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## METHODS FOR PRODUCING HARD ALLOYS FOR PREPARING CUTTING TOOLS USED IN THE PROCESSING OF PARTS USED TO CHANGE THE DESIGN OF TECHNOLOGICAL MACHINES

**Abstract:** Hard alloys are one of the most common materials that are in demand in production. The reason for the high demand is the high strength properties during processing of the material. A wide range of composition and properties of hard alloys has led to the emergence of various classification systems, the most relevant of which is ISO TC. The properties of hard alloys are determined by a combination of various characteristics, for example, a soft and ductile Co-based binder with hard and wear-resistant WC or cubic carbides. A wide range of mechanical properties can be achieved by choosing the appropriate raw material, its composition and certain processing parameters of the material during operation.

**Key words:** design, operation, machines, high strength.

**Language:** English

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### Introduction

Hard alloys are in great demand in production, due to the fact that they combine such properties as hardness and toughness. A hard alloy consists of refractory carbides, nitrides or carbonitrides embedded in a matrix of a plastic metal binder. The main phases present in hard alloys are the hexagonal WC phase, the mixed cubic carbide/carbonitride phase (also called the  $\gamma$ -phase or FCC-phase), and the

binder Co, which can also be based on Ni or a combination of Fe-Co-Ni metals. The gamma phase consists of carbonitrides of groups 4 and 5 of the periodic table. WC has high electrical and thermal conductivity. In the  $\gamma$ -phase, and forms solid solutions with a wide range of homogeneity of both interchangeable and interstitial elements. The properties of common carbides and nitrides used in the production of hard alloys are given in Table 1.

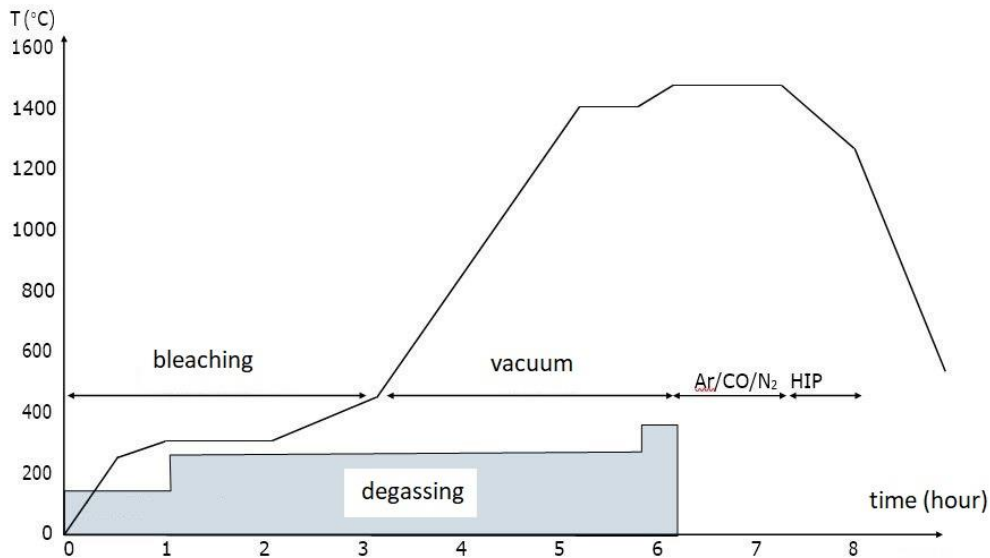
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**Table 1 - Values of selected properties of metal carbides and nitrides for the production of hard alloys.**

Co togetherness	Symbol	Lattice parameter	Density	Microhardness	Melting point	Young's modulus	Thermal conductivity
WC	hP2	a=0.29058 c=0.28365	15.72	23	2776	707	120
Mo <sub>2</sub> C	hP3	a=0.30233 c=0.47344	9.18	17	2520	530	15
Cr <sub>3</sub> C <sub>2</sub>	oP20	a=0.28290 b=0.55329 c=1.14719	6.68	27	1810	380	14
TiC	cF8	0.4328	4.93	28	3067	450	28.9
ZrC	cF8	0.4700	6.46	25	3420	350	24.6
HfC	cF8	0.4638	12.3	20	3930	420	25.1
VC <sub>0.88</sub>	cF8	0.4164	5.36	26	2650	430	26.8
NbC	cF8	0.4470	7.78	18	3610	340	27.0
TaC	cF8	0.4455	14.48	16	3985	290	22.1
TiN	cF8	0.4242	5.39	17	3050	420	29

