Synthesis, structure, and behaviour of a new CVD TiB_2 coating with extraordinary properties for high performance applications

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Abstract

High performance metal cutting of difficult to machine materials requires new concepts regarding substrate and coatings. Especially the machining of titanium alloys generates specific demands on the metallurgical setup of the cutting grades. A new coating concept based on TiB_2 was developed which opens new application areas in metal cutting and wear applications. Because of the new possibility to generate this coating with a CVD process the hardness and chemical stability is significantly increased compared to conventional available TiB_2 coatings. Additionally the nano- structured composition of this coating leads to strongly improved tribological behaviours during cutting and wear processes.

In this presentation, manufacturing, metallurgical features, and the resulting performance of this new development will be presented and discussed which is considered as a technical reliable alternative to diamond coatings.

Keywords

Coating, CVD, TiB_2, high performance application

Introduction

Aerospace, energy and automotive industry are focussing more and more on the need to increase productivity for difficult to machine materials like heat resistant superalloys, high alloyed steels for turbine blade machining, and Titanium alloys. The tendency to increase the load and temperature during the application of these materials leads to highly sophisticated compositions and microstructures of the work piece materials. Machining of these materials is difficult because they generate extremely high temperatures and high cutting forces which tend to create rapid wear and micro fracture of the cutting edge of the cutting tools. Therefore new approaches regarding substrate materials, coatings, and tool concepts are needed to face the new demands.

Especially in the field of coatings conventional available PVD and CVD coatings based on TiAlN-compositions and $TiCN/Al_2O_3$ layer systems are used to solve cutting challenges regarding difficult to machine materials. Other coating systems like TiB_2 were only used in combination with the PVD process mainly for Aluminium machining. In this work, a new step in the TiB_2 coating system will be presented focused on the CVD process which provides superior coatings behaviour in cutting applications especially on difficult to machine materials like titanium alloys.

Demands on cutting grades for the machining of Titanium alloys

Weight reduction is the central requirement in the modern aerospace industry for civil and military aviation. The industry sector responds to this demand with new materials such as carbon fiber and glass fiber composite materials. In this context Titanium alloys become more and more important in aircraft construction. These structural components made out of Titanium alloys are used as connection elements between carbon fiber parts. Due to this fact structural components made out of aluminum will be less important in future.

Titanium alloys exhibit a poor thermal conductivity which is factor 10 lower compared to conventional steel materials. Therefore 75% of the temperature generated during cutting processes stays in the cutting tool material. The combination of high temperature and work hardening effects during the chip formation lead to the necessity of high hot hardness substrate materials and a specific, chemical resistant, and hard coating for this application. The pronounced adhesion of the chips on the surfaces of cutting tools especially in the area of high temperatures leads additionally to the demand of very smooth, mirror like coating surfaces with reduced chip welding properties. To obtain this, very fine grained structures in the coating are desired in combination with high wear resistance and pronounced coatings adhesion on the substrate material. Because of high cyclic cutting forces due to work hardening effects in front of the cutting edge during the cutting process the stability of the coating regarding micro flaking mechanisms and therefore the intrinsic stresses must be controlled in a proper way.

Method of TiB_2 deposition

Preliminary remarks

The number of advantageous properties of TiB_2, like high hardness at high and low temperatures, a very high young's modulus and good thermal and chemical stability, makes it interesting as a material for wear and cutting applications. Various researches have been done to investigate the possibilities to create a TiB_2 containing hardmetal as an alternative for WC-Co based cemented carbide /1/. Limited sinter ability, especially because of the reactivity of TiB_2 with metallic binders and formation of brittle eutectic phases, is one reason which made it difficult to develop tools for cutting applications on an industrial scale /2/.

Nevertheless, TiB_2 is a candidate with high potential for wear applications, and lead to many activities to use this substance as a coating material as well. From the start of the manufacture of hardmetal parts having wear resistant coatings, the use of borides as layer material has been desired. Many attempts have been undertaken to deposit borides by CVD-processes but an advantageous technique still has not been developed to effectively utilize the advantages of TiB_2 as protective wear resistant CVD coating /3/.

Deposition method

Basic experiments

To investigate the possibilities generating a useable CVD-TiB_2 layer system on cemented carbide tools for cutting applications the consideration of some important requirements, shown in this chapter, were necessary. The high reactivity of boron-halogenides, e.g. with iron containing hot wall reactor materials but also with the cemented carbide substrate /4/, were most important factors which have to be solved.

For basic experiments a small laboratory graphite reactor was used as shown in Fig. 1.

