elemental composition is reported Tungsten ≥94, Carbon ≤2, Iron ≤0.03 (H. C. Starck, 2003)
- CAS Number: 12070-12-1
- IUPAC Name: Tungsten carbide
- Molecular Formula: WC
- Structural Formula: WC
- Molecular Weight: 195.85 g/mol

Several phases of the binary system W-C have been described in literature (Gmelin, 1993). Of major importance is tungsten carbide (WC) which forms homogeneously only when tungsten and carbon are present in a nearly exact stoichiometric ratio of 49.5-50.5 mol % C (Tulhoff, 2000).

Fig. 1: Identification of the Material

2) Physico-Chemical Properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
<th>IUCLID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance type</td>
<td>Inorganic compound</td>
<td>H. C. Starck, 2003</td>
<td>1.1.1</td>
</tr>
<tr>
<td>Physical state</td>
<td>Grey metallic powder</td>
<td>H. C. Starck, 2003</td>
<td>1.1.1</td>
</tr>
<tr>
<td>Melting point</td>
<td>2776 °C</td>
<td>Tulhoff, 2000</td>
<td>2.1</td>
</tr>
<tr>
<td>Boiling point at 1013 hPa</td>
<td>6000 °C</td>
<td>Lide, 1991</td>
<td>2.2</td>
</tr>
<tr>
<td>Density</td>
<td>15.63 g/cm³ at 18 °C</td>
<td>Lide, 1991</td>
<td>2.3</td>
</tr>
<tr>
<td>Vapor pressure</td>
<td>Not determinable</td>
<td>H. C. Starck, 2004</td>
<td>2.4</td>
</tr>
<tr>
<td>Partition coefficient</td>
<td>Not calculable</td>
<td>Bayer Industry</td>
<td>2.5</td>
</tr>
</tbody>
</table>

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octanol/water

(log $K_{ow}$)

<table>
<thead>
<tr>
<th>Water solubility</th>
<th>&lt; 0.1 mg/l at 20 °C</th>
<th>Cassella 2.6.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash point</td>
<td>Non-flammable</td>
<td>H. C. Starck, 2005 2.7</td>
</tr>
<tr>
<td>Auto flammability</td>
<td>Inflammable at &gt; 300°C</td>
<td>H. C. Starck, 2005 2.8</td>
</tr>
<tr>
<td>(ignition tempera)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Physico-Chemical properties

B. Development of Binderless Cemented Tungsten Carbides (WC):

The Binder Phase Property plays the vital role for cemented carbides. It increases the materials toughness by introducing a metallic component into the microstructure. It controls the bonding between WC grains and it make possible the sintering to a completely dense body.[41]

The metallic binder phase is responsible for hinder the performance of such materials, particularly in demanding good high temperature properties and high hardness.[84] Moreover, the use of a binder results in degradation in the corrosion and oxidation resistance. Hence, the performance of the cemented carbide based tools is limited by the metallic phase. It also restrict the life of the instruments due to excessive wear or corrosion.[85] Hence, both the problems of densification and brittleness will be solved simultaneously under the development of Binderless WC which require material design.[42]

C. Development of Nanostructure Cemented Tungsten Carbides:

Bulk nanostructured materials are defined as bulk solids with nanoscale or partly nanoscale microstructures. This category of nanostructured materials has historical roots going back many decades but has a relatively recent focus due to new discoveries of unique properties of some nanoscale materials.

The great interest in the mechanical behavior of nanostructured materials originates from the unique mechanical properties first observed and/or predicted for the materials prepared by the gas condensation method. Among these early observations/predictions were the following:

- lower elastic moduli than for conventional grain size materials—by as much as 30 - 50%
- very high hardness and strength—hardness values for nanocrystalline pure metals (~ 10 nm grain size) are 2 to 7 times higher than those of larger grained (>1 μm) metals a negative Hall-Petch slope, i.e., decreasing hardness with decreasing grain size in the nanoscale grain size regime
- ductility—perhaps superplastic behavior—at low homologous temperatures in brittle ceramics or intermetallics with nano scale grain sizes, believed due to diffusional deformation mechanisms the present or near-term applications for nc materials, the hard material WC/Co is an example of several important trends.

