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Chapter 12

Properties and Testing of Cemented Carbides

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Additional information is available at the end of the chapter

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Abstract

This chapter deals with selected properties of cemented carbides and their testing. It consists of three main sub-chapters. The first one covers the degradation processes associated with grinding of cemented carbides. Among those, the focus is on the effects of thermal loads and reactions with the environment—the atmosphere. The second main sub-chapter describes the origin of residual stresses and their impact on cemented carbide properties. Finally, the third main sub-chapter explores the corrosion of cemented carbides in various environments. The choice of these topics was inspired by the impression that many users have of cemented carbides: indestructible materials in which no degradation takes place either during the production of cutting tools or during their use. As evidenced by the authors' experience described below, which has been acquired over many years in the field, damage in cemented carbides is a very frequent occurrence. Despite that it still receives very little attention, and especially the damage in cemented carbide cutting tools tends to be ascribed to various other factors, such as the applied coatings, the cutting process conditions and the material of the workpiece.

Keywords: cemented carbide, degradation, oxidation, residual stresses, mechanical properties

1. Introduction

Cemented carbides have been in use for almost a century. Over this period, they have become a common material to make cutting tools and for all applications where high hardness is required together with a certain level of toughness. As they tend to be known under various names, their users sometimes mistake them for other materials. This proves the general lack of adequate knowledge of cemented carbides. Their evolution has accelerated in recent years, spurred by the demand for greater hardness without toughness being compromised, and by requirements for a greater ability to be formed and treated by various processes: grinding, thin film deposition, along with special routes leading to the minimization of residual stresses, for instance.

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The sub-chapters following the introduction outline the mechanical properties, manufacturing routes and methods of testing the characteristics of cemented carbides which are required by industry. The behaviour of these materials during grinding is explored in the next main sub-chapter. Effects of the grinding process on near-surface properties are analysed because these are decisive in industrial applications of these materials, not only in their uncoated but also in their coated variants. Such effects include thermal degradation and surface oxidation, which impact on the condition of the cobalt binder.

The second main sub-chapter deals with residual stresses. These can be induced by grinding but also by other manufacturing operations which so far have not received adequate attention, such as tumbling and polishing. Effects of thin film deposition on residual stresses are described, as well as the impact of these stresses on the properties of the resulting physical vapor deposition coatings, namely their adhesion and cohesion. All of the above dictate the ultimate life and performance of cutting tools and the quality of machined surfaces.

The topic of the last main sub-chapter is the corrosion of cemented carbides in various alkaline and acid environments. The environments described here were chosen on the basis of real-world service conditions of cemented carbides. Many users believe that—from the chemical viewpoint—cemented carbides are indestructible. Some of the environments used for testing were intended to simulate mine waters. Others included cutting fluids in which cemented carbide cutting tools operate, often as exchangeable inserts, e.g. in circular saws for cutting wood. In these applications, cemented carbides are exposed to corrosive substances released from wood which affect the life of the cutting edge.

1.1. Historical development of cemented carbides

Cemented carbides were introduced to market in the early twentieth 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 [1, 2].

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 [1].

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 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.

http://dx.doi.org/10.5772/66871

These improvements are mainly provided by the addition of TiC and TaC to the basic types of cemented carbides [3, 4].

As shown in **Figure 1**, 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 **Figure 2**. Fine-grained microstructures play their role in tool grinding as well. The finer the grain, the easier it is to achieve the desired sharp edges without the risk of chipping, crumbling or cohesion failures.

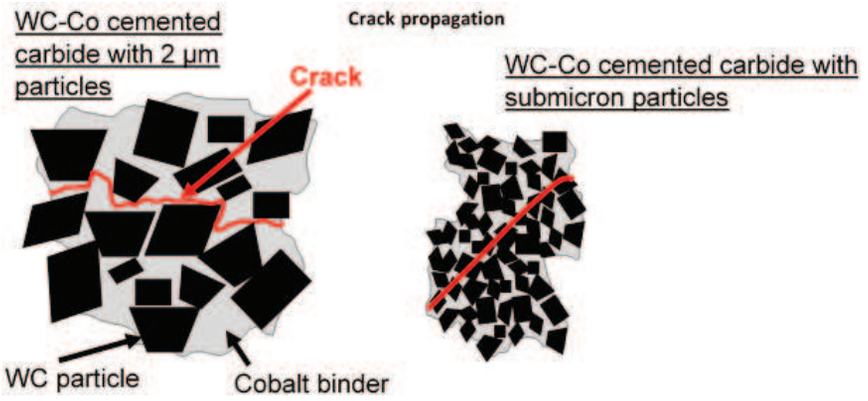


Figure 1. Structure of a cemented carbide and the formation of bonds between the hard carbide and the binder metal. The second micrograph illustrates a new trend in cemented carbides, where vanadium carbide serves to impede the propagation of cracks [5].

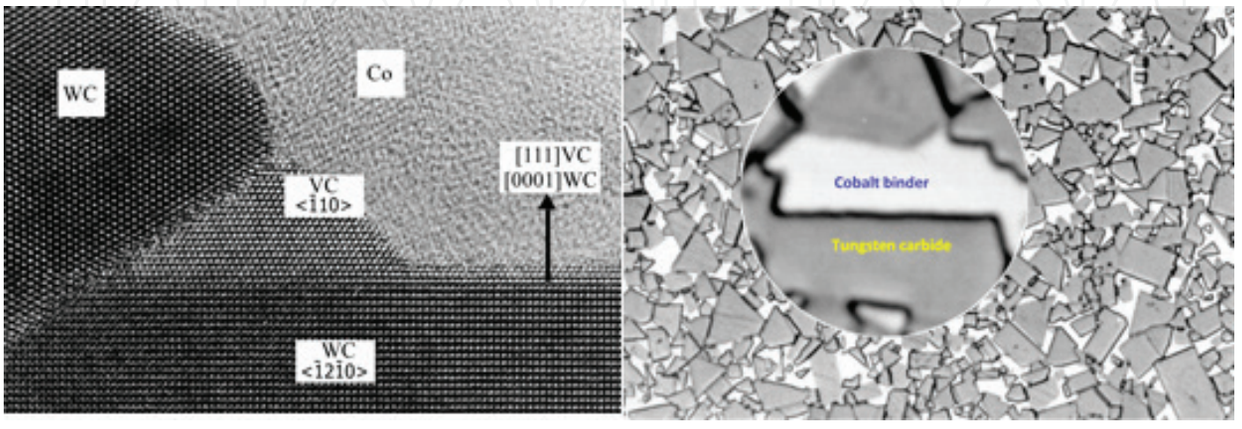


Figure 2. Crack propagation paths depending on the carbide grain size [5].

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].

1.2. Manufacture of cemented carbides

All properties of cemented carbides, and indeed of all powder metallurgy products, are governed by the type and purity of the primary raw materials used in their production. Primary constituents for the manufacture of WC-Co grades include, for instance, calcium tungstate $CaWO_4$ (scheelite) for the carbide powder and heterogenite for the cobalt powder. These days, powders are often manufactured from recycled cemented carbides. As a rule, the customer should be notified of the kind of raw material used, i.e. whether the product was made from pure or recycled raw materials. Although tests carried out by the authors have not revealed large differences between the properties of cemented carbides made from pure and recycled raw materials, data on machining performance reported by tool manufacturers have proved that there are such differences [1, 4, 6].

Various technologies are employed for converting carbide and binder powders into products—which therefore exhibit correspondingly varied characteristics. Powders used for this purpose are obtained by production methods which provide various particle shapes and sizes. These aspects have a bearing on the sinter activity and the chemical reactivity of the powder. The latter depends on the number of internal defects within the particles and on their surface energy. Internal defects include mainly crystallographic point defects, i.e. vacancies and interstitial atoms, and line defects, i.e. dislocations. In order to obtain sintered products of adequate density and low porosity, powders with high sinter activity and high reactivity should be used [4, 7, 8].

Once the powders have been produced, classified and mixed, they are shaped and sintered. Technologies by which the desired shapes of cemented carbide parts are achieved involve various forming operations, such as hot isostatic pressing, cold isostatic pressing and extrusion. Powder parts can also be pre-sintered during these operations. Pressing to the desired shape is followed by sintering. Sintering serves the purpose of homogenization of the cemented carbide. This is facilitated by the capillary action and good wettability of the binder with carbide particles [4, 7].

Once sintering has been completed, the product is ready for the finishing operations: grinding and, where relevant, the deposition of thin films. Thin film deposition is typically the last operation before the cemented carbide product is shipped to the customer.