Fig. 1: CVD reactor for experimental studies as schematic representation

Based on the theoretical thermo-chemical reaction for the formation of a TiB_2-film from vapour phase

$$TiCl_4 + 2BCl_3 + 5H_2 \rightarrow TiB_2 + 10HCl \quad (1)$$

a gas mixture consisting of the above mentioned precursors was used. Under atmospheric pressure, coating temperatures, gas compositions, and gas flow velocities were investigated. Appropriate coating conditions for the deposition of a uniform coating were found at a temperature below 900 °C. To obtain a perfect coating quality the gas ratio of TiCl4:BCl3 and therefore the partial pressure of the reactants must be controlled in a specific regime by using additional inert gas contribution to reduce said partial pressure under a maximum value. The successful outcome of the method was a smooth and uniform coating without any formation of brittle tungsten cobalt boron phases or η-phases in the substrate. The absence of any precipitations, e.g. consisting of free carbon, boron, or of C-porosity at the interface leads to a perfect adherence of the coating directly on a cemented carbide substrate. Fig. 2 shows the structure in a cross section micrograph of the developed TiB2 coating, deposited directly on a substrate of a cemented carbide with the composition of 11% Co, 12% Ti(Ta,Nb)C, and balance WC by this new CVD process.

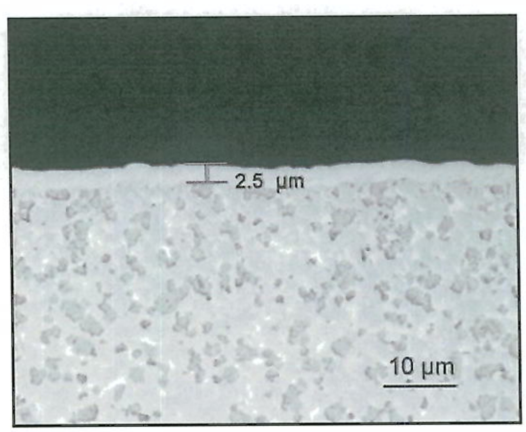


Fig. 2: CVD TiB2-layer on cemented carbide [11% Co, 12% Ti(Ta,Nb)C, rest WC]

Up scaling for mass production

For the deposition of the coating on a production scale an existing hot wall CVD production plant from CERATIZIT Austria was used. As mentioned before, considering the specific demands, e.g. the high reactivity of boron, a new suitable reaction chamber has been constructed to obtain a stable process. Fig. 3 shows the coating plant schematically.

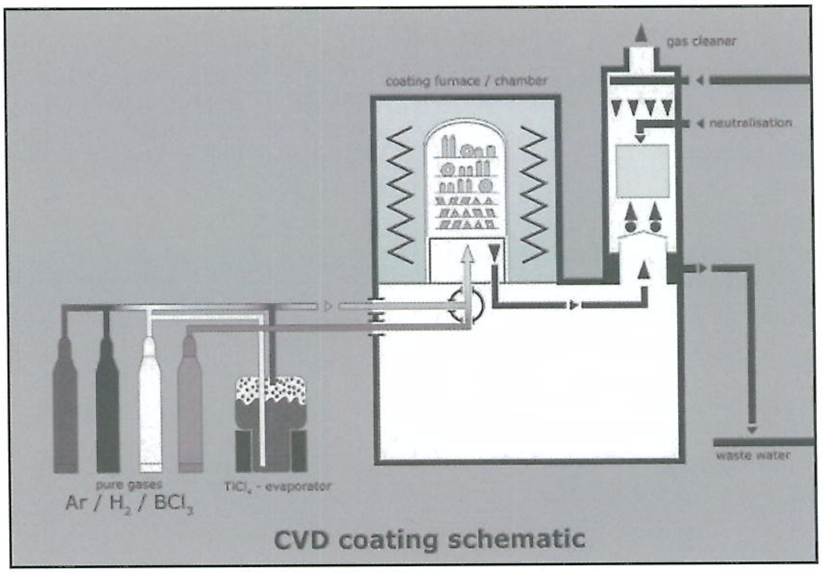


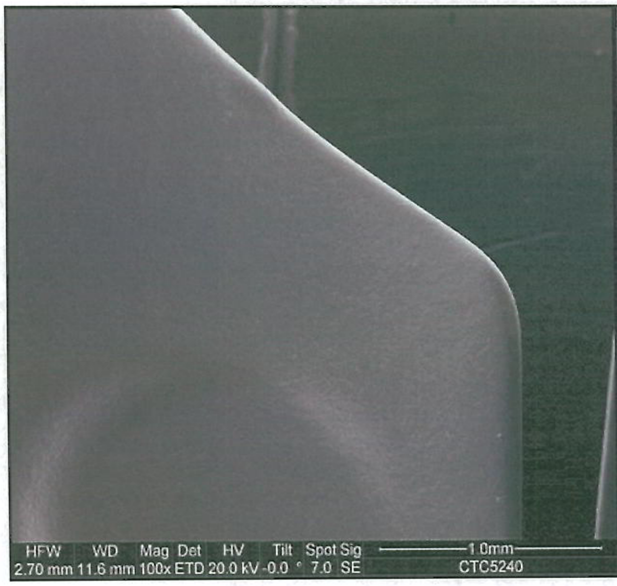
Fig. 3: schematic representation of coating plant

Process development

An adaptation of the coating device mentioned above including the gas supply system and a new set up of the automated control system for gas regulation was necessary.