The production of hard alloy products is a complex that includes many technological stages: production of raw powder, mixing and grinding of powders, spray drying for obtaining granulated powders ready for pressing, pressing, pressing or shaping to the final form, dewaxing and pre-sintering, sintering, after sintering, for example grinding or shot blasting. All production processes are interconnected, which means that any change at any stage of

production in the production chain will affect the subsequent process and the quality of the final product. Therefore, when designing hard alloy microstructures, it is necessary to take into account all stages of production [1,2]. From the point of view of regulating the microstructure and mechanical properties of hard alloys, the sintering stage is one of the most important processes in their production (Fig. 1).



**Fig. 1. Schematic description of the sintering process for obtaining cemented carbides. Areas for decontamination, vacuum, reactive and protective gases, and hot isostatic pressing (HIP) are shown. The area of evolution of gas release during sintering is also indicated.**

Decrease occurs during sintering to obtain a non-porous microstructure and final component dimensions. Hard alloys are obtained by liquid-phase sintering, there are four main stages in the sintering process. At the initial stage, shrinkage occurs mainly

due to the reduction of oxides and degassing of the binder and impurities. At the second stage, as the temperature rises, solid-state sintering begins. The binder phase begins to wet the WC grains, and the dissolution and transport of the material occurs by

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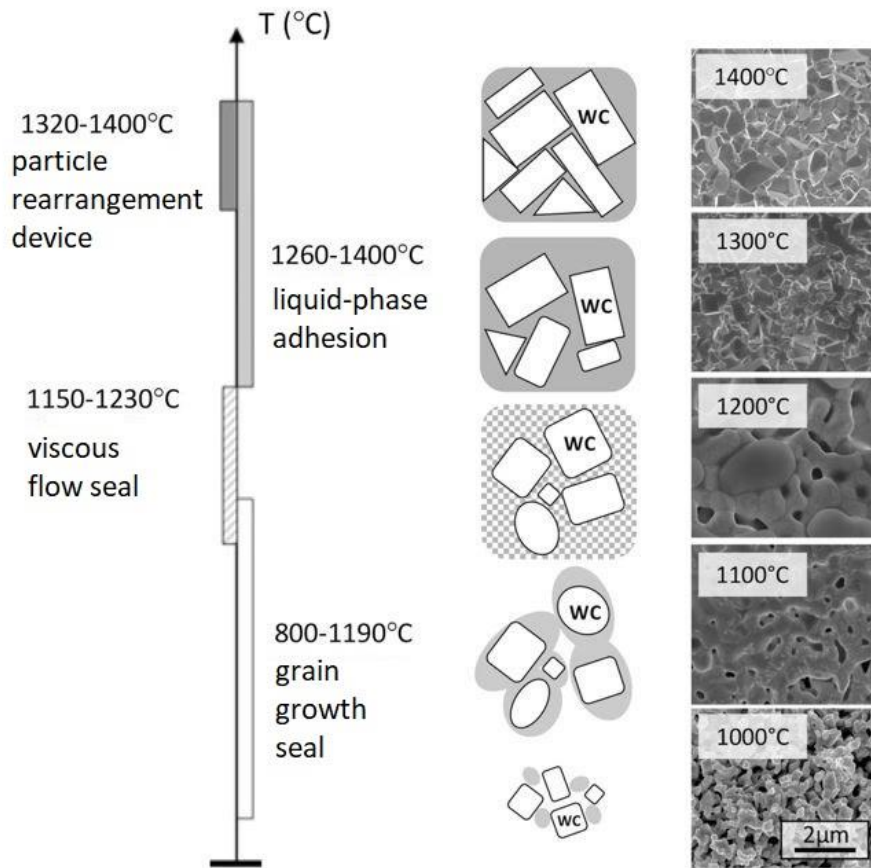
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solid-state diffusion. The porosity decreases as the temperature rises, and the material dissolved in the binder begins to re-deposit on undissolved grains. Compaction is enhanced by the redistribution of particles. This is accompanied by further shrinkage. At the third stage, the melting temperature is reached (for a typical WC-Co alloy saturated with carbon, ~1300°C) and liquid-phase sintering begins. The

grains dissolve in the binder phase until it is saturated, which is controlled by the solubility of the product. Smaller grains dissolve preferentially, and larger grains (which do not dissolve) dissolve at the expense of smaller grains [3,4,5]. This Ostwald ripening process leads not only to coarsening of the WC grain, but also to complete compaction, see fig. 2.