In some cases, however, the sintered part is still no more than a semi-finished product whose final shape must be imparted by grinding. Nowadays, the capabilities of some other

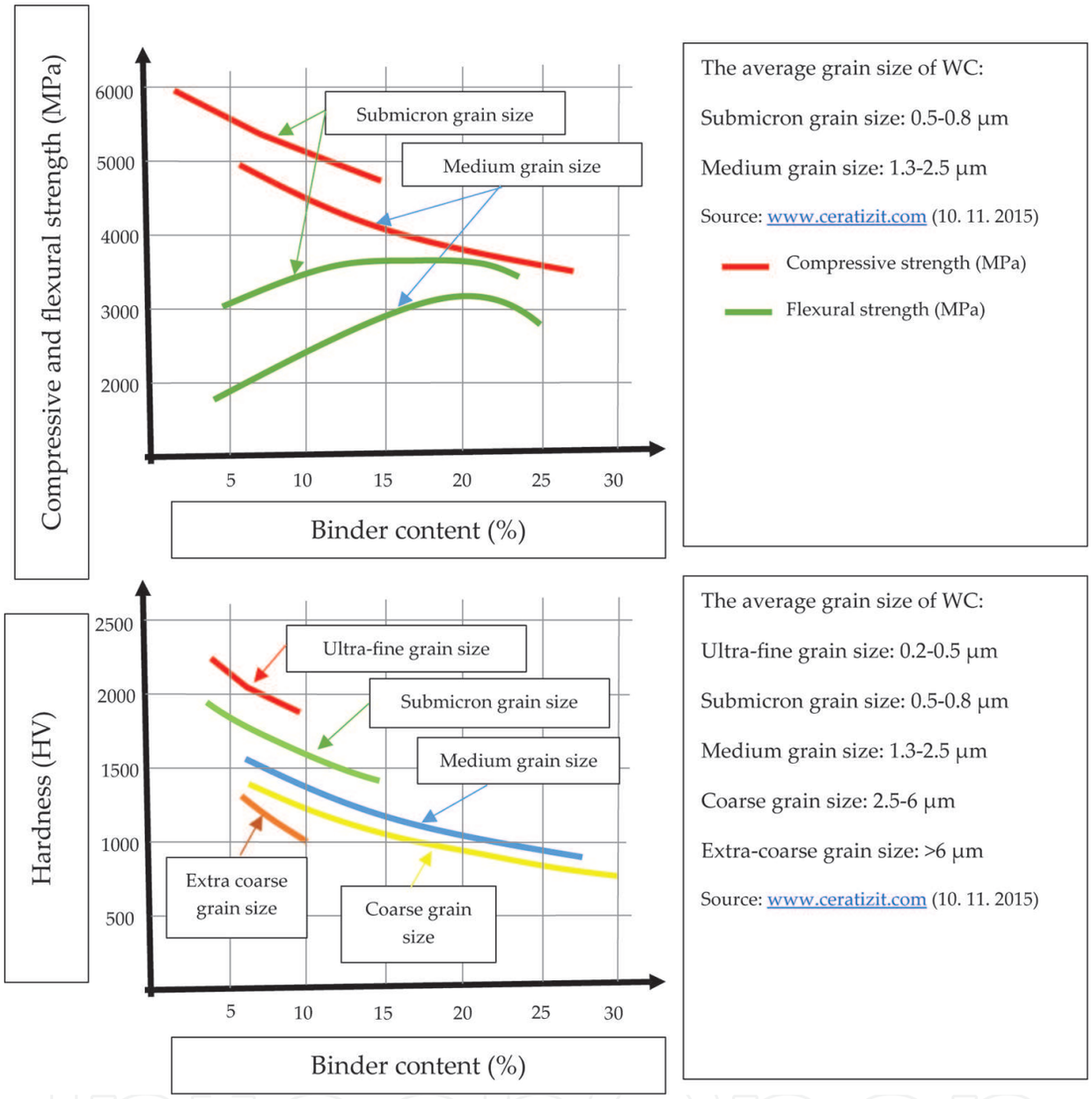
cutting processes are studied to ascertain their potential for making complex-shaped tools of cemented carbides. One of the viable options is milling. Thanks to tailored milling tools and conditions, it allows machining of materials whose hardness exceeds 85 HRC.

The technologies used for producing cemented carbides have a bearing on their mechanical properties. These properties are controlled by the carbide particle size, particle distribution (gradient cemented carbides), the type and proportion of the binder, the resulting structure (brittle phase content, porosity) and impurities (oxides), which may enter or form within the cemented carbide during processing [1, 4, 7].

Cemented carbides belong to a class of brittle materials. The reason for this classification is their inability to undergo extensive plastic deformation on the macroscale. However, some plastic deformation takes place within microvolumes, namely in the cobalt binder. This is why the condition, purity and content of the binder deserve attention. There should be no admixtures with the potential for forming intermetallic phases. To enable a more effective description, the concept of mean free path (MFP) has been introduced. This criterion is used instead of grain size because the bonding material (Co) is present in the form of a network in which the tungsten carbide particles are embedded. At high bonding metal levels, or large MFP values, the binder can undergo plastic deformation and work hardening. The propagation of cracks induced by elevated stress is hindered to some extent in the tough bonding metal, depending on the mean free path (MFP). Once the ductility of cobalt is used up (due to the rising stress), macroscopic failure may set in. By contrast, decreasing cobalt content leads to expansion of the areas of contact between tungsten grains. The grains may therefore become the source of microcracks. The very thin cobalt film (between 100 and 300 nm) grows brittle, as the movement of dislocations within the film is confined, and the growth of microcracks is not arrested [9]. Mechanical properties which are evaluated in cemented carbides include flexural strength, compressive strength and fracture toughness. They are measured by destructive tests on standard specimens in special testing machines. Microstructure (carbide grain size, distribution of carbide types and microstructural homogeneity) and chemical composition are studied by means of optical and electron microscopy methods. The data gathered in this manner give an overall picture of the properties of cemented carbides. In addition to the above-mentioned techniques, non-destructive testing methods are employed. Examples include X-ray, ultrasonic and eddy current inspection. X-ray diffraction is a representative of X-ray-based methods used in this context. It is advantageous in the cases where residual stresses in the cemented carbide surface need to be quantified or when checking for the presence of the eta phase. This is a brittle phase which impairs the mechanical properties of cemented carbides. It can be identified by this method because its diffraction properties differ from those of the binder and the carbide grains. It can also be detected using eddy current inspection on account of the different magnetic properties [3, 9].

Variation in the mechanical properties of WC-Co cemented carbides (hardness and flexural strength) as a function of carbide grain size and Co binder content is illustrated in **Graph 1.**

Graph 2 shows fracture toughness and hardness levels of three WC-Co cemented carbides with carbide grain sizes in the range of 0.5–0.8 μm, and a Co binder content of 10%. These



Graph 1. Effect of carbide grain size and Co binder content on hardness and flexural strength of cemented carbides [10].

specimens were provided by three different suppliers in order to compare the actual levels of mechanical properties of the materials and of those given in catalogues. The differences result from the differences between the manufacturing processes. They may arise as early as in the production of powders and their mixtures. For instance, one manufacturer may be using attritors, whereas another may be using atomization. Another source of variation is the final inspection, where one manufacturer might permit a higher fraction of coarse carbide grains of 0.8 μm than the other. The other product will therefore contain a greater amount of carbide grains of the 0.5 μm size [3].

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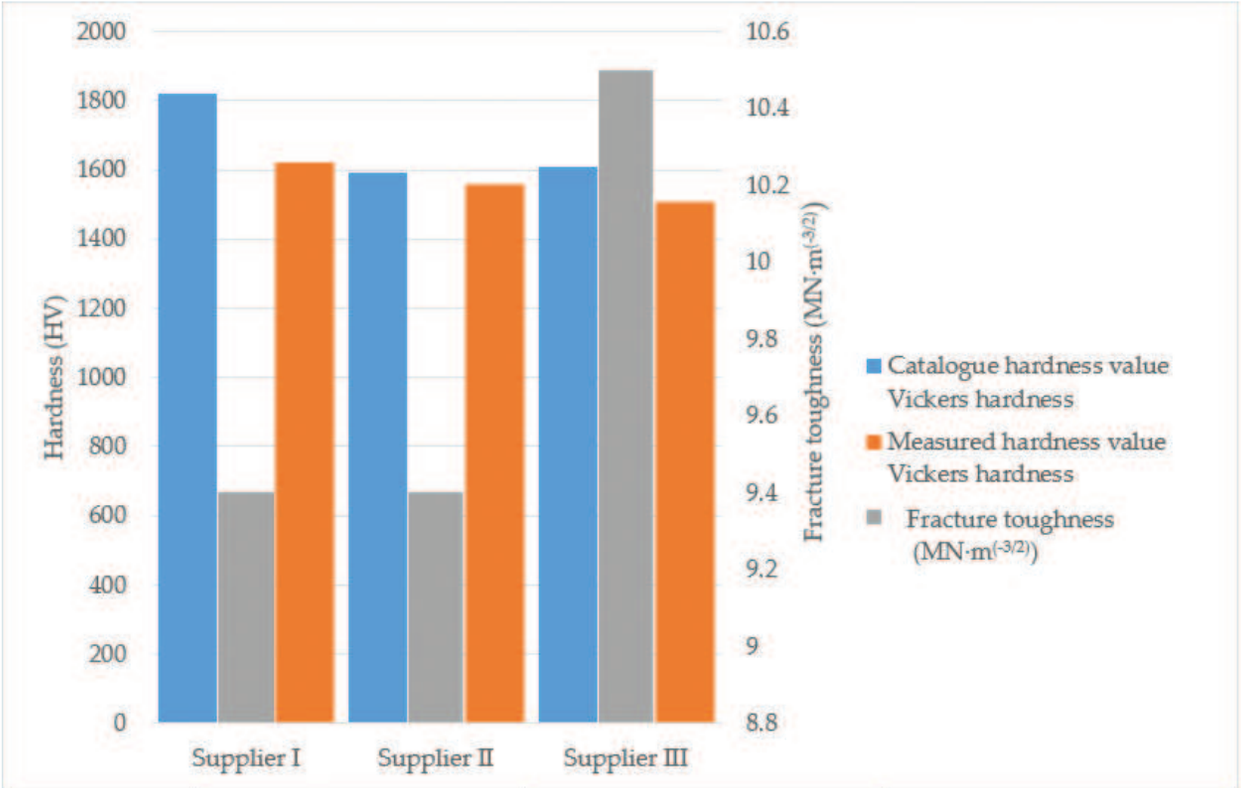

Supplier:	Catalog hardness value:	Measured hardness value:	Fracture toughness:
	Vickers hardness:	Vickers hardness:	(MN·m$^{(-3/2)}$)
Supplier I:	1820	1620	9.4
Supplier II:	1590	1558	9.4
Supplier III:	1610	1507	10.5

Graph 2. Comparison between fracture toughness and hardness levels of cemented carbides of identical composition provided by three different suppliers [3].