The process development for a uniform coating in a production environment comprised the usual range of relevant parameters like gas quantities, gas composition, flow speed, and deposition temperature as well, to be investigated. The goal to achieve a constant, reproducible quality is even more important as to be able to produce a modern coating in an economic way. So, the deposition rate is one of the most important factors for an economic manufacturing process. For the new coating the deposition rate was found to be >1µm/h TiB_2. This is remarkable in so far as the deposition temperature is lower than for known conventional CVD coatings up to now, and, as it will be shown in the following pictures and in the next chapter, the coating is characterized by an extremely fine grain size and high surface smoothness.

Fig. 4a and Fig. 4b show the surface morphology of a CVD TiB_2-coated hardmetal cutting insert. The investigation was done by scanning electron microscopy [SEM].



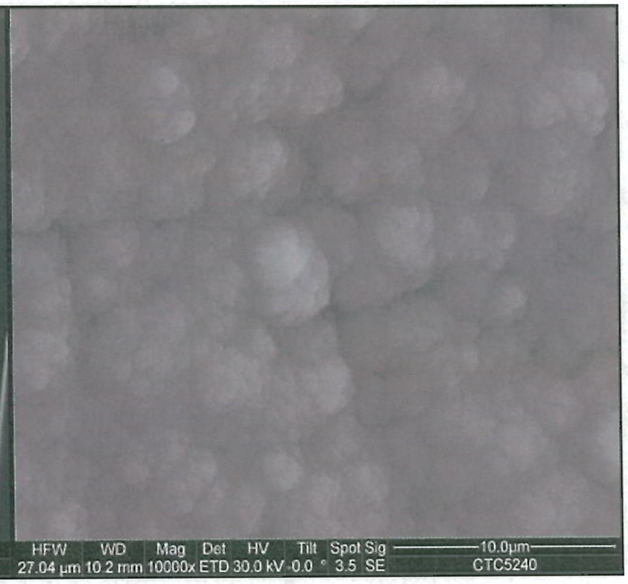


Fig. 4a: CVD TiB2-coated surface

Fig. 4b: CVD TiB2 coated surface

Secondary electron [SE]-pictures

Product development

To fulfil the specific demands on the wear resistance and the stability of the cutting edge as described above the potentials of development regarding substrate, tool geometry and coating were focused. For the coating itself different compositions and combinations including Al_2O_3-containing and Ti(C,N,B)-based layers were investigated. For the special focus on milling of Titanium alloys extensive cutting tests showed that there is an optimum in the performance which can be achieved by a monolayer TiB_2 coating, or, in combination with a basic layer, e.g. TiN.

Fig. 5 shows a photograph of a coated indexable insert of the new CERATIZIT grade CTC5240 which is coated with this new CVD TiB2-layer.

Fig. 5: CVD TiB_2-coated insert

Fig. 6 shows a microphotograph representing the structure of the new CVD coating with the coating thickness of 1µm TiN / 3µm TiB_2 on a cemented carbide substrate with a composition of WC with 10 % binder (CTC5240).

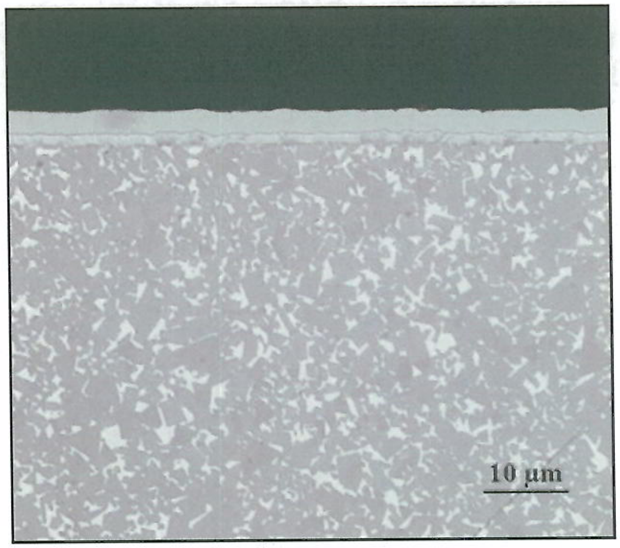


Fig. 6: CVD TiN/TiB_2-coated cemented carbide

Characterization of the coatings and properties

Chemical composition

Glow discharge emission optical spectroscopy [GDOES] is a method to obtain a chemical depth profile. Samples with the new coating with a structure of 1µm TiN / 3µm TiB_2 were analyzed by the GDOES method. An area of several mm^2 was sputtered for 200 seconds. The sputtering time is corresponding to a penetration depth of the coating thickness and the outer zone of the substrate. The detected element specific optical signal is characteristic for the quantitative composition of the sample.

Fig. 7 shows the results of the GDOES analysis for Boron and Titanium, corresponding to the thickness of about 3µm TiB_2. The measured values show basically the theoretical stoichiometric composition of TiB_2, which is approximately 33 At.-% Ti and 66 At.-% B. The constant signal - except of an outermost, little oxygen contaminated zone - until the TiN layer (thickness of about 1µm) proves the homogeneity of the TiB_2 coating. Additionally, no Boron at the interface or in the substrate was detected.