**Fig. 2. Temperature ranges for the densification stages, as well as a schematic description of the evolution of the microstructure and the corresponding fracture images (scanning electron microscopy (SEM) during sintering of cemented carbide a WC-Co).**

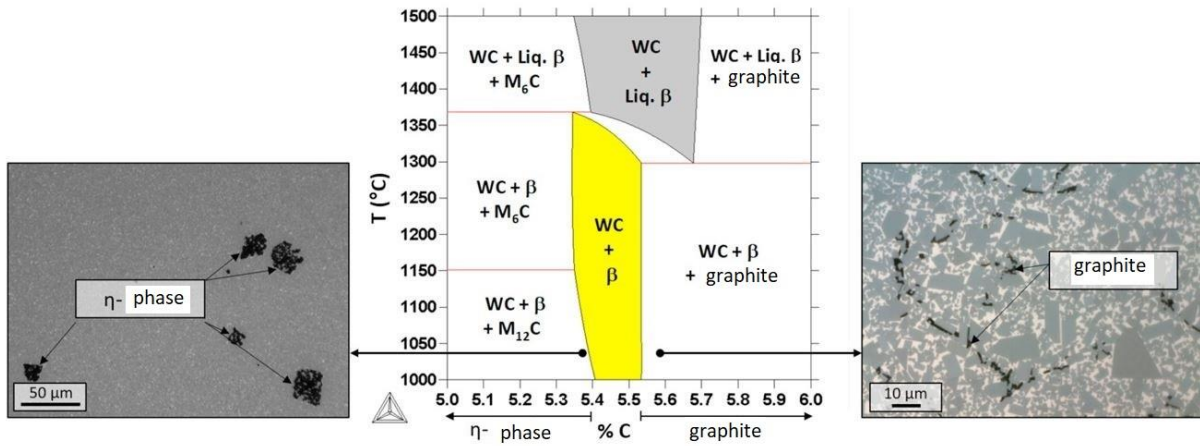
At the fourth stage (cooling), the binder phase solidifies. Reprecipitation is present in the last step leading to further enlargement. Usually sintered by controlled conditions of temperature, pressure, atmosphere and sintering time [4,6,7,8].

The key aspect is the consideration of the carbon content in the solid alloy. At a low carbon content, a

sub stoichiometric carbide phase, called the η-phase, can form. This phase tends to decrease in hardness in the hard alloy, especially if it is deposited in the form of large dendrites. Or, on the contrary, free carbon is expected in the form of graphite and in the resulting hard alloy, with a high carbon content, the mechanical properties of the material decrease (Fig. 3).

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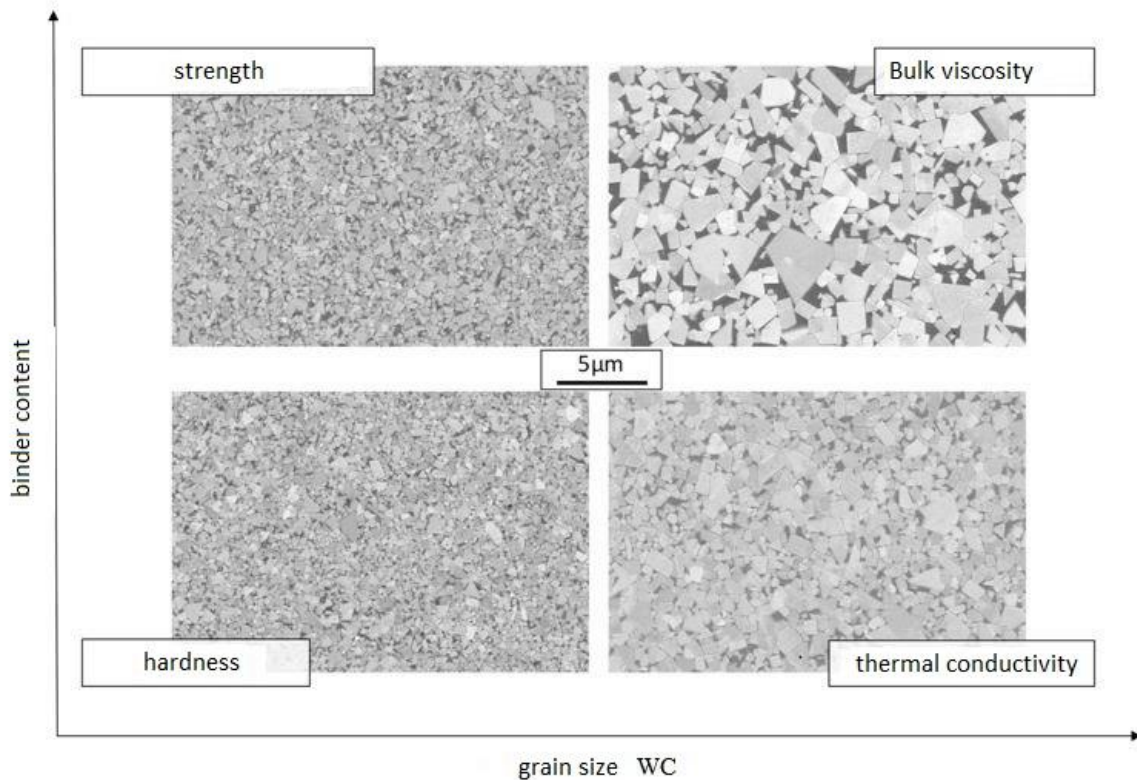