2. Effects of grinding on cemented carbide properties

With their hardness levels close to 85 HRC, cemented carbides belong to the class of hard materials. As a result, the main method used for shaping them after sintering is grinding. In the production of cemented carbide tools, the grinding operation provides the desired tool geometry. It can be subsequently modified in terms of microgeometry by laser processing, tumbling, blasting or brushing. A tool prepared in this way can be coated using the PVD or CVD methods.

During grinding, the surface of a cemented carbide is removed by the action of a multi-edged tool: a grinding wheel. Grinding wheels for shaping cemented carbides consist of diamond grains bonded by resin or metal (e.g. copper) [11].

The wheel is pressed against the cemented carbide surface and their movement relative to each other and the associated friction cause heating. The surface of the cemented carbide is removed by abrasion in amounts which are directly proportional to the downforce and the contact area, and inversely proportional to the ratio of the hardness of the cemented carbide surface and that of the abrasive particles of the wheel. The abrasive action scratches and gradually removes the surface layers of the cemented carbide [11, 12].

The abrasion or grinding process in fact comprises several mechanisms, occurring due to the different responses of the binder and the carbide grains to the mechanical loading imposed by the grinding wheel. One of them is brittle fracture, which occurs in carbide particles once their compressive strength is exceeded (the values reported for WC grains are up to 5000 MPa). Another operates in the binder, normally a metal, which may lose its ductility under load. As a result, a crack initiates in the binder, and an entire carbide grain may be dislodged. The stress that eventually causes a crack to form in the cemented carbide may increase suddenly or gradually, by high-cycle or low-cycle fatigue processes [11, 12].

The above mechanisms are responsible for degradation of the cemented carbide surface during grinding. Once the binder loses ductility, its bond to the carbide grains becomes weaker. The carbide grains thus become dislodged and are carried away by the cutting fluid (coolant). Depending on the grinding conditions, the loose binder and carbide particles may build up on the cemented carbide surface and form a thin work-hardened layer with a thickness of several micrometres [11] (**Figure 3**).

Along with the above-described degradation, the temperature of the cemented carbide increases during grinding. The highest temperature is in the area of contact with the grinding wheel. However, the entire volume of the cemented carbide heats up gradually. The rising temperature of the cemented carbide surface and the interaction with the environment lead to surface oxidation. The fresh oxides are stripped during grinding. Apart from grinding,

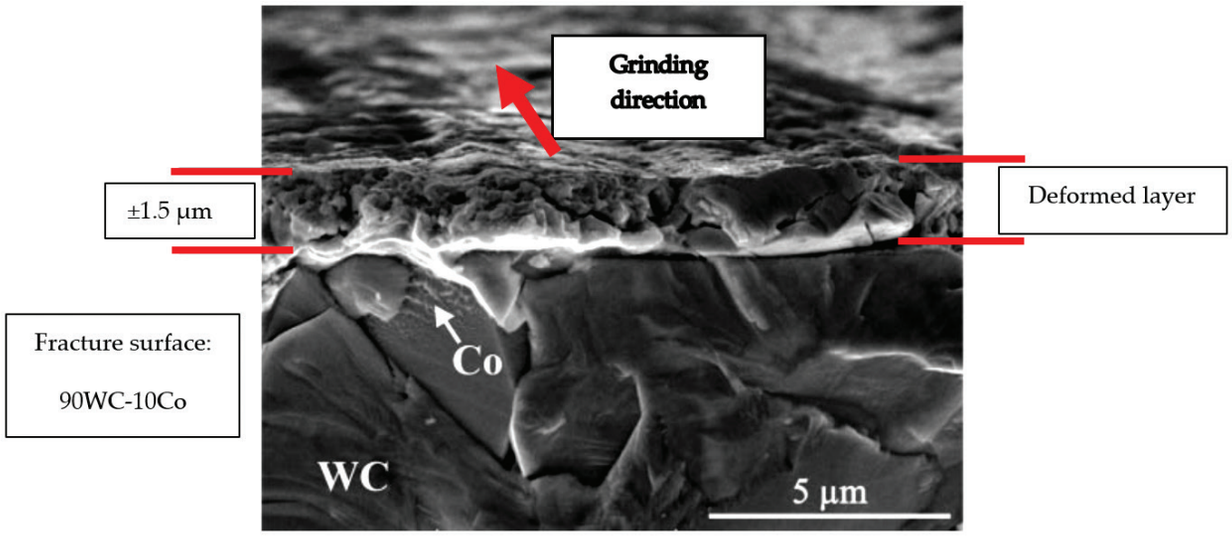

Figure 3. Deformed layer on the surface of WC-Co after grinding [13].

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oxidation of cemented carbide may occur during other machining processes, and the new oxide layer may change the geometry of the cutting tool and impair the machining conditions.

The oxidation behaviour of cemented carbides is dictated by a range of variables. The structure-related ones include the type and content of the binder, the types and sizes of carbide particles and the content of impurities. Then there is the atmosphere, the temperature to which the cemented carbide is heated, and the rates of heating and cooling.

Finally, the oxidation behaviour of a cemented carbide depends on its surface finish. For instance, thin films applied to cutting tools prevent their oxidation during machining. Cutting tools can, however, oxidize while they are being manufactured, particularly during grinding. When a used coated tool is being reconditioned, the protective film is removed by grinding and oxidation again threatens. Consequently, the largest risk of oxidation is not associated with the actual use of a cemented carbide tool but with its production or reconditioning. Temperature, along with the chemical composition of the material, affects the progress of oxidation. Since cemented carbides are composite materials, the behaviour of their constituents, i.e. the binder and the base material, will be decisive in the progress of oxidation. In particular cases, the combined behaviour of both constituents will be the governing factor.

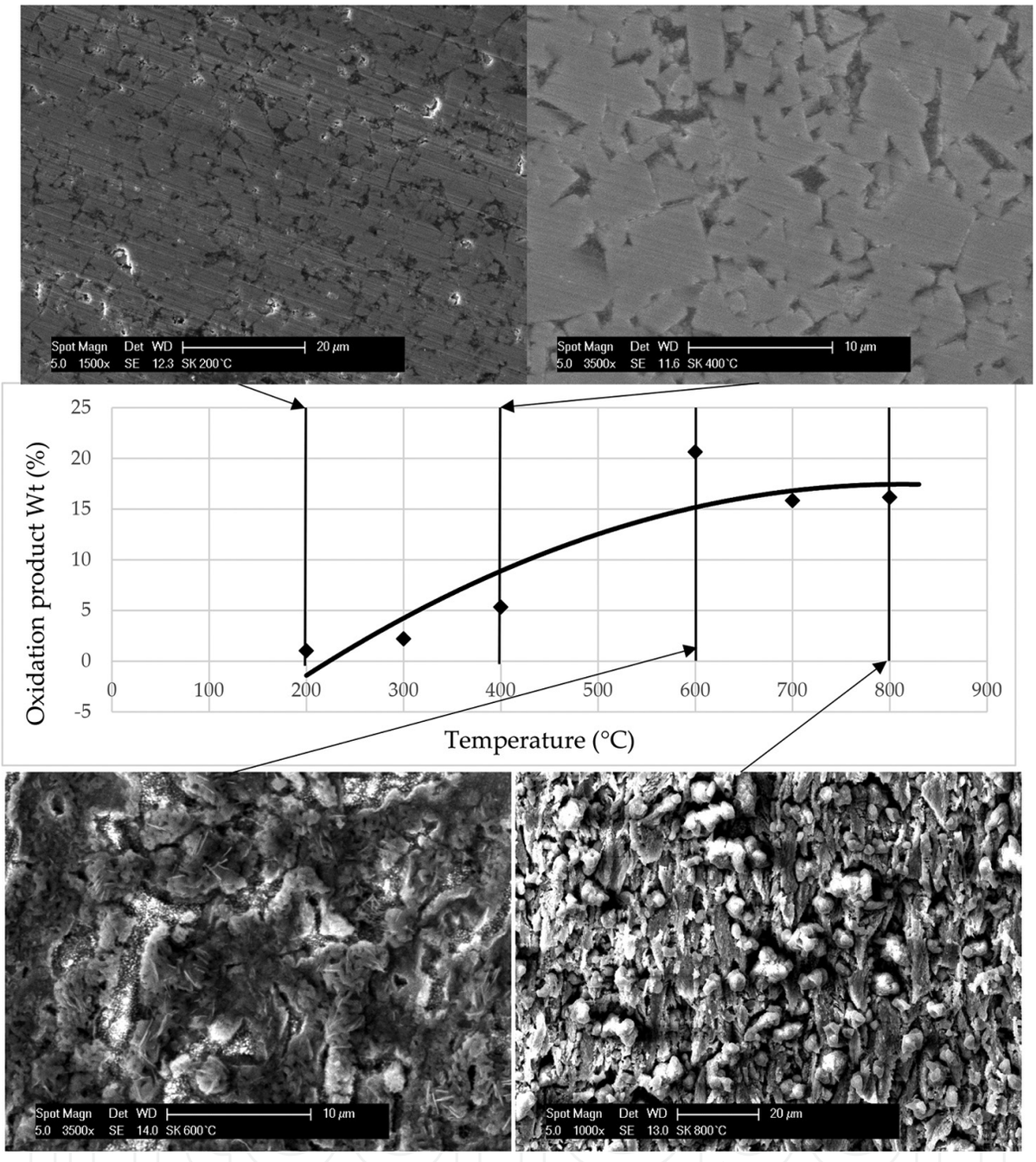
Cemented carbides develop a porous oxide layer on their surface consisting mainly of tungsten trioxide WO_3 in those cases where there is a low binder content. The porosity of this layer is thought to be related to gaseous CO and CO_2 being released at the interface between the cemented carbide and the atmosphere. At higher binder levels, the layer becomes less porous, more compact and consists of the complex oxide $CoWO_4$ [14–17].