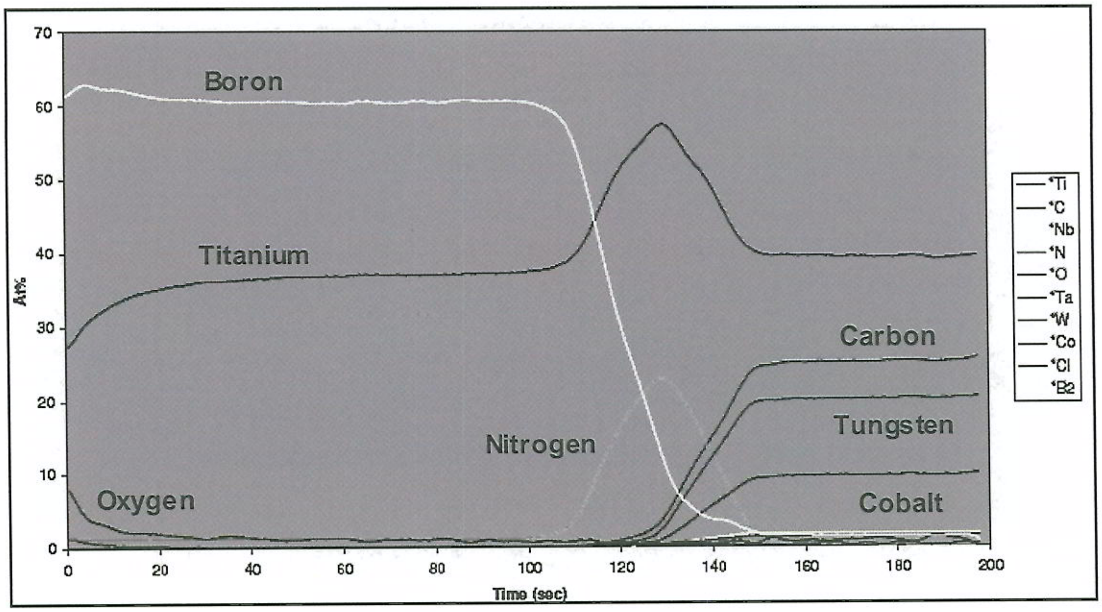


Fig. 7: Chemical analysis of the CVD TiN/TiB_2 layer [GDOES method]

Crystalline structure and phase identification

X-ray diffraction [XRD] is an analytical technique for the identification and determination of crystalline phases in solid materials. By this method X-ray radiation is diffracted by the crystal planes of the sample, resulting in a characteristic diffraction pattern for the crystal structure. To identify the crystal structure of the new coating samples were analyzed by XRD. Fig. 8 shows exact peaks for the TiB_2-phase without any shift which indicates hexagonal structure of the TiB_2 layer.

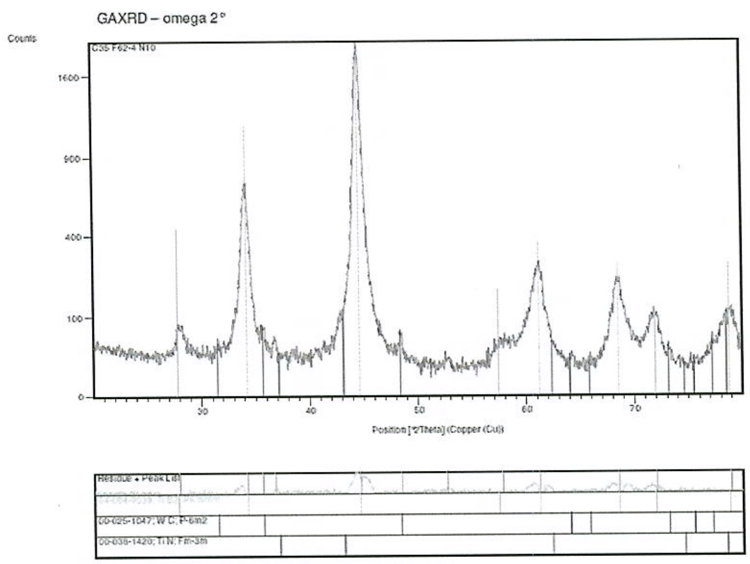


Fig. 8: XRD diagram of the CVD TiN/TiB_2-layer

Hardness

Hardness and Young's modulus were measured by nano indentation by using a CSM system. Precise hardness and elastic modulus of thin films and hard coatings by using this method can be determined.

Samples were polished because an absolutely even surface is necessary to achieve exact reproducible results.

Fig. 9 shows the diagram of the measurement of a TiB2 coated cemented carbide sample.

