

The Potential for Heat Treating Cemented Carbides

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The focus at the outset was on nothing more than cryogenic treatment of cemented carbides. Then, in relation to additional findings arising from heating of cemented carbides, this paper was expanded to include the results of heat treatment and the behaviour at elevated temperatures. Although heat treatment is applied to diverse materials, no profound study of heat treatment has been dedicated to cemented carbides. This is despite the fact that both cryogenic treatment and heating to elevated temperatures have been proven to cause changes in their properties. Not all these changes are favourable. If precisely-defined rules are not followed, the changes may be adverse. The interest in heat treatment of cemented carbide has been very low. This paper not only provides comprehensive information on the properties of heat-treated cemented carbides but also presents the processes which take place in cemented carbides under load.

Keywords: Cemented Carbides, WC-Co, Heat Treatment, Cryogenic Treatment, Wear

1 Introduction

Cemented carbides exhibit properties which are beneficial in applications involving cutting tools. These properties include high hardness. Some authors also incorrectly mention temperature resistance. Findings suggest that cemented carbides lack good temperature stability. Nevertheless, they are used for cutting tools because temperature resistance can be improved appreciably by surface treatment (thin film deposition). The films used for this purpose include, for instance, those which contain silicon, an element which markedly enhances oxidation resistance. Hardness is provided by the substrate, whereas the resistance to thermal loads arises from the surface film acting as a thermal barrier. Both properties combine to generate high cutting performance and wear resistance of the cutting part of the tool. On the other hand, high hardness results in decreasing toughness, which in case of cemented carbides is expressed in terms of fracture toughness. It is many times lower in cemented carbides than in tool steels. This is manifested in machining and during the manufacture of the tool. In the first case, excessive load, such as in interrupted cutting, leads to chipping in the cutting part. Grinding of the tool blank increases its residual stress levels. Once the critical stress is exceeded, the tool fails. Failure sometimes occurs after thin film deposition. Such failures used to be frequent, leading to disputes about who is to blame. Unfortunately, thin film deposition companies were often on the losing side. Studies [1; 2] were extensively involved with brittle behaviour and heat treatment of cemented carbides. They were motivated by the promise of cemented carbide annealing which might relieve residual stresses below critical levels. A brief summary of their findings is given in another section below. The nature of the cemented carbide is that of a composite material, which is why experience acquired with steels does not apply here. For better understanding, the nature of cemented carbides from both microstructural and historical viewpoints must be described.

2 Historical development of cemented carbides

Cemented carbides were introduced to market in the early 20th century. Although they still comprise two fundamental constituents, the base material and the binder, they have evolved since their early days. This evolution led to alternate bonding materials, such as nickel-based and multi-component binders. One of today's multi-component binders is the Co-Ni-Cr type. Nickel-based and multi-component binders are used in applications where cobalt binders would be inadequate, e.g., in corrosive environments, or at higher temperatures. On the other hand, nickel-based binders are gradually being abandoned even in the above applications due to the health hazards associated with nickel, which causes contact dermatitis. One of the available substitutes is manganese, which is not carcinogenic and exhibits corrosion properties similar to nickel. [3, 4]

Besides the binders, the base materials of cemented carbides continued to be developed. Nowadays, not only tungsten carbide (WC) but also other carbides (VC or TiC) are used as the base materials. In addition to these basic carbides, complex carbides are employed thanks to advances in their processing technology. [3]

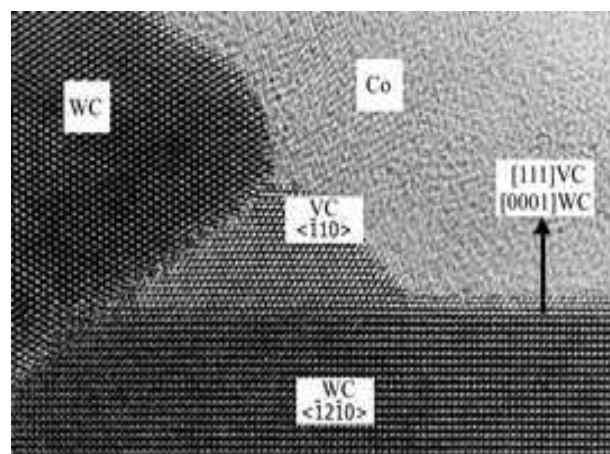




Fig. 1 Structure of a cemented carbide and the formation of bonds between the hard carbide and the binder metal. The second micrograph illustrates a new trend in cemented carbides, where vanadium carbide serves to impede the propagation of cracks [5].