H. C. Starck, Aktiengesellschaft, 1995

Nanostructured WC/Co composites have been prepared that can have the following characteristics:

- nanoscale grain sizes after consolidation of powder
- hardness values about twice that of conventional micrograined WC/Co
- enhanced wear resistance and cutting performance

While this material has increased hardness and strength, preliminary reports from Stevens Institute of Technology in Hoboken, NJ, and the Royal Institute of Technology in Stockholm, Sweden, point to similar or increased fracture toughness values for nanostructured WC/Co. As noted earlier, single-phase nanostructured materials studied to date have exhibited high strength and hardness but brittle behavior at low homologous temperatures (< 0.5 TM). The results of these studies of WC/Co two-phase nanostructured materials suggest that the combination of high hardness/strength and toughness/ductility may be possible in multiphase nanostructured materials. Other examples that point to this possibility come from the work of Professor A. Inoue at Tohoku University in Japan, whose lab the WTEC panel visited (see Appendix D). Inoue and coworkers have synthesized a variety of multiphase Al, Mg, and Ni-base alloys with nanoscale microstructures. Many of these alloys consist of nanocrystallites in an amorphous matrix. Some Al-rich alloys contain nanoscale quasi-crystalline particles surrounded by crystalline face-centered cubic Al. The fascinating properties of these multiphase nanostructured alloys include extremely high strength coupled with some ductility. Ductility is high in compression, but uniform elongation in tension is limited. Again, this behavior is analogous to that exhibited by ductile amorphous alloys. These results suggest the possibility for development of nanostructured multiphase composites that combine extremely high hardness and strength with toughness and ductility. Such materials could have many applications as unique structural materials. Multiphase ceramic nanocomposites are the focus of several efforts. One significant effort is underway at the Research Center for Intermaterials of the Institute of Scientific and Industrial Research at Osaka University in Japan (see site report, Appendix D). Professor Koichi Niihara has a large effort studying micro-nano composites such as Al2O3/SiC that have enhanced toughness and also a variety of hard
matrix/soft dispersion or soft matrix/hard dispersion nanocomposites. The enhanced toughness in some ceramic nanocomposites observed by Prof. Niihara has been verified by parallel studies of Dr. Steve Roberts at University of Oxford in England.

II. LITERATURE REVIEW

A. Fracture and Strength of Hardmetals WC-CO at Room Temperature (Alex V. Shatov, S.S. Ponomarev, S.A. Firstov) (2014) [8]:

Crack initiation, crack propagation, fracture modes, fracture toughness, strength, and critical defects of hardmetals at room temperature are reviewed. The state of the art for the structure-property relations that are based on a variety of chemistry, geometry, residual stresses and defects of the microstructure is discussed with major emphasis on the modern models and understanding of the processes and mechanisms behind the mechanical properties of hardmetals. Future research directions that seem appropriate at the moment are outlined.

B. Potentials of Nanostructured WC-Co Hardmetal as Reference Material for Vickers Hardness (Tamara Aleksandrov Fabijanica, Željko Alara, Johannes Pötschke) (15 December 2014)[9]:

The potential of nanostructured WC-Co hardmetal as reference material for Vickers hardness was researched in this paper. Preliminary reference Vickers hardness blocks were developed from a WC-9-Co mixture. The WC powder used was nanoscaled and had a grain size of 150 nm and a specific surface area of 2.5 m2/g. Hardness blocks were consolidated using Sinter-HIP process. Properties of the sintered material were obtained by using standard measurement techniques like magnetic properties or the SEM analysis of microstructure. Special emphasis was placed on hardness uniformity of the test surface as it is the most important property placed on reference hardness blocks. Hardness uniformity was tested by analysis of variance, ANOVA, for single factor in order to determine if significant hardness variations across the block surface were present. From the conducted research it was concluded that hardness distribution over the whole test surface was uniform. The achieved superior properties of the material, such as full densification, nanosized homogeneous microstructure, high hardness and good fracture toughness, influenced the metrological characteristics of the reference Vickers hardness block. Hardness non-uniformity is nearly two times lower when compared to commercially available standard reference material made of ultra-fine WC-Co. Material response does not involve chipping, cracking or any other imperfections. The research opens a new area of application for nanostructured WC-Co hardmetals as reference material for Vickers hardness for high hardness range.