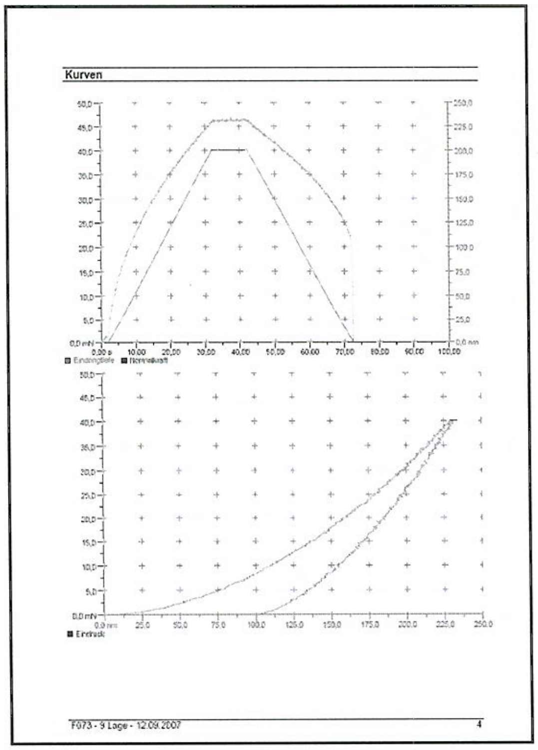


Fig. 9: Nano indentation measurement of hardness and elastic modulus (CSM)

Table I shows the results of the measurements of a conventional commercial available PVD TiB_2 coating and the new CVD coating [hardness calculated into HV].

	penetration depht [µm]			hardness [$HV_{0,04}$]			elastic modulus [GPA]		
	value	*min.*	*max.*	**value**	*min.*	*max.*	**value**	*min.*	*max.*
conventional PVD coating	**0,266**	*0,261*	*0,284*	**2957**	*2560*	*3229*	**601**	*520*	*705*
new CVD coating	**0,23**	*0,227*	*0,235*	**4977**	*4784*	*5148*	**669**	*617*	*709*

Table I: Results of the hardness measurements (CSM)

A significant difference of the hardness between the different coatings was found. The hardness of the new CVD-TiB_2 coating is 2000 HV units higher than the conventional PVD-TiB_2 coating.

Adherence

The adherence of the new coating on the substrate was measured by the scratch test method. This is an usual method for the characterization of coatings adhesion for hard coated materials. By scratching the coated surface with a diamond at given speed and increased load the "critical load" is defined when failures in the coating occurs. This can be detected by optical and/or acoustic measurements.

Fig. 10a shows the result of the measurement on a new CVD-TiB_2 coated cemented carbide sample, Fig. 10b shows the result on a conventional PVD-TiB_2 coated sample.

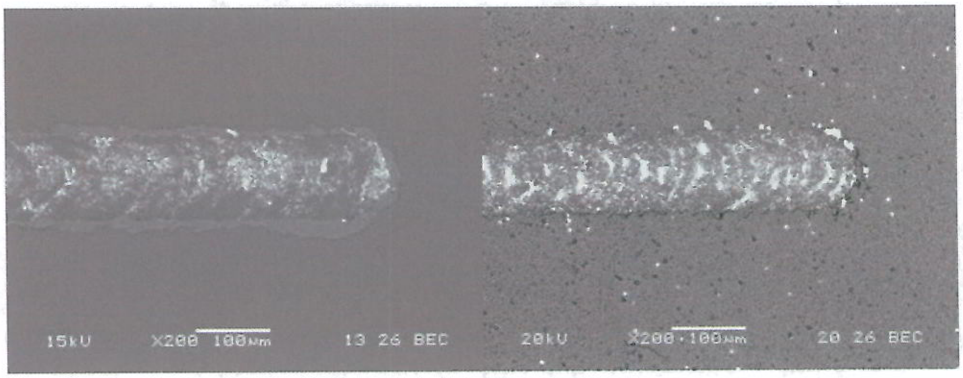


Fig. 10a: CVD-TiN/TiB_2 coated

Fig. 10b: conventional PVD TiB_2 coating

[Scratch test, load 100N]

Slight advantage of the adherence of the CVD coating has been seen at a load close to 100N. The critical load for both coatings was observed at >60N.

Structure

The structure of the coating was investigated by using scanning electron microscopy [SEM] and by transmission electron microscopy [TEM] as well.

Fig. 11a and Fig. 11b show the secondary electron [SE] -pictures representing the structure of the new CVD-TiB_2 coating and of a conventional PVD-TiB_2 coating on a cemented carbide substrate.