In terms of thermal loads, the oxidation behaviour of cemented carbides at temperatures below approximately 720°C depends on the properties, chemical composition and content of the binder. It is because at these temperatures, the oxidation ability of the carbide phase is limited. The situation is reversed at higher temperatures: the oxidation ability of the binder is limited, and tungsten trioxide WO_3 readily forms [14–17].

Graph 3 reports data from a test which explored the oxidation behaviour of a cemented carbide. Specimens of WC-Co were heated over the range 200–800°C in an air furnace. The chemical composition of the surface layer was measured by an EDX probe in a scanning electron microscope [2].

The micrographs in **Graph 3** show that at lower temperatures (below 400°C), there is no extensive surface oxidation. Below 400°C, scratches from grinding are still visible on the surface. At higher temperatures, above 600°C, a notable oxide film forms and covers the surface. As the cemented carbide is heated to these temperatures, the scratches from grinding continue to disappear due to advancing surface oxidation. The volume of the oxides grows and they alter the surface relief.

In addition to oxidation to which cemented carbides are subjected during grinding due to the introduced heat, their surfaces also experience thermal cycles resulting from the immediate removal of this heat by the coolant. This rapid thermal cycling generates temperature gradients throughout the volume of the cemented carbide and causes thermal shocks.



Graph 3. Cemented carbide surface at various heating temperatures [2].

Thermal cycling in the surface layer leads to dramatic variations in stress distribution, and to alternate tensile and compressive stresses. The occurrence of these stresses is associated with volume changes, where heating is accompanied by expansion, whereas cooling leads to contraction.

After a certain time, these continuously alternating stresses cause the binder to lose ductility. At that point, even moderate loads may cause the cemented carbide to develop cracks which threaten failure. Cracks may also form within carbide grains if the load exceeds their ultimate

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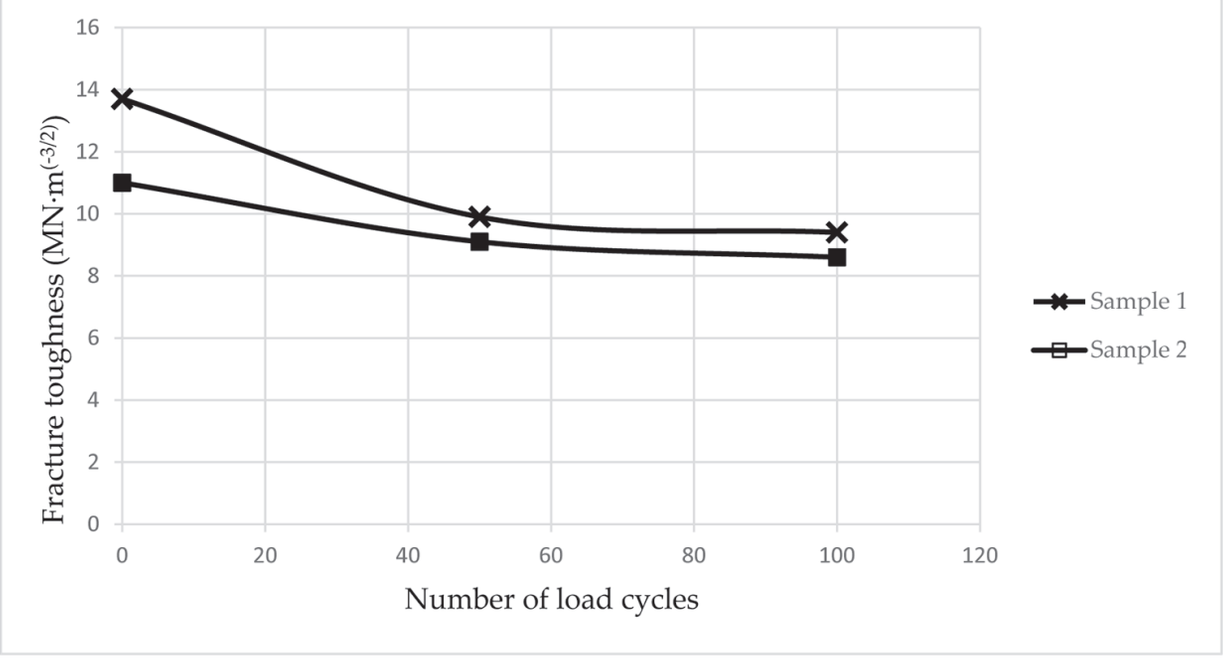
strength. Microcracks frequently initiate at the interface between the carbide particle and the binder, as this location is energetically most favourable for crack formation. As such intergranular microcracks gradually propagate, carbide particles become dislodged during grinding and the cemented carbide may eventually fail through brittle fracture.

Degradation caused by cyclic thermal loading in a 90WC-10Co cemented carbide with carbide particles in the range of 0.5–0.8 μm is illustrated in **Graph 4**. The specimens were resistance heated to 450°C at a rate of 80°C/s in a thermomechanical simulator. When this temperature was achieved, they were immediately cooled at 10°C/s. Degradation was evaluated by measuring the mechanical properties of the specimens (hardness and fracture toughness) after 50 and 100 cycles. **Graph 4** shows a plot of fracture toughness after 50 and 100 cycles [3, 18].

Graph 4 shows the progress of degradation caused by cyclic thermal loading. Both specimens exhibited a decrease in fracture toughness of approximately 20%. In a real-world application of this cemented carbide, the additional mechanical load would lead to an even greater decline in mechanical properties. The difference between the initial mechanical properties of these specimens is given by their slightly different compositions. The first specimen had a larger content of coarse carbide particles. The second one contained a larger proportion of finer carbide grains, and therefore showed lower fracture toughness. The decline in fracture toughness indicated in the graph can probably be attributed to a gradual loss of ductility of the binder. Its mechanism was described above [3].

The ability of cemented carbides to withstand thermal shocks can be enhanced in various ways. One of them involves using another carbide grade with a higher binder content, or substituting a complex-grade cemented carbide, such as WC-Co-Ni-Cr, with the straight grade



Graph 4. Degradation of cemented carbide due to cyclic thermal loading [3].

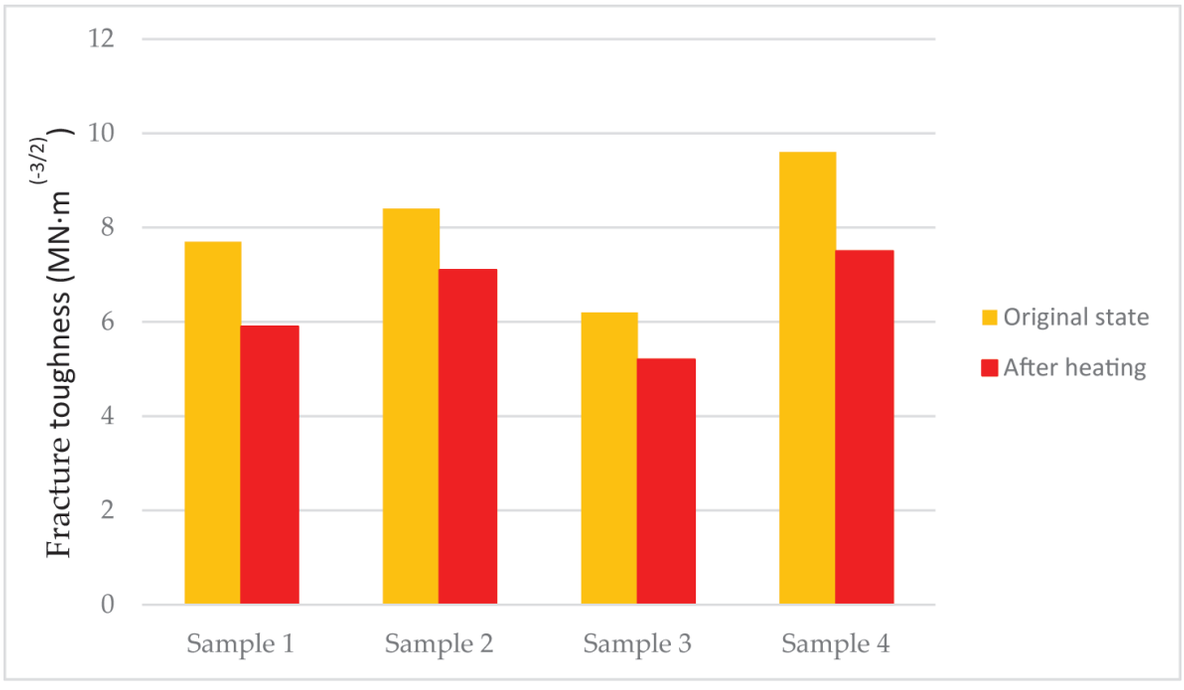
WC-Co. Another option is the deposition of a suitable thin film. Such a film can either dissipate heat, distributing it across a larger area or create a thermal barrier which prevents heat from entering the cemented carbide [3, 18].