In cutting operations performed with cemented carbide tools, mechanical properties and chemical and physical processes play important roles. The temperature of the chip can rise to up to 1000 °C. In addition to wear resistance and an ability to sustain impact loads, one has to consider the resistance to oxidation and diffusion processes between the tool tip and the chip. These improvements are mainly provided by the addition of TiC and TaC to the basic types of cemented carbides. [6, 7]

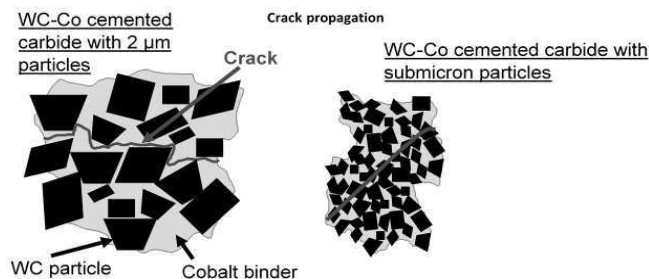


Fig. 2 Crack propagation paths depending on the carbide grain size [3]

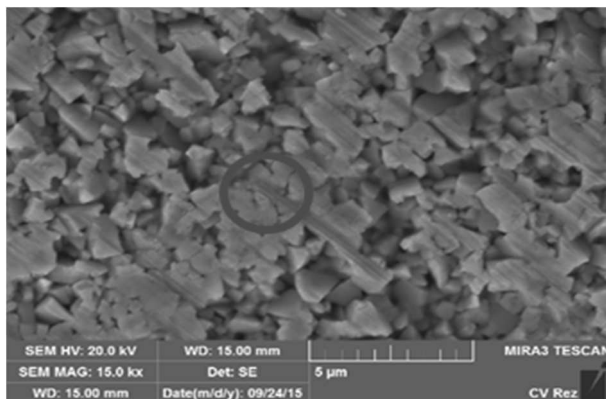


Fig. 3 Surface condition upon grinding. Examination by EDX has shown a notable loss of cobalt.

As shown in Fig. 2, a crack spreads more readily through a material with smaller grains. In such case, the resistance to crack propagation, as expressed by fracture toughness, drops. On the other hand, hardness and flexural strength increase with decreasing carbide grain size.

At the beginning of this century, efforts to achieve the

highest possible hardness in cutting tools led to the use of carbide particles with sizes on the order of several hundred nanometres. Practical experience proved that such materials are only suitable for very specific applications. In some cases, the fine-grained microstructure was even revealed as the cause of extreme damage suffered by the tool. In response to this and other findings, the Ceratizit company combined multiple carbide types to improve the crack resistance of the resulting material, while maintaining high hardness thanks to fine particle size, as illustrated in Fig. 1. Fine-grained microstructures play their role in tool grinding as well. The finer the grain is, the easier it is to achieve the desired sharp edges without the risk of chipping, crumbling or cohesion failures.

Despite the years of progress, the WC-Co grade, the oldest cemented carbide type in industrial use, remains the most widespread representative of the class. Its origin dates back to 1922, when the company Widia came up not only with the carbide itself but also with its unique name, Widia, derived from the German words “wie Diamant” or “like diamond”, referring to the hardness of the material. This carbide’s constant popularity is down to its internal structure. The cobalt binder is the best choice for wetting the WC particles, and therefore provides uniform pore-free products. If present, internal pores impair the mechanical properties of the material. Since cobalt has a hexagonal crystal structure that resembles the structure of the WC carbide, the bonding forces between them are very high. [1] Although WC has a major impact on brittle-fracture properties, the decisive role in the behaviour of cemented carbides as a whole is played by cobalt. As the following section shows, the behaviour of the cobalt phase dictates not only corrosion properties but, above all, the degradation of the material by oxidation under high thermal loads. Cobalt also causes brittle failure when residual stresses exceed critical levels.

3 Thermal loading on cemented carbides

In order to understand the processes that take place in cemented carbides under thermal loads, one has to return to the manufacture of the cemented carbide. It comprises the production of powders and the binder, the mixing of both constituents, compacting and sintering. An important aspect in this context is the use of W₂O₅ tungsten-bearing ore for the production. Pure tungsten is obtained by reduction and then combined with carbon at temperatures of 1400-1500 °C to produce WC grains. This reaction employed in the production of cemented carbides is very important with respect to their behaviour under thermal load. First experiments conducted at the author’s facility have shown that once the cemented carbide is heated above 800 °C in an oxygen-containing atmosphere, it suffers thermal degradation due to tungsten-oxygen reaction and reverts to the stable compound from which it was made. This experiment was designed to ascertain the integrity of a thin film deposited on an exchangeable cutting insert. In the locations where the film was damaged, tungsten oxidation occurred [7].