C. Mechanisms for the degradation of strength and wear-resistance of WC based cemented carbides due to faster cooling (S.S. Ponomarev, A.V. Shatov A.A. Mikhailov, S.A. Firstov) (18 October 2014) [10]:

Faster cooling after sintering or the heat-treatment like brazing and high temperature joining can cause the formation of the layers of free carbon at the carbide–binder interface of the WC based cemented carbides. Formation of the free carbon layers at the carbide–binder interface decreases the transverse rupture strength by up to 10–15%, dramatically decreases the wear-resistance, but does not affect the hardness of the cemented carbide. This paper concentrates on the possible mechanisms of the reduction of the transverse rupture strength and the degradation of the wear-resistance of cemented carbides when the free carbon layers are formed due to the faster cooling. The microcracking along the carbide–binder interfaces that are weakened by the presence of the brittle free carbon layers plays the role of the additional defects for the strength and facilitates the initiation and growth of the macrocracks that can form the “reptile skin” pattern on the wear surface that is associated with the dramatic decrease of the wear-resistance of cemented carbides.

D. Characterisation of WC-Co with cubic carbide additions (Jonathan Weidow a,b , Jenni Zachrisson b , Bo Jansson b , Hans-Olof Andrén b) (March 2009) [11]:

In order to understand the effect of cubic carbide additions on the microstructure of WC-Co, six different materials were manufactured using the same WC powder and milling time. Four of the powder mixtures contained additions of TiC, ZrC, NbC or TaC and one of the powder mixtures contained both TiC and ZrC. All materials were designed to contain 20 vol% cubic carbide and 10 vol% binder phase as sintered. A WC-Co reference material containing 10 vol% binder phase was also manufactured. With electron backscatter diffraction (EBSD) it was seen that the best effect of grain growth inhibition was achieved when TiC was added to the powder mixture. The materials with addition of both TiC and ZrC had the highest hardness and coercivity of the materials manufactured. The fraction of low energy Σ2 WC/WC grain boundaries was seen to decrease as the Ostwald ripening proceeded during sintering.

E. On plastic deformation mechanisms of WC–15 wt% Co alloys at 1000 °C (X. Han a,b, N. Sacks a,b, Y.V. Milman, S. Layeck ) (March 2009)[12]

WC–15 wt% Co samples with and without VC doping have been tested in three-point bending at 1000 °C. The strain at fracture was found to be as high as 4.7%. Fractographic as well as macrostructural and microstructural investigations have been carried out on the tested samples to identify the mechanisms leading to the high strain. Up to 10% of the strain has been found to be due to cracks which initiated at or near the tensile face of the samples. Majority of the strain was found to be due to the drifting of the binder phase, which at 1000 °C appears to acquire a viscous consistency. No evidence of grain boundary sliding was found, but is expected to occur, on the basis of previous work. In the case of VC-doped samples a large number of WC/Co interfaces exhibiting steps were observed on the fracture surfaces which are possible preferred sites for fracture propagation.

F. Measurement of residual thermal stress in WC–Co by neutron diffraction (D. Mart a,b,c , B. Clausen b,c , M.A.M. Bourke b,c , K. Buss) (March 2009)[13]

The temperature dependence of residual stresses in a WC–17.8vol.%Co cemented carbide was measured by neutron diffraction. The comparison of the WC lattice parameter
within the WC–Co and within stress-free WC reference provides a measurement of lattice elastic strains and, using Hooke’s law, stresses. WC is found to be under hydrostatic compressive stresses of about ~400 MPa at room temperature, which decrease monotonically with temperature to a near-zero value at 800 °C. Residual stresses in cobalt also decrease with increasing temperature, but show an apparent increase above 800 °C, which is attributed to an increase in lattice parameter due to W dissolution in the Co phase.