**Fig. 3. Light optical micrographs showing the  $\eta$  phase (left) and graphite formation (right) on cemented carbide WC-10% Co. The phase diagram in the center shows the possible phases. The two-phase region without defects (WC: tungsten carbide,  $\beta$ : Co binder) is highlighted in yellow.**

Therefore, the carbon content in the sintered alloy must be kept within narrow limits, in which neither the  $\eta$ -phase nor graphite is deposited, which really depends on the total composition of the material. It should be noted that the solubility of W in liquid Co decreases with increasing carbon activity. If the content  $c$  of cemented carbide is less than the ideal ratio  $[C] / [W] = 1$ , the amount of tungsten dissolved in Co increases. In modern production lines, carbon can be controlled in the range of 0.05 wt.% [1,9,10].

Hard alloys are in many respects a unique class of materials. It is most remarkable that the phase of the matrix, i.e., binder is the minority phase. The interaction between the binder and carbide phases determines the final microstructure.

By adjusting the binder content and grain size of WC, certain properties can be achieved, i.e., grain size, mechanical properties, impact strength, hardness and thermal conductivity (see Fig. 4).



**Fig. 4. Correlation between binder content and WC grain size with the main properties of cemented carbides.**

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These properties may vary depending on the application, i.e., the processing of alloyed, stainless and austenitic steels; cast iron or composites.

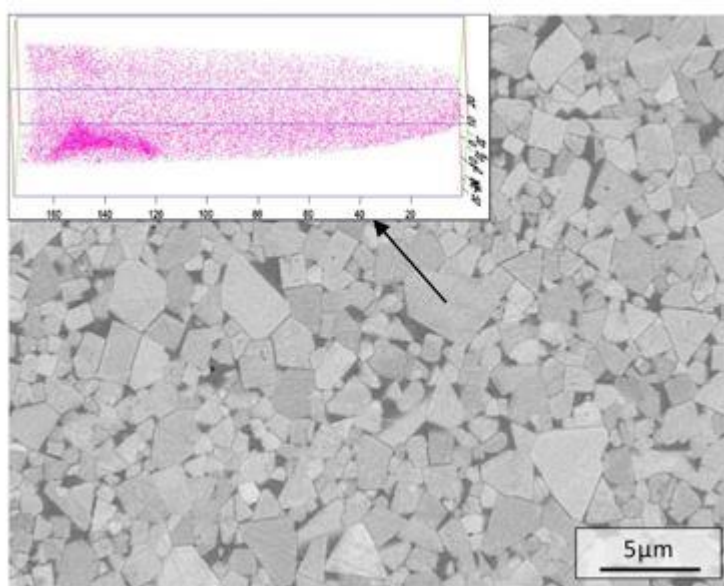
Bonding is an indication of the degree of WC/WC bonding in the microstructure that effectively forms the WC framework. Many unique properties of hard alloys are due to the formation of the WC frame.