The purposes of follow-up experiments were to explore the degradation of cemented carbides at elevated temperatures and to design a heat treatment route which

could lead to reduced residual stresses in ground solid-carbide tools. Another impetus for monitoring the processes that take place in cemented carbides was the finding that in specific cases that involve grinding, cobalt is lost from the surface. Fig. 3 shows the surface of a cemented carbide upon grinding, which lacks cobalt. Examination by EDX showed a decrease in the Co content from the initial 5% to 0.6%. The surface relief of WC grains offers evidence of cobalt loss.

The reduction in cobalt content was monitored down to the depth of several micrometres. Its consequence is an increase in surface brittleness, as evidenced by fracture toughness values K_{IC} . Those dropped from the starting 12.2 ± 0.1 to $5.4 \pm 0.4 \text{ MN} \cdot \text{m}^{-3/2}$.

As mentioned above, the particular properties of cemented carbides arise predominantly from the fact that they are composite materials. Considering thermal loads, the differences between the behaviour of the cobalt binder (metallic bond) and tungsten carbide (covalent bond) must be taken into account. For this reason, it is necessary to track the behaviour of each constituent of the composite at a particular temperature. Generally, oxidation is faster at higher temperatures because the system transitions into an energetically more favourable state. As shown by the research by Liyong Chen, in the oxidation process, the oxygen content rises preferentially in the cobalt phase, whereby a porous layer with microcracks is formed which impairs wear resistance. This case was confirmed by experiments in which the onset of oxidation was observed in the cobalt phase at 450°C . A literature search shows that three phases of oxidation of WC-Co can be distinguished. Up to approximately 600°C , preferential attack is seen in the cobalt phase which develops cobalt oxides. The same mechanism operates in WC-Co during machining when cobalt binder is gradually lost, leaving a skeletal structure of tungsten carbides (see Fig. 3). At higher temperatures (above 600°C), WO_3 tungsten oxides begin to form which, with increasing temperature and at longer times, lead to formation of the CoWO_4 phase. These changes are associated with the energy barrier which must be overcome for a particular stable phase to form. The CoWO_4 phase leads to the largest energy drop but a large amount of energy must be supplied [9; 10]. These processes were corroborated in an extensive study presented at the conference entitled 25. DNY TEPELNÉHO ZPRACOVÁNÍ S MEZINÁRODNÍ ÚČASTÍ (25th NATIONAL CONFERENCE ON HEAT TREATMENT) [2]. The conclusion is that a thermal load applied in the presence of oxygen leads to appreciable degradation due to formation of the above-described oxides. Nevertheless, the motivation for these experiments was to improve the post-grinding stress state in the cemented carbide. Evidently, a sintered material must be annealed in a protective atmosphere or in vacuum. The following section is devoted to the relationship between thermal loads acting on the cemented carbide and the decrease in residual stress.

4 Residual stress in ground cemented carbides

Today, residual stresses receive major attention. It is because they can be quite well quantified and their impact

on final properties (such as fatigue strength and corrosion behaviour) are known. Furthermore, today's instruments' capabilities are such that even the residual stresses between individual phases in the microstructure can be identified (e.g. using EBSD). In cemented carbides, the matter of residual stresses is somewhat complicated. The reason is that, like composites, they comprise two dissimilar constituents (carbide grains and cobalt binder). Residual stresses must be considered in other operations as well.