As mentioned above, grinding causes cyclic thermal loads in the surface of a cemented carbide. As a result, temperature rises gradually throughout the carbide workpiece.

The difference can be several hundred degrees Celsius in some locations. The maximum temperature is given by the parameters of the grinding process, and by the thermal conductivities of the cemented carbide, the workpiece and the environment. When a cemented carbide is the material of a cutting tool, the temperature at the tool tip may reach 1300°C. Thermal conductivity determines the rate at which heat is transferred from a location of higher temperature to locations of lower temperatures. In cemented carbides, this physical property is affected mainly by the operating temperature and by carbide grain size. The thermal conductivity of a cemented carbide decreases with decreasing grain size and with increasing temperature. By contrast, it is not particularly sensitive to the binder content [3].

As temperature rises within cemented carbide, diffusion processes set in. Their intensity is directly proportional to the heating intensity. At temperatures near the solidus of the binder, creep occurs in cemented carbides, depending on the binder type, chemical composition and impurity content. Creep causes loss of adhesion between the binder and the carbide grains. As a result, the surface of the carbide grains becomes exposed and oxidized. All these processes lead to a failure of the cemented carbide.

Graph 5 shows the results of an experimental study of degradation of a cemented carbide. The specimens were slowly heated to 450°C and held for 10 min to allow their temperature



Graph 5. Degradation of cemented carbides due to heating [3].

to homogenize. Then they were cooled by water at 15°C to simulate the effect of the coolant during grinding [3].

The specimens were made of WC-Co-type cemented carbides with identical carbide grain sizes of 0.5–0.8 μm but with various binder levels.

The resistance of cemented carbides to thermal loads can be enhanced by coating them with thin films. CrAlSiN films, for instance, create an effective thermal barrier. By contrast, TiN films provide good conditions for distributing heat across a large area. Another way of controlling the thermal degradation of a cemented carbide involves altering the machining operation. When dry machining or machining with waterless cutting fluids is used, the surface of the cemented carbide is cooled less severely, and the stress gradients will be less steep [3].

Grinding and other post-sinter surface finishing operations have yet another consequence: the formation of residual stresses in the surface of cemented carbide.

3. Residual stresses and their impact on the properties of cemented carbides

Residual stresses develop within the body of a material as a result of external loads, both thermal and mechanical. In essence, they are caused by non-uniform elastic or elastic-plastic deformation of the cemented carbide surface. For residual stresses to occur, the material must experience some of the following [11]:

- Non-uniform plastic deformation, for instance, during machining;
- Non-uniform heating of the surface, which may be caused by the coolant as a cutting tool is retracted from the machining location;
- Transformational stresses related to, for instance, changes in crystal structure;
- Interaction between the surface and the atmosphere and the absorption of substances from the atmosphere by the surface of the cemented carbide.

Residual stresses induced by the above processes lead to changes in the utility properties of cemented carbides. They may also give rise to areas of high stress concentration, distort the shape or alter the product's corrosion resistance.

The magnitude of residual stresses is mainly governed by these three factors:

- Amount of absorbed heat;
- Mode of mechanical loading;
- Changes in material structure;

3.1. Magnitude and type of residual stresses

Not only the absolute value of stress but also the stress type, tensile or compressive, must be considered.

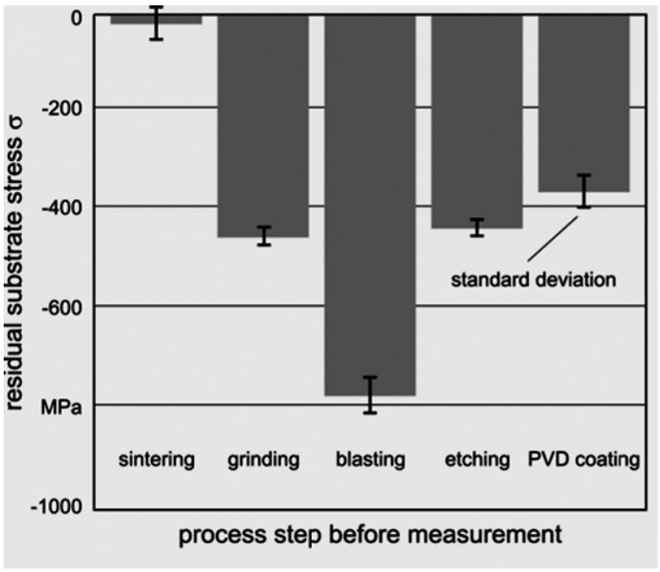
Compressive residual stresses in the cemented carbide surface are favourable for the service application. Such stresses close cracks which have formed due to thermal loads. However, if compressive stresses are to be beneficial to the cemented carbide, their magnitude must remain below a certain limit. If this limit is exceeded, which means that the compressive strength of carbide grains has been exceeded or the binder ductility has been lost, cracks will spread despite compressive stresses being present in the surface of the cemented carbide under load. One must also bear in mind that if there is compressive stress within a carbide grain, there is tensile stress in the binder (**Graph 6**). As the material is more sensitive to tensile stress, large compressive stresses within carbide grains threaten failure in the binder on account of tensile stress [11].

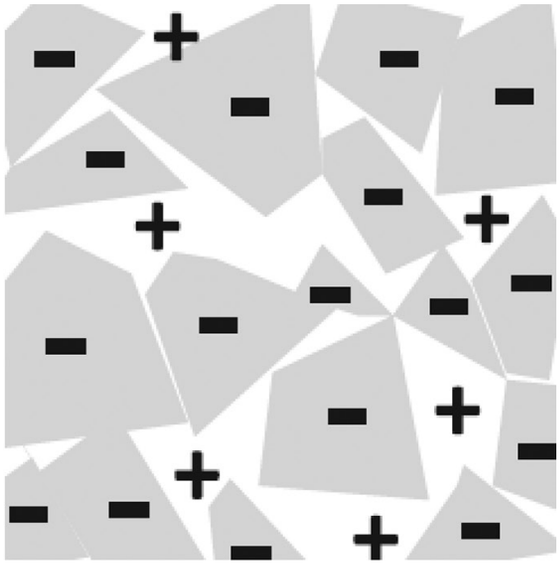
For instance, cracks may spread due to a compressive load applied after the cemented carbide surface has been coated with a thin film. The film imposes additional compressive stress which, after superposition on the compressive stress already present in the substrate, may exceed the ultimate strength and cause a failure of the cemented carbide.

Tensile stresses pose a greater threat to a cemented carbide surface under load than compressive stresses. The reason for this is that the former cause incipient cracks to open, which accelerates the degradation of cemented carbide properties and causes earlier failure.

When an external force acts on a cemented carbide surface, first-order residual stresses arise, causing eventual changes in the geometry of the cemented carbide product. These changes may lead to substantial distortion.

External loads, whether mechanical or thermal, cause movement, growth and decrease in the volume of individual microstructure constituents of a cemented carbide. Differences between the expansion factors of individual constituents and their relative movement lead to residual stresses between the carbide grains and the binder. This residual stress





Graph 6. Effects of process steps carried out prior to measurement of residual substrate stresses in cemented carbides. The results were obtained using X-ray diffraction [19].

that arises at the interfaces between the grains (crystals) and the binder is referred to as second-order stress. It is also capable of causing changes in the cemented carbide geometry [11].

Furthermore, external load causes movement of dislocations, vacancies and interstitial atoms within the crystals. All these defects and their movements cause third-order residual stresses, which alone do not induce changes in the product geometry.

It follows from the above description that if external forces act on a cemented carbide, these three types of stress coexist within its volume, and the resulting residual stress is given by their superposition.

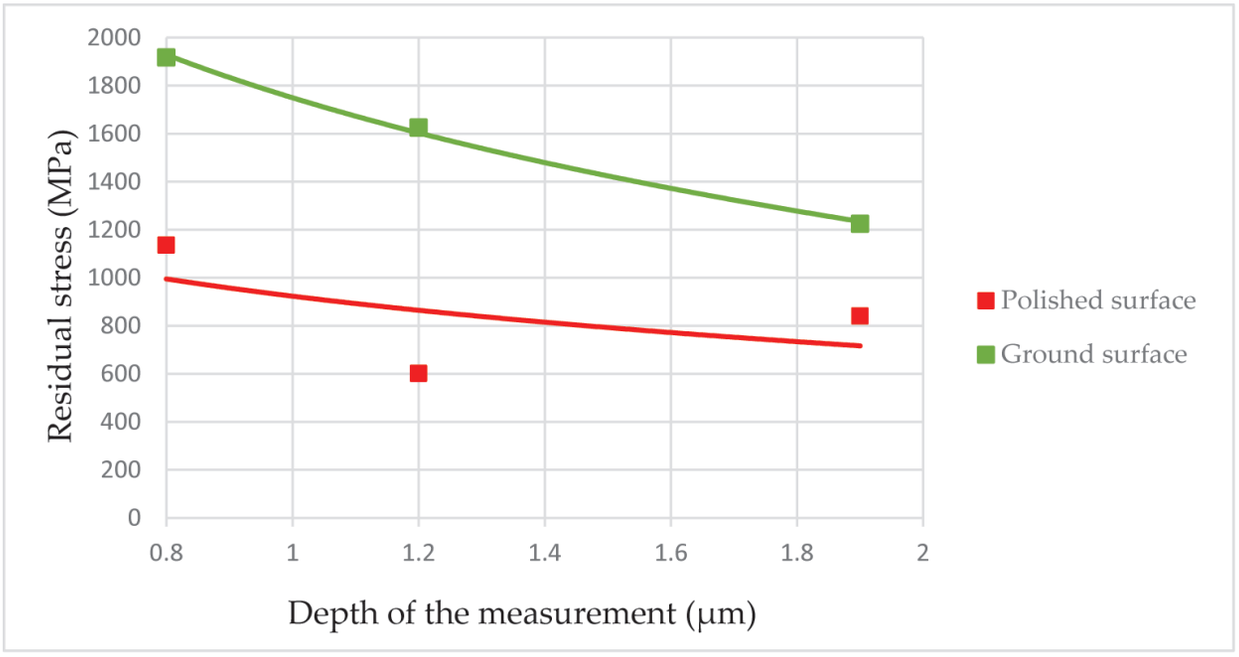
The magnitude of residual stresses can be determined by destructive and non-destructive testing methods. The former include successive etching of the cemented carbide surface or the hole-drilling method.