G. Microstructure and wear resistance of WC–Co by three consolidation processing techniques (J.A. Picaa, Y. Xiongb, M. Pansera, L. Ajdelstajnb, A. Fornt, J.M. Schoneuna) (March 2009)[14]

Tungsten carbide–cobalt (WC–Co) has been extensively employed as an abrasion/wear protective material. However, carbon loss (decarburization) of WC–Co powders during processing reduces the efficiency of the material against abrasive wear. This paper examines the efficiency of three consolidation processing techniques to obtain coatings and bulk samples from WC–Co powder. In this work, high velocity oxy-fuel (HVOF) spray forming and laser engineered net shaping (LENS®) were applied to make WC–Co coatings; spark plasma sintering (SPS) was used to produce bulk WC–Co samples for comparison. The microstructures of two types of coatings and one bulk sample were analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) to recognize material modification. In addition, porosity and tribological properties of the WC–Co samples were tested. The ultra-microindentation technique was applied to measure the universal hardness and the elasto-plastic properties of the samples. Experiments using a tribometer (ball on disc configuration) under dry conditions have been performed in order to evaluate the friction and wear properties of the different systems.

H. Grain growth during the early stage of sintering of nanosized WC–Co powder (Xu Wang, Zhigang Zafang, Hong Yong Sohn) (May 2008)[15]

Rapid grain growth during the early stage of sintering has been found in many nano material systems including cemented tungsten carbide WC–Co. To date, however, there have been few reported studies in the literature that deal directly with the kinetics or the mechanisms of this part of grain growth. In this work, the grain growth of nanosized WC during the early stages of sintering was studied as a function of temperature and time. The effects of other influencing factors, such as the initial grain size, cobalt content, and the grain growth inhibitor VC, were investigated. The kinetics of the grain growth process was analyzed and the evolution of the morphology of WC grains during heating-up was studied using high resolution scanning electron microscopy. The results showed that the grain growth process consists of an initial stage rapid growth process which typically takes place during heat-up and the normal grain growth during isothermal holding. The initial rapid grain growth is at least partially attributed to the process of coalescence of grains via elimination common grain boundary. The preferred orientation between WC grains within the aggregates is considered a favorable condition for coalescence of grains, hence rapid grain growth. The solution–reprecipitation process is considered a mechanism of coalescence.

I. Ultrafine hardmetals prepared by WC–10 wt.% Co composite powder. (Zhen Xiong, Gangqin Shao, Xiaoliang Shi, Xinglong Duan, Li Yan) (May 2008)[16]

Ultrafine tungsten carbide–cobalt (WC–10 wt.% Co) composite powder was synthesized via spray-drying and direct reduction and carburization process in vacuum, which includes precursor preparation by spray-drying of a suspension of ammonium metatungstate (AMT) and cobalt carbonate (CoCO3). Calcination to evaporate volatile components, formation of tungsten–cobalt mixed oxide powder (CoWO4/WO3), ball-milling with carbon black, and subsequent direct reduction and carburization reaction in vacuum. The synthesis temperature of WC–10 wt.% Co composite powder without η or graphite phases is lower than 1000 °C. The calculated particle size by BET test is 0.29 μm. Coarse WC powder (FSSS: 0.9 μm) and Co powder (FSSS: 1.0 μm) (WC:Co = 9:1 in mass) were added into the obtained WC–10 wt.%Co composite powder with addition of 30 wt.%, 50 wt.% and 70 wt.%, respectively. Results show that the hardmetal fabricated from 70 wt.% (WC–10 wt.%Co composite powder) + 30 wt.% (90 wt.%WC + 10 wt.%Co) coarse powder) mixed powders exhibits a fine microstructure as well as optimum mechanical properties.