Thus, most of the properties of hard alloys can be explained by the content of Co and the average grain size of WC. Hardness, and hence impact strength, can be described as a function of average WC grain size and Co content. It should be noted that the ratios presented here are empirical in nature and most often do not take into account the scatter due to the shape of the WC grain, the width of the particle size distribution (this was indeed noted by Golov Chanom and Litoshenko) or multimodal distributions,

as well as any other carbide phases that may appear in the microstructure [11,12].

Recently, an alternative method has been developed, consisting of alloying WC grains while maintaining their hexagonal structure (hexagonal). The goal is to change the internal properties of the hex-WC, as well as to control the WC grain size by doping already in the WC phase. However, it was difficult to change the properties of the hexagonal WC phase itself. Molybdenum forms a continuous solid Mo compound in WC at temperatures below 1170 °C. The solubility of other transition metal atoms in WC is so low that it is usually neglected.

WC powder, pre-alloyed with Ta, is successfully used to obtain both coarse-grained and fine-grained cemented carbides based on WC - Co with a confirmed high concentration of ta, octa in the WC structure (Fig. 5).



**Fig. 5. SEM micrograph of sintered material (W, Ta) C-Co.**

**The light areas correspond to WC, as well as (Ta, W) C. The dark areas correspond to the phase of the binder based on Co, in the form of a needle, part of the grain (W, Ta) C in the same material (upper left corner). Each dot represents one Ta atom.**

Young's moduli of doped crystals were significantly lower than for undoped WC. They were measured by nanoindentation in accordance with the decrease in elastic constants from non-empirical calculations. When added, some materials with a high amount of Ta in WC grains had a lower hardness than expected for their grain size, which is consistent with the hypothesis that Ta doping in WC crystals has a softening effect on the material and can improve the ductility of the WC phase.

Theoretical calculations Suetin predicted that among the 3d transition metals, Cr, V, Ti, and Mn should be the closest in energy to form a solid solution with W in hexagonal WC.

Several authors have reported the solubility of Cr in the WC lattice. Gladyshevsky et al. have already described cubic carbide (W, Cr) C formed in the W-Cr-C ternary system with a carbon content of 40–50%. However, Tükör found that the dissolution of Cr in hexagonal WC is possible during powder cementation. The authors found a hexagonal (W, Cr) c phase with a higher Cr content than previously reported (W<sub>0.85</sub>, Cr<sub>0.15</sub>) C corresponds to 5% CrC. Weidow confirmed the results of theoretical calculations using atomic probe measurements, giving the solubility Cr in WC  $1.85 \cdot 10^{-3}$  after sintering at a temperature of 1410 °C.

The main task in alloying hexagonal WC, from the point of view of processing, is to control the

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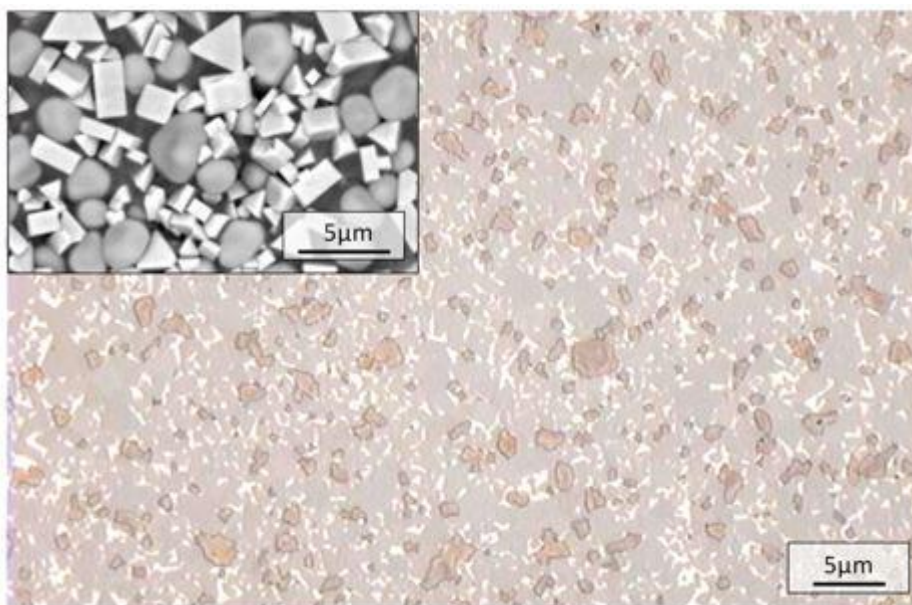
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deposition of cubic carbides or carboxylic acids from alloyed hexagonal -WC, since how this precipitation will affect the viscosity of the resulting sintered product. Methods for producing hard alloys using alloyed hexagonal WC, as well as for adjusting the transition thickness by combining alloyed hexagonal WC and nitrogen, have been proposed [1,5,8,13].