The latter comprise X-ray measurement of strain, where residual stresses are determined from changes in interatomic and interplanar distances, which in turn are determined from changes in the scattering angle under Bragg's law.

The microstructural aspects that affect residual stresses in cemented carbides include the type and amount of binder and the type and size of carbide grains. Cracks initiated by internal stresses may occur at the interface between the binder and the carbide particle. This is the case mainly in fine-grained cemented carbides. In coarse-grained cemented carbides, cracks may also initiate within carbide particles. Apart from the overall content of binder, the binder distribution among grains plays a role as well. It is characterized by means of the mean free path parameter. Where the amount of binder between the carbide grains is larger, the mean free path is longer and the plasticity of the cemented carbide increases. Under applied loads, new dislocations form, move and interact, which results in work hardening and deformation of the binder. If cracks developed within the binder, their propagation would require—due to the above processes—a continuous supply of energy until the ultimate strength is exceeded. Beyond that point, the substrate will suffer macroscopic failure. At low binder levels, i.e. short mean free paths, the ductility is lost sooner. The reason for this is that in such a system, the movement of dislocations is confined when compared to systems with higher binder levels. Therefore, cracks initiate and propagate faster and the cemented carbide fails more rapidly [11].

Residual stresses develop in the surface layer of cemented carbides during post-sinter operations such as grinding, polishing, tumbling, pickling or thin film deposition. These operations impose thermal and mechanical loads on the surface. Unlike in sintering, the loads are not in balance and do not cancel each other out. Therefore, they cause stresses in the surface of the sintered part.

The largest residual stresses occur in the surfaces of those cemented carbide parts which were finished by operations such as grinding or blasting (surface micro-conditioning). The depth profile of residual stress in cemented carbide starting at the surface is shown in **Graph 7.** Compressive stresses of up to 2000 MPa are introduced to the cemented carbide surface



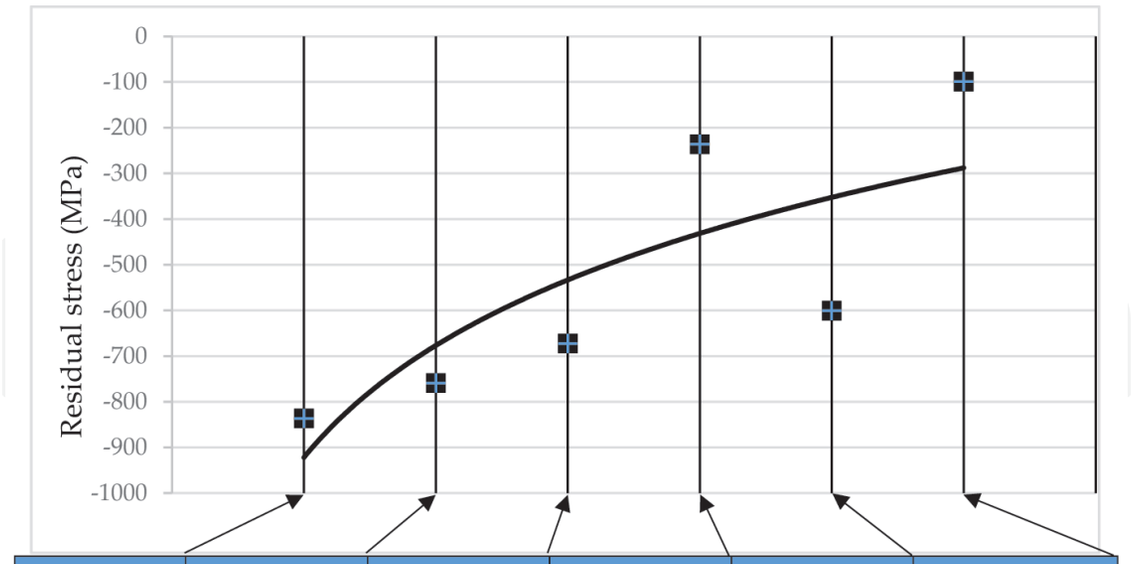
Graph 7. Depth profiles of residual stress in surfaces finished by various methods [11].

during grinding. It has been confirmed by experiments that the severity of grinding, i.e. the depth of cut, has no substantial effect on the increase in residual stress in the surface.

This high value of residual stress arises from the fact that grinding imposes predominantly mechanical load on the cemented carbide surface. Thermal loads are minimized by the use of coolant. Polishing, by contrast, is characterized by the dominance of thermal loads over mechanical ones. Polishing of cemented carbides relieves a great part of their residual stresses, as indicated by **Graph 7.** The reason for this is that polishing removes the most heavily deformed layer with the highest residual stress. Moreover, the heat that is generated in the process causes the remaining residual stress in the cemented carbide surface to relax [11].

Residual stresses in the surface upon grinding can also be reduced by annealing. Important annealing parameters include the temperature, holding time, heating and cooling method, protective atmosphere and some others. **Graph 8** illustrates the effect of annealing on the residual stress in a cemented carbide surface. The specimens were annealed in an air furnace in the range of 200–500°C. Some of them were annealed at 500°C in an ammonia atmosphere. Residual stresses were measured at 100°C intervals [11].

It is clear from the graph that at the same holding times, higher temperatures lead to better relaxation of residual stress. It is also apparent that annealing is more effective when carried out in an appropriate atmosphere. In this case, annealing in ammonia gas led to maximum stress relief. It is important to prevent oxidation of the cemented carbide surface during annealing. Any oxides on the surface impair the adhesion of thin films deposited on the cemented carbide. The surface can be protected against oxidation by using an adequate



After cutting up (0 ^{0}C):	Annealing (200 ^{0}C):	Annealing (300 ^{0}C):	Annealing (400 ^{0}C):	Annealing (500 ^{0}C):	Annealing atmosphere: Ammonia (500 ^{0}C):
-837	-759	-673	-236	-601	-99

Graph 8. Effects of various annealing schedules on the relief of residual stress in a cemented carbide surface [11].

protective atmosphere, by removing the oxide layer, or by applying a protective coating, to give a few examples [11].

Thin films deposited by PVD methods on a cemented carbide surface show high compressive residual stresses ranging from 2000 to 8000 MPa. Stresses this high are beneficial to the films because they close the cracks which form in them during service. At the same time, however, they affect the substrate as well. The impact of the deposited film on residual stresses in the cemented carbide substrate is illustrated in **Table 1** [11].

A thin film deposited by the PVD method is characterized by compressive residual stress and by an inability to relax this stress. As a result, it shows high levels of residual stress. In the resulting thin film-substrate system, the residual stress levels in the film and the substrate (the cemented carbide) differ greatly. The difference is accommodated by the substrate, whose initial residual stress shifts towards tensile stress. This is illustrated in **Table 1**, where the film deposition leads to a considerable reduction in stress. This was encountered in both ground and annealed specimens. However, there is a difference in that the annealed specimens exhibit tensile residual stresses upon deposition. This is due to their prior heat treatment. Obviously, there is a thermal effect of the PVD deposition itself, but it is weaker than the force exerted by the film. The change in the stress level can be explained in terms of Newton's third law of action and reaction. The appreciable compressive stress within the film induces an opposite reaction within the substrate to establish equilibrium of forces. Hence, the value of the prior stress within the substrate changes in order to counter the stress in the

Grinded samples				
Thin film	**Thin film thickness (μm)**	**Residual stress ground samples (MPa)**	**Residual stress after annealing (MPa)**	**Residual stress after thin film deposition (MPa)**
TiN	2–3	−1657	–	−690
TiN	4–5	−1509		−403
TiCN	2–3	−1689		−346
TiCN	3–4	−1545		−501
Annealed samples				
Thin film	**Thin film thickness (μm)**	**Residual stress ground samples (MPa)**	**Residual stress after annealing (MPa)**	**Residual stress after thin film deposition (MPa)**
TiN	2–3	−1410	−266	371
TiN	4–5	−1603	−383	310
TiCN	2–3	−1380	−262	143
TiCN	3–4	−1008	−245	275

Table 1. Changes in residual stress levels induced by thin film deposition, grinding and heat treatment [11].

thin film. Another important finding is that annealing led to a decrease in stress similar to that achieved by the PVD method.