Nanocrystalline WC–Co materials have been the subject of interests and focus of research programs around the world for the past two decades owing to the expectations that the mechanical behavior of the material may improve significantly when grain sizes reduce to nanometer scale. However, although numerous technologies are available for making nanosized tungsten carbide powders, obtaining true nanocrystalline WC–Co (average WC grain size <100 nm) has been a great challenge due to the difficulties of controlling grain growth during sintering. Evaluation of the mechanical properties of nanocrystalline WC–Co materials is also difficult because there is little published data that are based on specimens with truly nanoscale grain sizes. In this review, the challenges and results of sintering nanocrystalline WC–Co powders will be examined as well as the various technologies for producing nanosized tungsten carbide powders. It will be discussed that the key challenge to the production of bulk nanocrystalline cemented tungsten carbide materials is to control the rapid grain growth during the early stage of sintering. The current understanding on the mechanical properties of cemented tungsten carbide made from nanoscaled WC–Co powders will also reviewed.

K. Evolution of the WC grain shape in WC–Co alloys during sintering: Cumulated effect of the Cr addition and of the C content Aurélie Delanoë, Sabine Lay March 2009[18]

The evolution of the WC grain shape in Cr doped WC–Co alloys are studied at several stages of the sintering treatment. The common shape of WC is a prism based on a truncated
triangle. The habit planes are two prismatic facets and the basal plane. In this work, the WC grain morphology is quantified using transmission electron microscopy at several temperatures. Two shape factors are used to measure the anisotropy between the two prismatic facets and between the prismatic and basal facets. The cumulated effect of the Cr addition and C content is studied. The Cr addition increases the anisotropy between prismatic facets in the W rich alloy. A significant increase of the elongation factor is recorded in the C rich alloy while the effect is more limited in the W rich alloy. The results are discussed as a function of the factors influencing the grain shape: grain growth and difference in energy between the facets.


Since nanocrystalline WC–Co powder was produced over a decade ago, the sintering of nanocrystalline powders remains a technological challenge. The goal of sintering nanocrystalline powders is not only to achieve full densification but also to retain nanocrystalline grain sizes. This is difficult because of rapid grain growth at high temperatures. Previous studies on the sintering of nanocrystalline WC–Co have shown that grains grow rapidly during the early stage of sintering. But there are few studies on the mechanisms of grain growth and densification during this stage. This paper presents the results of an experimental investigation on grain growth and densification of nanocrystalline WC–Co powders during heat-up at equilibrium solid-state temperatures. The results have shown that nanocrystalline WC grains grow rapidly during this period concurrently with rapid densification. The rapid densification and grain growth are partially attributed to the surface energy anisotropy of tungsten carbide. The effects of vanadium carbide on grain growth at solid state during heat-up are also discussed.

III. SUMMARIES

In this paper author have discus about the identification or chemical composition of WC-CO hard metal [2,3], in this review author have also did brief discussing on about varies research work with respect to property of tungsten carbide (WC-Co) that, Crack propagation, Critical defects, Fracture toughness ,Strength,[8] Vickers hardness, sinter–HIP,[9] strength and the degradation of the wear-resistance of cemented carbides, [10] grain growth, [11] Plastic deformation, viscous consistency,[12] Residual stresses; Thermal expansion,[13] HVOF thermal spray; Laser engineered net shaping,Spark plasma sintering, Tribology [14], Nanocrystalline powder ,Sintering, Grain growth,[15,18] Ultrafine tungsten carbide–cobalt (WC–10 wt % Co) composite powder was synthesized via spray-drying and direct reduction and carburization process in vacuum. [16] Grain shape development ,Effect of C/W ratio and Cr addition,[19]

IV. CONCLUSIONS

It has seen that there is very much wield research work have been done with conversional WC – CO walker or powder [8,9,10,11,12,13 ] also a higher research work perform with binder less or fine or altar fine (500 to 100 nanometer grain size) WC material , but there is very much space to perform research work with nanostructure( > 100 µ ) with or without binder tungsten carbide material.

V. ACKNOWLEDGEMENT

The author would like to thank Prof. Dr. S.K.Jha, formerly with the Department of Mechanical Engineering, B.I.T. sindari, for fruitful discussions and help during the preparation of this paper.

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