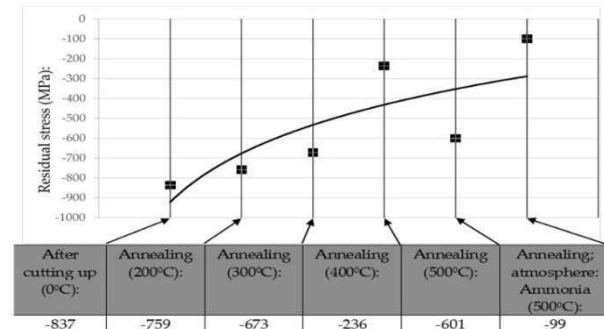


Fig. 4 Effect of heat treatment sequence on the reduction of residual stress in the surface layer of cemented carbide [11]

The manufacture of exchangeable cutting inserts did not involve large volumes of cemented carbide stock being removed by grinding. In addition, this step was followed by CVD deposition whose high temperature (1000°C) relieved the residual stress generated grinding. Today, "full-width" grinding method is often used for tools which, together with high demands on cutting productivity, means that large-scale residual stresses are introduced. To understand the processes which are taking place during grinding, one has to focus on what precedes the creation of new surface. During grinding, the grains of WC fracture and become crushed due to large tensile stresses imposed by diamond grains in the grinding wheel. Examination of the ground surface at high magnification reveals how carbide particles are pulled out from the stock. During grinding, the pliable cobalt binder with WC fragments is smeared and removed by the process fluid. The surface develops a deformed layer which consists of tungsten carbide fragments and smeared cobalt binder. Moreover, high temperature is generated at critical grinding conditions, leading to cobalt oxidation. The resulting oxide is very brittle and tends to spall, rendering the surface and the regions below depleted of cobalt. Grinding generates residual stress which, in some cases, may reach up to 3000 MPa . It is a compressive stress component whose magnitude is measured on WC grains. The reaction generated in the cobalt binder is a tensile stress component. Whereas tungsten carbide can sustain compressive loads up to 5000 MPa , the strength of cobalt is approximately 1200 MPa (in tension). Consequently, high compressive stresses cause the cemented carbide to fail in the cobalt binder phase. To prevent failure, these stresses must be reduced: either by reducing the grinding parameters (removal rate, wheel speed, cooling, grinding wheel sharpness) or by incorporating some stress-relieving operation. One of the available options is annealing.

As shown in Fig. 4 below, an appropriate thermal load can relieve residual stresses. The right heat treatment sequence supports reduction of residual stresses in the surface layer of cemented carbide. Specimens were annealed in an air furnace at 200–500°C. At 500°C, cobalt oxides form which do not contribute to reducing residual stress. If their formation is prevented at this temperature (by introducing ammonia), the reduction continues all the way to almost zero.

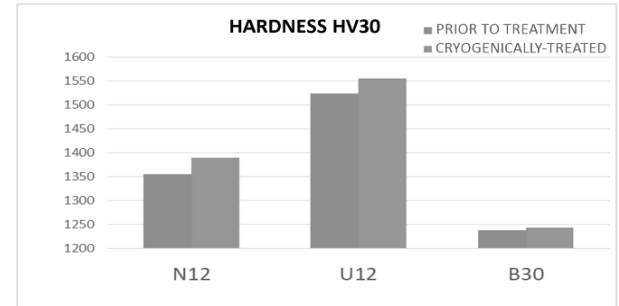
5 Cryogenic treatment of cemented carbides

Although it may appear that no cryogenic treatment of cemented carbides has ever been performed, there is a large number of such studies. Most of them were conducted by the Department of Mechanical Engineering at Beant College of Engineering & Technology, India, where several decades of effort have been dedicated to this process [12; 13; 14]. Their papers report definite improvement in the utility properties of cemented carbides deployed in cutting processes. These papers provided an impetus for an experiment that involved cryogenic treatment of three different cemented carbides. The materials were as follows: N12 – binder: 12% Ni, WC grain size 0.8 µm; U12 – binder: 12% Co, WC grain size 0.8 µm; B30 – binder: 10% Co, WC grain size 3-9 µm. These specimens were subjected to special cryogenic treatment (freezing to -186°C – holding for 24 hours, slow reheating to 150°C – holding for 6 hours). For the first experimental run, this process was adopted from the company 300 Below, Inc. It will be reviewed and updated. Nevertheless, the first results confirmed favourable changes in the cemented carbide. Cryogenic treatment leads to changes in not only the cobalt binder but also in tungsten carbide. Lattice defects are reduced in the cobalt (nickel) binder. In addition, minute precipitates of tungsten and carbon form in the binder, strengthening it. In carbides, a change occurs in the ratio of the η phase (CO₆W₆C) – in the case of the cobalt binder. These carbides have not