An important factor contributing to failures of coated cemented carbides is the stress state in regions of stress concentration, such as in the cutting edges of tools. In the cutting edge, residual stresses present in the thin film are superposed on other pre-existing stresses. The resulting stress has a severe impact on the cutting edge and may lead to a cohesion failure of the substrate. A schematic sketch of this phenomenon is shown in **Figure 4**. It illustrates an

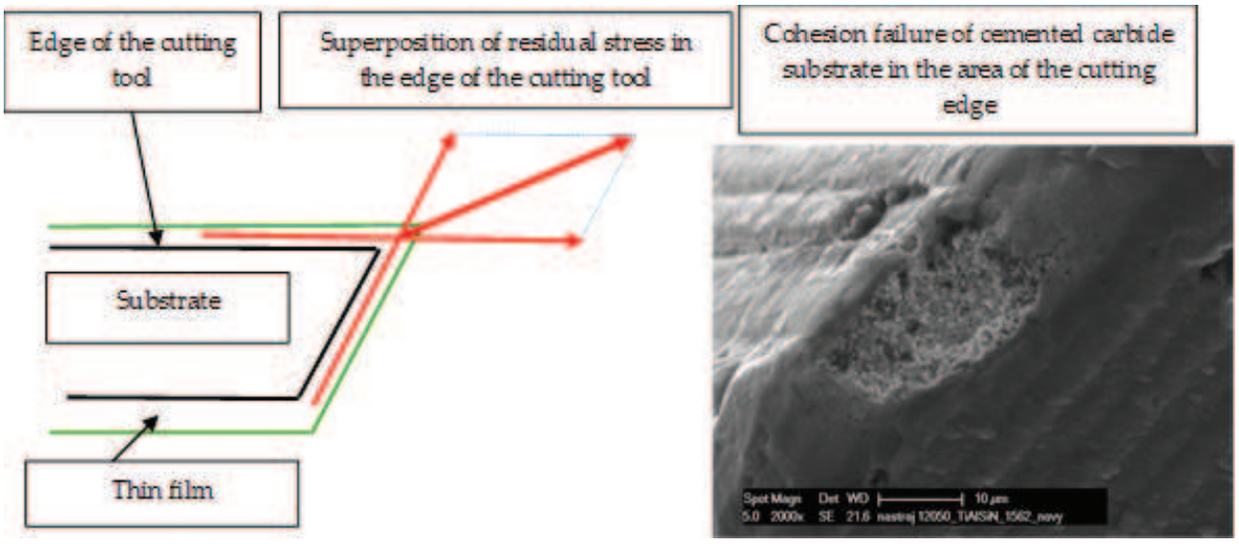


Figure 4. Cohesion failure of cemented carbide cutting edge caused by increasing residual stresses upon grinding [11].

available approach to dealing with this issue which, however, has not been elaborated yet by in-depth research [11].

If the stress that is concentrated in the cutting part of the tool exceeds the ultimate strength of the substrate, the cutting edge immediately fails through chipping. The stress in the cutting part of the tool can continue to rise during the cutting process owing to additional stresses which develop in the process. **Figure 4** shows the chipping of the cutting edge in a coated cemented carbide tool. Clearly, this failure was not an adhesion failure at the interface between the film and the substrate but a cohesion failure of the substrate. In terms of physics, the stress concentration will be dictated by the cutting edge geometry and the resulting superposition of stresses.

4. Corrosion of cemented carbides

Corrosion is a degradation process based on the interaction between the surface of a material and the environment. It is associated with a potential gradient which develops in the surface layer of the material [2].

Four essential components are required for electrochemical corrosion to occur: a cathode, an anode, a corrosive environment provided by an electrolyte and an electrical path between the anode and the cathode. Two chemical reactions, oxidation and reduction, occur between the anode and the cathode, forming the basis of the corrosion attack. Oxidation takes place at the anode, whereas reduction occurs at the cathode. The first involves the loss of electrons from the electron shells of atoms at the anode, whereas the latter is the gaining of electrons by atoms [2, 20].

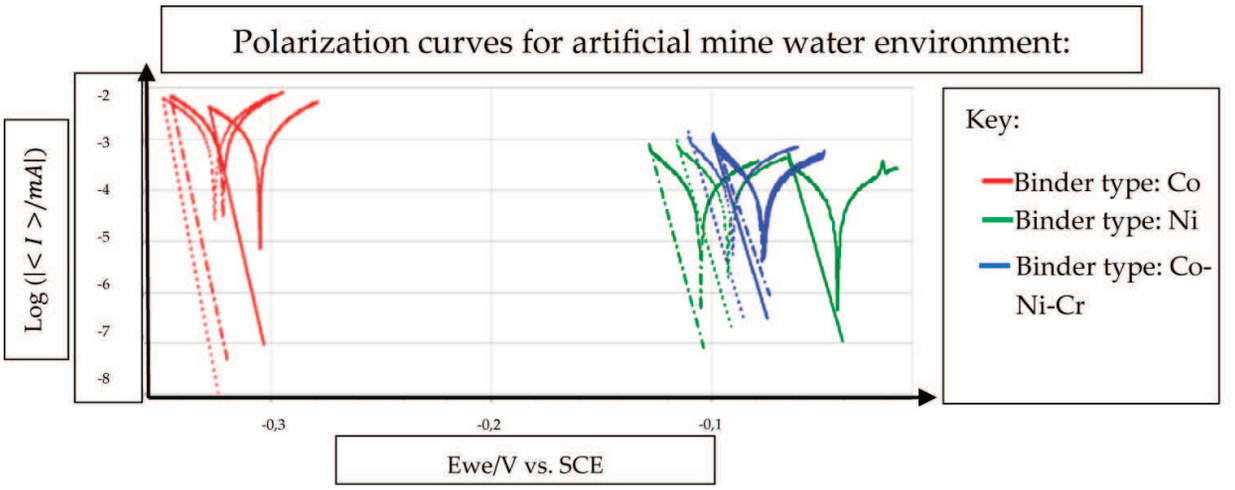
Corrosion attacks are classified according to their fundamental principles as either chemical or electrochemical corrosion.

Cemented carbides suffer this type of degradation in wood machining processes or in the mining industry.

Cemented carbides possess a heterogeneous structure, where corrosion occurs predominantly in the binder, which has lower corrosion resistance than the base material. For instance, the most common cobalt binder has poor corrosion resistance in corrosive acids, such as sulphuric acid or formic acid. By contrast, it withstands corrosion attacks in acetone, ammonia or weak acids.

If the cobalt binder proves inadequate, other binder types are available. **Graph 9** shows a comparison between three types of cemented carbides containing different binders. The first one is the ordinary WC-Co grade. The second one is a WC-Ni type and the last one is a WC-Co-Ni-Cr cemented carbide. The grain size was identical in all specimens: 0.5–0.8 μm. The binder content was the same as well: 8%. Testing was carried out in artificial mine water with a pH of 5, and in a sodium hydroxide solution of pH = 14. **Table 2** shows the measured data [2].

These results confirm the conclusions of earlier studies on which **Table 3** is based. **Table 3** describes the corrosion resistance of cemented carbides with cobalt and nickel binders in



Graph 9. Polarization curves for the corrosion test in artificial mine water [2].

Environment			Type of binder								
			Co			Ni			Co-Ni-Cr		
			E_{cor} (mV/SCE)	Rp (Ω cm²)	I_{cor} (μA)	E_{cor} (mV/SCE)	Rp (Ω cm²)	I_{cor} (μA)	E_{cor} (mV/SCE)	Rp (Ω cm²)	I_{cor} (μA)
Artificial mine water	pH	5	−316	2268	6.06	−78.3	34836	0.4	−78.2	23081	5.6
NaOH	pH	14	−286	8378	1.61	−296	17570	0.79	−290	7072	2

Table 2. Corrosion behaviour of cemented carbides containing various binders. The readings were obtained using a potentiostat [2].

pH	Co binder	Ni binder
12	Very good	Very good
11		
10		
9	Good	
8		
7	Sufficient	
6	Poor	
5	Very poor or no corrosion resistance	Good
4		
3		Sufficient
2		
1		Poor
0		

Table 3. Corrosion resistance of cemented carbides with cobalt and nickel binders at various pH levels [20].

environments of various pH levels. The corrosion resistance of multi-component binders is governed by the proportions of the constituents. For instance, the presence of cobalt in the multi-component binder listed in **Table 3** impairs its corrosion resistance in these environments. By contrast, the presence of chromium improves the resistance to oxidation [2].

Other factors that play a role in the corrosion behaviour of a cemented carbide include the binder content and the size of the carbide particles. They were studied on WC-Co and WC-Ni specimens. **Table 4** lists the measured data [2].

These results confirmed experimental studies carried out by other researchers. Those showed that in acid environments, it is cemented carbides with higher cobalt binder levels which suffer more severe degradation. In alkaline environments, the corrosion rates were similar. In the case of the nickel binder, the corrosion rate increased with its content. This occurred in both acid and alkaline environments.

Carbide grain size affects the corrosion resistance of cemented carbides as well. **Table 4** confirms that fine-grained cemented carbides have better corrosion resistance in both alkaline and acid environments.

Environment			Type of binder						Co			Amount of binder		(%)	8
			Grain size of WC particles												
			(μm)						(μm)						
			3–6									0.2–0.5			
			E: (mV/SCE)		Rp: (Ω cm²)		I: (μA)		E: (mV/SCE)			Rp: (Ω cm²)		I: (μA)	
Artificial mine water	pH	5	−385		802		16		−316			2273		6	
NaOH	pH	14	−259		3194		4.4		−285			8380		1.6	
Environment			Grain size of WC particles											(μm)	0.5–0.8
			Type of binder												
			Co						Ni						
			Amount of binder						Amount of binder						
			(%)			(%)			(%)			(%)			
			4			12			8.5			12			
			E: (mV/SCE)	Rp: (Ω cm²)	I: (μA)	E: (mV/SCE)	Rp: (Ω cm²)	I: (μA)	E: (mV/SCE)	Rp: (Ω cm²)	I: (μA)	E: (mV/SCE)	Rp: (Ω cm²)	I: (μA)	
Artificial mine water	pH	5	−350	1796	7.5	−345	1218	11	78	34836	0.4	−71	19862	0.67	
NaOH	pH	14	−287	5180	2.5	−292	5631	2.4	−296	17570	0.79	−293	9319	1.7	

Table 4. Corrosion behaviour of cemented carbides with various carbide grain sizes and binder contents. The readings were obtained using a potentiostat [2].