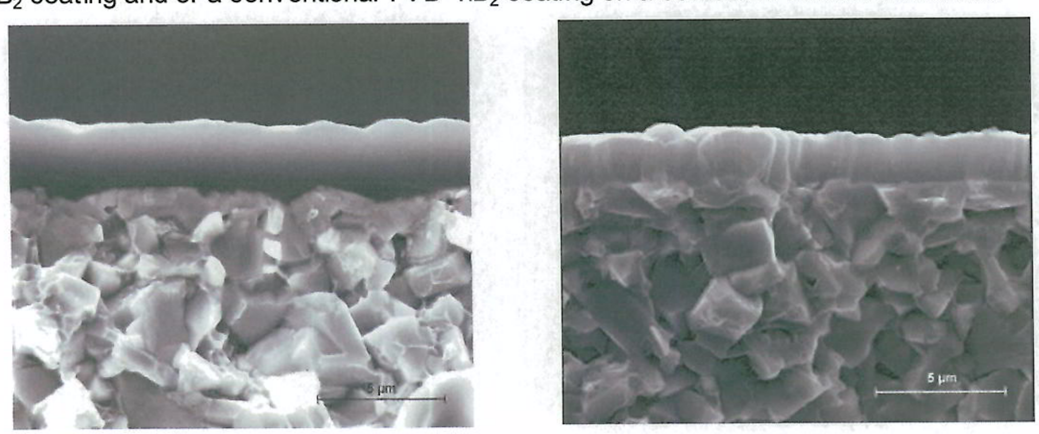


Fig. 11a: CVD-TiB_2 coating

Fig. 11b: PVD-TiB_2 coating

[SE-pictures]

The fracture cross sections show a big difference between the coatings. The new CVD coating shows no features and a high homogeneity.

For exact identification of the coating structure extensive investigations have been done by TEM at the Austrian Centre for Electron Microscopy and Nanoanalysis – Technical University Graz. The following pictures show the comparison between the new CVD-TiB_2 coating [Fig. 12a, Fig. 13a, and Fig. 14a] and the commercial available PVD-TiB_2 coating [Fig. 12b, Fig. 13b, and Fig. 14b].