Addition of TiC, TaC, NbC and in some cases VC, ZrC or HfC to cemented WC-Co carbides will result in a secondary mixed (M, W) with cubic carbide phase (here  $\gamma$ -phase is denoted), where M = Ti, Ta, Nb, Zr, Hf, V depending on the added carbides. The

$\gamma$ -phase does not change in the microstructure of hard alloys in terms of a distinct round morphology and a brownish color in the cross-sectional images (Fig. 6).

The solubility of these carbides in the liquid phase at typical liquid phase sintering temperatures is also limited. and thus, incomplete dissolution of the added carbide particles can be observed. This often leads to the formation of the  $\gamma$ -phase, which is the structure of the core, although much less pronounced than, for example, for cermet materials. The formation of such a structure as a core-rim depends on the composition and processing.



**Figure 6. Optical light microscopy image of WC- (Ta, Nb)c-Co cemented carbide showing grains of WC (gray phase), Co bonding phase (white) and (Ta,Nb)c  $\gamma$ -phase (brown phase). Surface SEM backscattered electron image of WC-(Ta,Nb)C-Co showing different morphology of WC (faceted grains) and cubic carbide phase (rounded grains) (upper left corner).**

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Only very small additions of these carbide formers can be allowed if secondary precipitation of carbide is undesirable, then due to the very low solubility of cubic carbide formers in the solid based on co-binder on high carbon activities in typical cemented carbide materials.

The effect of adding cubic carbides to cemented carbides was revealed. TiC is a very hard and stable carbide that provides wear resistance in the toilet together. Compared to WC, the addition of TiC increases the hardness of cemented carbides. Accessory for improving the cracking resistance of

stainless steel, which forms abrasion and is often accompanied by chemical attack and diffusion wear due to high temperature near the cutting edge. On the other hand, TaC, NbC and ZrC increase resistance to plastic deformation, especially TaC, due to higher wear resistance and hardness at high temperatures.

Barbatti studied the effect of partial replacement of WC by cubic refractory carbides (TiC and (Ta, Nb) C) on the resistance to oxidation of cementing carbides WC - Co at 600 and 800°C. Oxidation kinetics causes an increase in the oxidation rate of (Ta, Nb) C at higher temperatures, oxidation resistance at 800 °C is achieved only by adding TiC; Thus, after the replacement of the carbide, WC is mixed and passivated by the action of Ti, Ta, and Nb oxides.

At present, due to the main type of cemented carbide grades coated with CVD and PVD, the use of cemented carbides containing a significant proportion of this mixed cubic area carbide, limited. Fields of application - milling (continuous cutting), where there are cubic carbides with a total content of no more than