	Type of binder			**Co**	**Amount of binder**		**(%)**	**10**
	Grain size of WC particles			**(μm)**	**2.5–6**			
Environment	**Residual stress after grinding (average value) (MPa)**			**Residual stress after annealing (average value) (MPa)**				
	−1687			**−265**				
	E: (mV/SCE)	**Rp: (Ω cm²)**	**I: (μA)**	**E: (mV/SCE)**	**Rp: (Ω cm²)**	**I: (μA)**		
Artificial mine water pH5	−458	1256	68	−579	3319	6		

Table 5. Corrosion behaviour of cemented carbide vs. residual stress levels upon grinding and heat treatment. The readings were obtained using a potentiostat [2].

The corrosion behaviour of cemented carbides is, to a certain extent, governed by residual stresses, which were dealt with in the previous sub-chapter. Data obtained from a literature review suggest that larger residual stresses will promote corrosion attack as they are linked to higher activation energy, which the material strives to lower by oxidation.

Table 5, based on the authors' own experiments, shows the effects of residual stresses on the corrosion resistance of cemented carbides. The experimental material was the 90WC-10Co grade. Grinding of the specimens introduced residual stresses to their surface layers. Some of the specimens were subsequently annealed to relax the residual stress. **Table 5** shows the average stress levels in the surface layers of the cemented carbide specimens after grinding and annealing [2].

The comparison indicates that annealing improved the corrosion resistance of the specimens. As mentioned above, the reason for this is that at lower residual stresses, more energy is required to cause the corrosion attack and, therefore, a more aggressive environment must be used. In such case, corrosion resistance will be poorer and the attack on the cemented carbide surface will accelerate.

5. Conclusion

This chapter explores the properties of cemented carbides dictated by their internal structure. It also focuses on the degradation processes associated with grinding of cemented carbides. Degradation can also be studied in processes that precede grinding: powder production, mixing, shaping and sintering, as well as in industrial applications of the resulting products, such as machining. Besides oxidation and thermal degradation, great attention was paid to residual stresses and corrosion. The latter two have a profound impact on the service life of cemented carbides, e.g. in machining and mining. Residual stresses also play a role in PVD coating of cemented carbides, where they may lead to tool failure. Such failures used

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to be attributed to inadequate deposition processes but the present experiments showed that incorrect grinding procedures have the major impact. Therefore, these factors must be taken into account in machining applications where cemented carbides are used. Papers published by prof. B. Denkena show that it is beneficial to have as high as possible compressive stresses in the cemented carbide prior to thin film deposition. Such stresses, however, impair the corrosion resistance of the cemented carbide. The question arises whether grinding, which introduces large compressive stresses, leads to a loss of ductility of the binder. This is a plausible hazard because grinding imposes cyclic load on the surface of the cemented carbide, which may cause the loss of binder ductility and subsequent surface damage. This accelerates degradation processes such as corrosion. Besides corrosion, compressive stress can also affect the formation of tensile stress in cobalt. When combined with the added compressive stress imposed by a thin film, it may exceed the tensile strength of cobalt (binder), resulting in cohesion failure of the cemented carbide.

The ductility of the binder can be restored by annealing, a method which has been tested by the authors. Annealing relaxes the compressive residual stresses in the cemented carbide surface without changing its geometry. The disadvantages of this procedure include the risk of surface oxidation if an inadequate protective atmosphere is used, and possible degradation of the mechanical properties due to poorly chosen heating and cooling conditions. Another weakness is the risk that residual stresses in the cemented carbide may shift to the tensile stress region (as measured in the cemented carbide) during annealing or after thin film deposition on the annealed material. Tensile stress is hazardous for a tool in service, as it opens cracks that may have formed in the brittle carbide, and may initiate more cracks and impair fatigue strength under cyclic load. Such cyclic loads may include forces in machining, as well as forces resulting from rapid heating and cooling cycles. Therefore, these processes deserve adequate attention as they may lead to sudden degradation of a cutting tool. The resulting changes may then be misinterpreted and the proposed corrective measures may fail to improve the situation.

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References

[1] Upadhyaya G. Cemented Tungsten Carbides: Production, Properties and Testing. 1st ed. New York: William Andrew; 1999. 420 p. ISBN:0-8155-1417-4

[2] Janeček J. Corrosion properties of sintered carbides [thesis]. Pilsen: University of West Bohemia, Faculty of Mechanical Engineering; 2015. 85 p. Available from: https://portal.zcu.cz/stag?urlid=prohlizeni-prace-detail&praceIdno=63342

[3] Špirit Z. Selected properties and cutting tool applications of sintered carbides [thesis]. Pilsen: University of West Bohemia, Faculty of Mechanical Engineering; 2013. 90 p. Available from: https://portal.zcu.cz/stag?urlid=prohlizeni-prace-detail&praceIdno=52610

[4] Humár A. Materials for cutting tools. Publisher: MM Publishing VUT Brno. Brno. 2008. 235 p. ISBN: 8025422502

[5] Kathrein M. Grundlagen der Beschichtung. Kundenseminar Ceratiyit. Reutte 2002.

[6] Kurolov SA., Gusev A. Tungsten Carbides: Structure, Properties and Application in Hardmetals. New York: Springer; 2013. 242 p. DOI: 10.1007/978-3-319-00524-9

[7] Skotnicová K, Kursa M. Powder metallurgy. 1st ed. Ostrava: VŠB-Technical University of Ostrava. Ostrava; 2013. 153 p. ISBN: 978-80-248-3378-1

[8] Neikov O, Naboychenko S. Handbook of Non-Ferrous Metal Powders: Technologies and Applications. 1st ed. New York: Elsevier; 2008. 616 p. DOI: ISBN: 978-1-85617-422-0

[9] Kříž A. The effect of sintered carbide microstructures upon the life of tools and machine parts. Košice: Institute of Material Research of the Slovak Academy of Sciences; 2006. 8 p. ISBN: 80-968543-5-6

[10] Ceratizit. General Catalogue-Wear Parts [Internet]. Available from: http://www.ceratizit-j.co.jp/pdf/wear%20parts_catalogue.tif [Accessed: 10. 11. 2015]

[11] Palán J. Measuring of residual stress in relation to the technology of preparation [thesis]. Pilsen: University of West Bohemia, Faculty of Mechanical Engineering; 2015. 80 p. Available from: https://portal.zcu.cz/stag?urlid=prohlizeni-prace-detail&praceIdno=63341

[12] Suchánek J. Tribotechnika [Internet]. Available from: http://www.tribotechnika.sk/tribotechnika-12010/abrazivni-opotrebeni-kovovych-materialu.html [Accessed: 7. 12. 2015]

[13] Hegeman JBJW, De Hosson JThM, De With G. Grinding of WC-Co Hardmetals [dissertation]. Eindhoven University of Technology. Netherlands Elsevier; 2001. 10 p. Available from: http://linkinghub.elsevier.com/retrieve/pii/ S0043164800005615. DOI: 10.1016/S0043-1648(00)00561-5

[14] Voitovich VB, Sverdel VV, Voitovich RF, Golovko EI. Oxidation of WC-Co, WC-Ni and WC-Co-Ni hard metals in the temperature range 500–800 °C. International Journal of Refractory Metals and Hard Materials; 1996 pp 289–295. DOI: 10.1016/0263-4368(96)00009-1

[15] Gu W-H, Jeong YS, Kim K, Kim J-C, Son S-H, Kim S. Thermal oxidation behavior of WC–Co hard metal machining tool tip scraps. Journal of Materials Processing Technology; 2012. pp 1250–1256. DOI: 10.1016/j.jmatprotec.2012.01.009

[16] LOFAJ F, KAGANOVSKII Yu. S. Kinetics of WC-Co oxidation accompanied by swelling. Journal of Materials Science [online]. 1995. pp 1811–1817. DOI: 10.1007/BF00351615. ISSN 0022-2461. Available from: http://link.springer.com/10.1007/BF00351615

[17] Aristizabal M, Sanchez J M, Rodriguez N, Ibarreta F, Martinez R. Comparison of the oxidation behaviour of WC–Co and WC–Ni–Co–Cr cemented carbides. Corrosion Science; 2011. pp 2754–2760. DOI: 10.1016/j.corsci.2011.05.006

[18] Kříž A, Špirit Z. Properties of cemented carbides upon thermal exposure. 25th National Conference on Heat Treatment. Čerčany: ASSOCIATION FOR HEAT TREATMENT OF METALS 2013. pp.179–186. DOI: ISBN 978-80-904462-6-7

[19] Denkena B, Köhler J, Breidenstein B, Abrão AM, Ventura CEH. Influence of the Cutting Edge Preparation Method on Characteristics and Performance of PVD Coated Carbide Inserts in Hard Turning [dissertation]. Elsevier; 2014. 8 p. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0257897214005751 DOI: 10.1016/j.surfcoat.2014.07.003. ISSN 02578972

[20] Federal Carbide Company. Corrosion Resistance of Tungsten Carbide Grades [Internet]. Available from: http://www.federalcarbide.com/corrosion_resistant_tungsten_carbide_grades.html [Accessed: 16. 12. 2014]

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