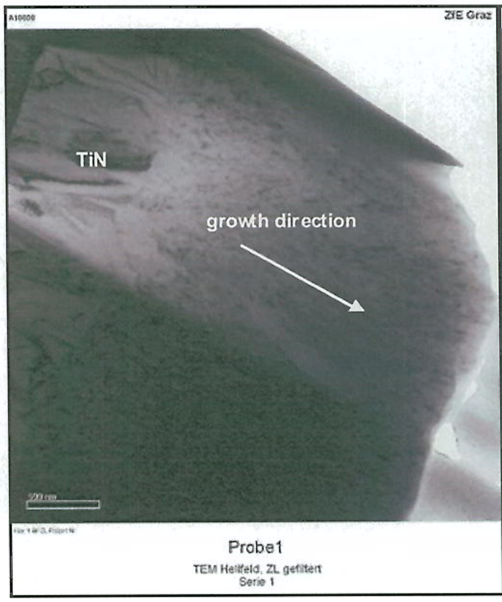


Fig. 13a: TEM, CVD-TiN/TiB_2

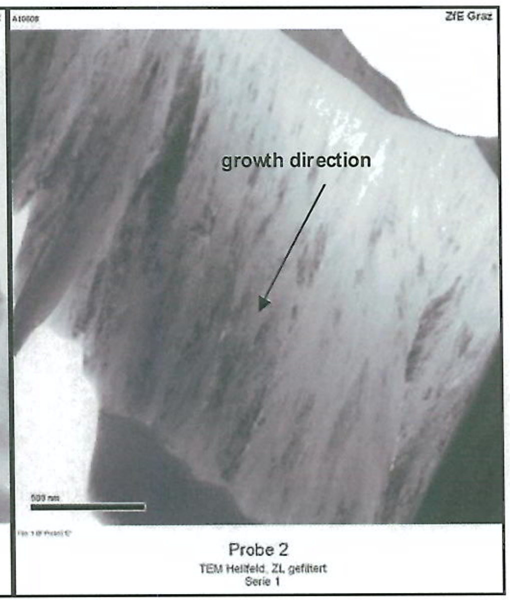


Fig. 13b: TEM, PVD-TiB_2

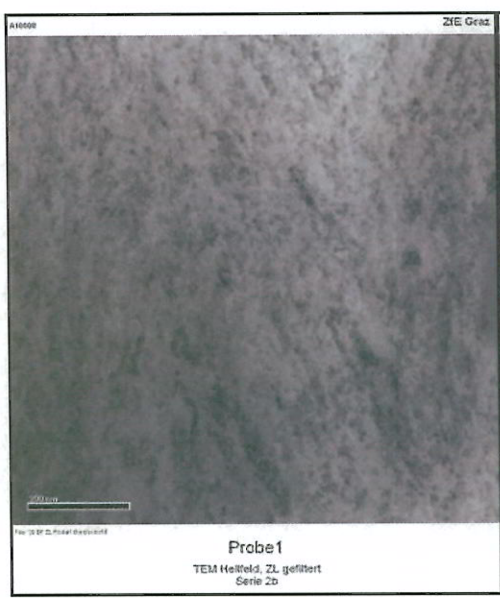


Fig. 13a: TEM, CVD-TiB_2

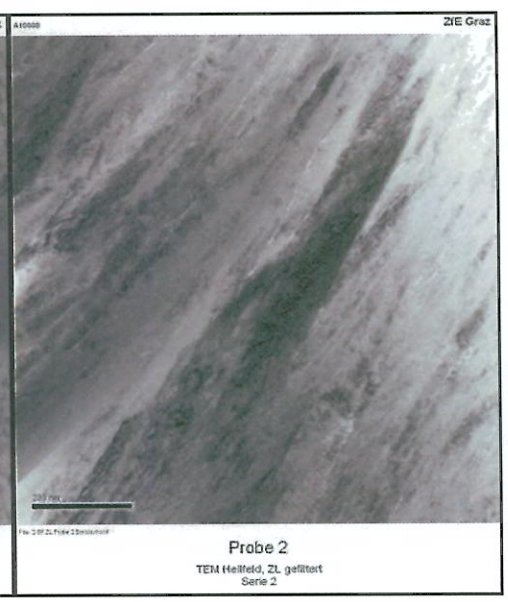


Fig. 13b: TEM, PVD-TiB_2

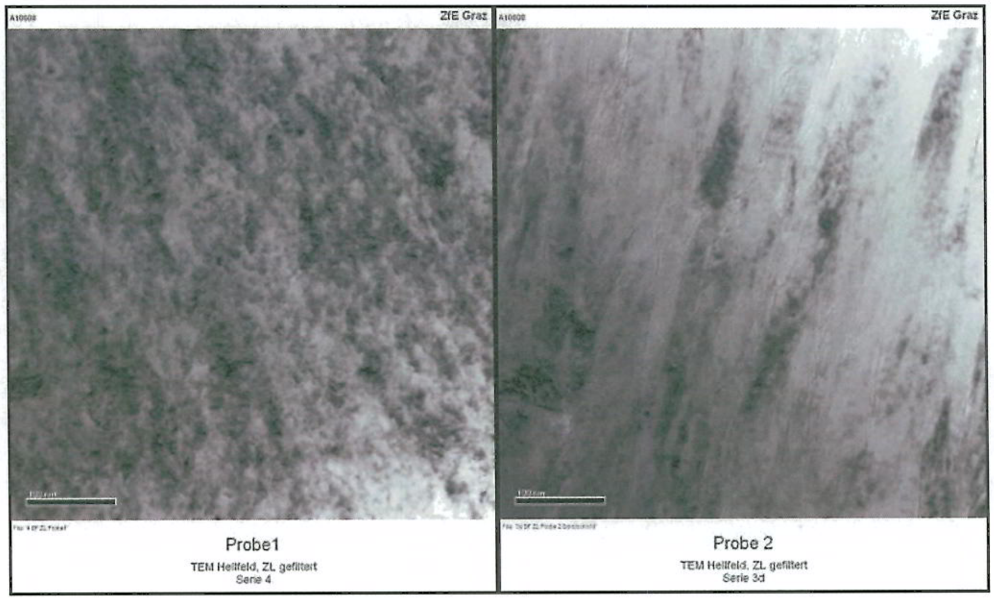


Fig. 14a: TEM, CVD-TiB_2 Fig. 14b: TEM, PVD-TiB_2

It was found that the CVD-TiB_2 coating has an extremely fine grained and regular nanostructure with an average grain size smaller than 50 nm. No texture of the microstructure was found in this coating, investigated by electron diffractometry, shown in Fig.15a. The PVD coating shows a coarse grained columnar structure with a texture as shown in the electron diffractometry pattern in Fig. 15b.

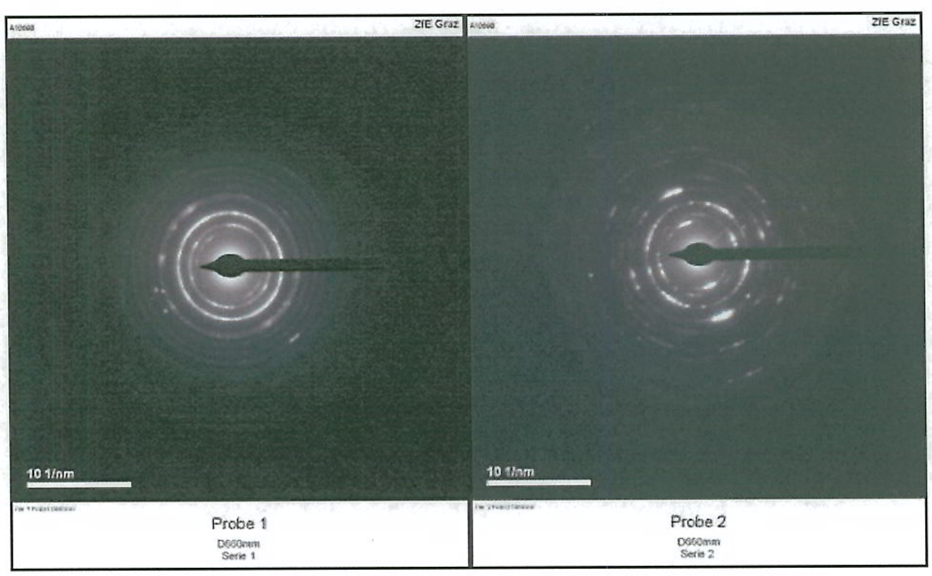


Fig. 15a: CVD-TiB_2 Fig. 15b: PVD-TiB_2

TEM, electron diffraction pattern

Surface topography

Measurements of the surface topography have been done by the optical wavelength dependent method [FRT – MicroProf®]. To avoid an influence of the substrate roughness on the different coated samples, the surface of the substrates has been polished prior to the coating process.