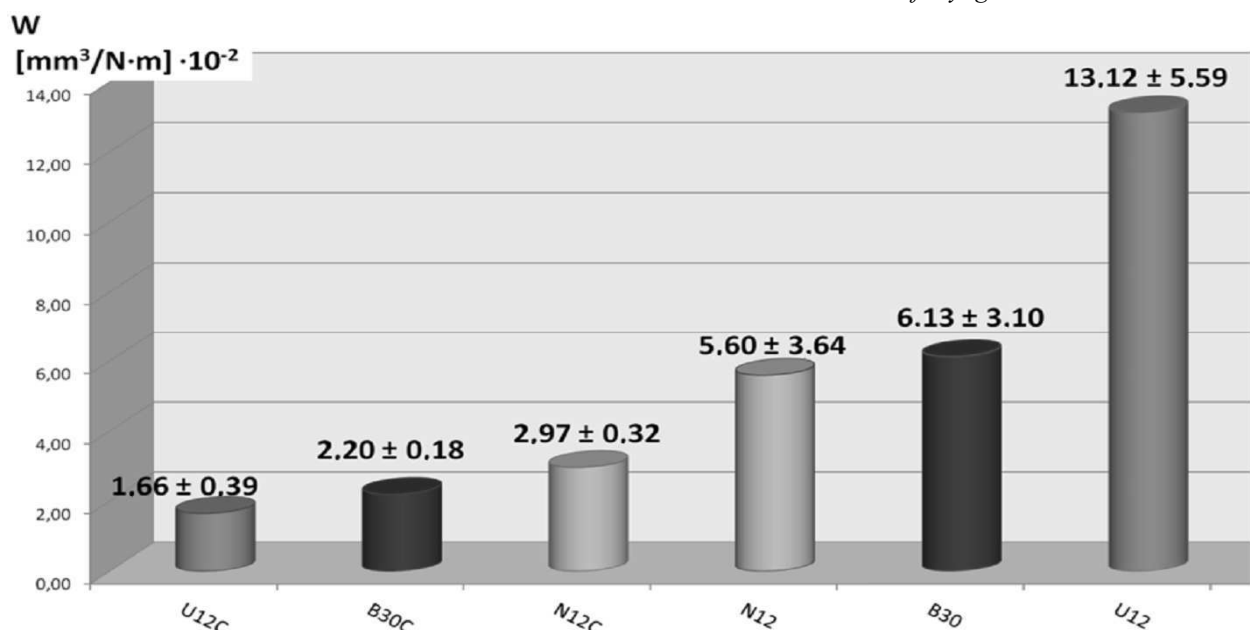
been described yet in the nickel binder. Owing to these changes, hardness increased in all the cemented carbides under examination. In N12 and B30, fracture toughness deteriorated slightly. In U12, it improved negligibly. These changes are smaller than the variance of the values. Resistance to contact loads was determined using the pin-on-disc test. The results were unambiguous: the wear rate in the cemented carbides upon cryogenic treatment was reduced. The first data on residual stress indicate a reduction from approximately -1500 MPa to between -700 and -950 MPa. It was found by X-ray measurement and will be verified by measurement taken at another facility. It will be specified further in relation to the depth profile of residual stress (measured by various X-ray generators).

Tab. 1 Changes in fracture toughness of cemented carbides as a result of cryogenic treatment

Cemented carbide type	Cryogenic treatment	Fracture toughness K_{IC}	
		K_{ICSH}	K_{ICPLQ}
N12 nickel	Before	19.1±1.5	19.4±1.5
	After	18.5±2.2	18.8±2.2
U12 cobalt	Before	12.8±0.2	13±0.2
	After	13.5±1.3	13.7±1.4
B30 cobalt	Before	26.3±3.0	26.8±3.1
	After	24.0±2.5	24.4±2.6



Graph 1 Changes in hardness of cemented carbides as a result of cryogenic treatment



Graph 2 Effect of cryogenic treatment on wear behaviour (material loss) found by the pin-on-disc test. Cryogenic-treated cemented carbides are indicated by the letter “C”.

6 Conclusion

Experiments have definitely shown that cemented carbides can be heat-treated much like conventional metallic materials. Heating must be performed under such conditions which eliminate oxidation, a process which starts in the cobalt binder and eventually spreads to tungsten carbide. If such conditions are provided, residual stress levels decrease. High residual stresses may lead to catastrophic failure of ground solid carbide tools. Further experiments were devoted to cryogenic treatment of cemented carbides. Tests confirmed improvement in properties. Although only one freezing and reheating sequence was tested, higher hardness and, above all, higher resistance to shear contact loads were obtained. These results are confirmed by data from a literature search which suggest up to 20% improvement in cutting edge durability in machining C45 steel.

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