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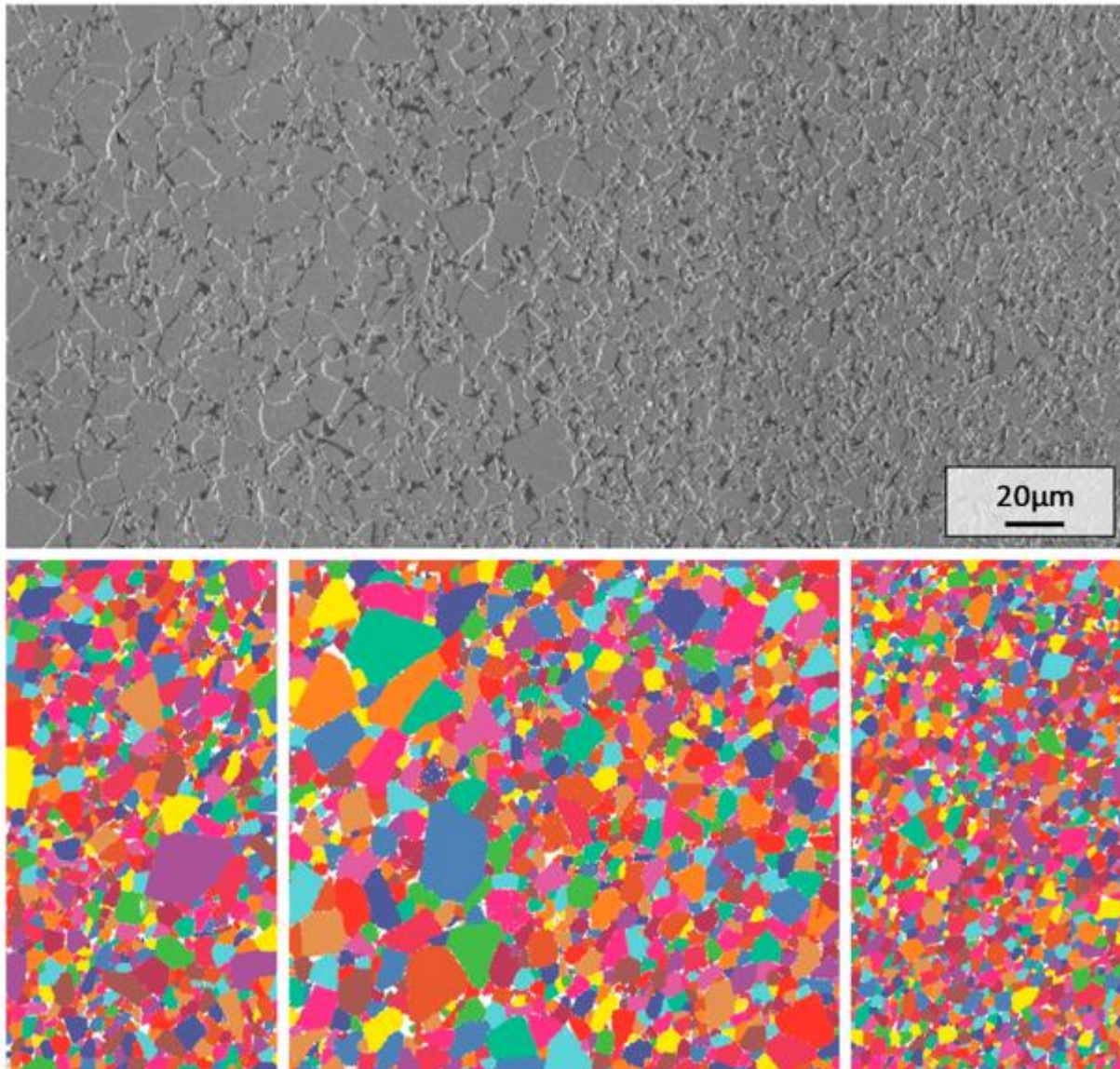
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a few percent by volume. The use of a nitrogen-containing  $\gamma$ -phase to obtain functionally graded hard alloys is a modern coating of inserts for turning steel.

Two-layer cemented carbides can be obtained by sintering two different parts of carbides with WC particle sizes, the appropriate binder, and composition (Fig. 7).



Ree c. 7. SEM image of two-layer cemented carbide WC-Co/WC-FeNi (top) and corresponding EBSD image showing two different grain sizes of WC and a clear interface (bottom).

This technology can be used to create two different microstructures. The phenomenon of the liquid phase in two-layer cemented carbides, which is under the conditions of joining two dissimilar cemented WC-Co carbides, is considered in detail. As a rule, grain size and carbon content affect the release of the liquid phase during sintering. In addition, the proportion of liquid binder in the 2nd half also affects the redistribution of the binder. These variables must be taken into account if the gradient is to be preserved or avoided. Depending on the swelling, if the migration of the liquid phase is not properly controlled, not only changes in the properties of the

half-layer material can occur, but also a harmful effect on an interface or connection.

### Conclusions

1. The empirical model is established based on the level of the liquid phase flow. Can be used to create multilayer cemented carbides. They showed that the redistribution of the binder can be prohibited as a result of the same pressure at which the liquid phase migrates into all parts of a two- or multi-layer material.

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2. Obtaining large-sized two-layer cemented carbides in WC particles and/or binders requires precise control of the sintering process.

3. When using bonds other than cobalt, the mutual diffusion gradients are also observed at a multilayer boundary (with a gradual change in mechanical properties).

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