The pictures from the measured surface of coated samples on an area of 5 x 5 mm are shown in Fig. 16 [new CVD-TiB_2 coating] and Fig. 17 [conventional MT-CVD Ti(C,N)/TiN coating].

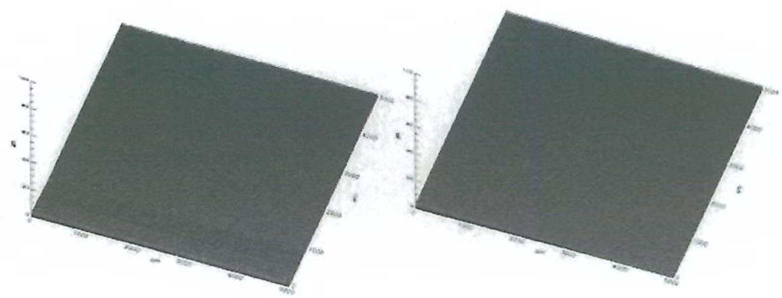


Fig. 16: surface of CVD TiB_2 Fig. 17: surface of conventional MT-CVD Ti(C,N)/TiN coating

Based on this analysis the roughness value of Ra can be calculated as shown in Fig. 18.

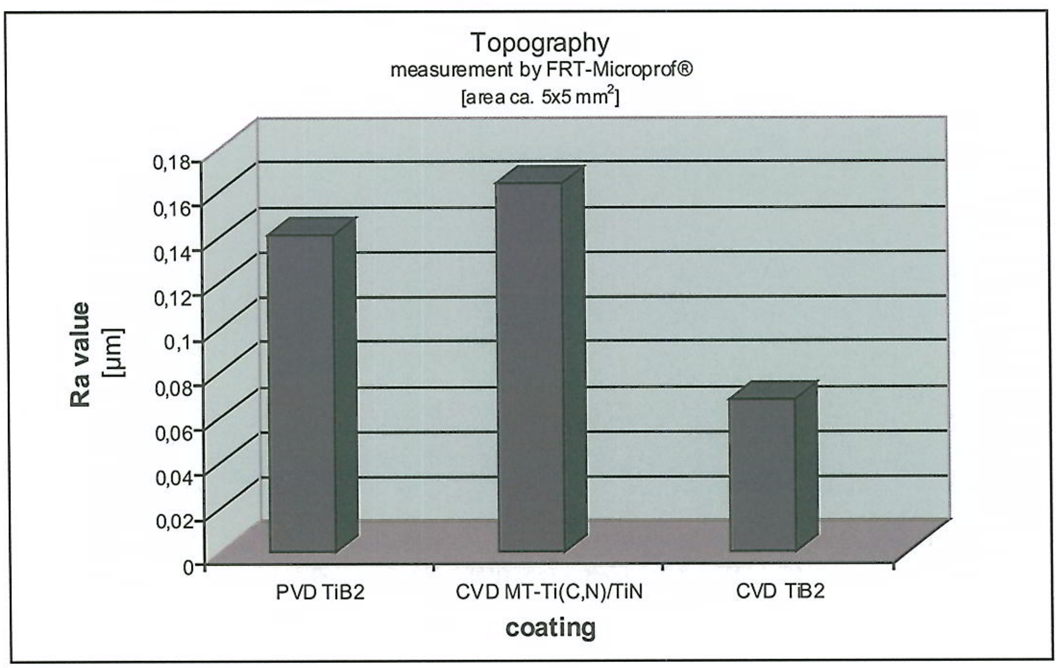


Fig. 18: surface roughness [Ra] of a PVD-TiB_2 coating, of a conventional MT-CVD coating, and of the new CVD-TiB_2 coating

The average roughness of the new CVD-TiB_2 coating was found to be significantly lower compared to the conventional MT-CVD Ti(C,N)/TiN coating and also lower than the conventional available PVD-TiB_2 coating.

Cutting tests

For cutting tests a variety of different milling inserts were produced and tested in different cutting conditions. In this paper one example will be presented which represents an average in the performance of this new developed product described above.

Test with edge milling system C211/XDKT11T325ER-F40 on TiAl6V4

For this experiment the edge milling system C211 was used as shown in Fig. 19 for the machining of TiAl6V4 on an EXCELLO milling machine with the cutting speed of 50 m/min, feed rate per teeth of 0.12mm at the entrance of the cut and 0.08mm at the exit of the cut with a depth of cut ap 5mm. Especially the comparison between the PVD TiB_2 coating and the new developed CVD TiB_2 was the focus of this experiment. Some life time results of competitive systems are shown also in Fig. 19 for completion of this overview. The life time criteria for this experiment was a flank wear of 0.3mm.

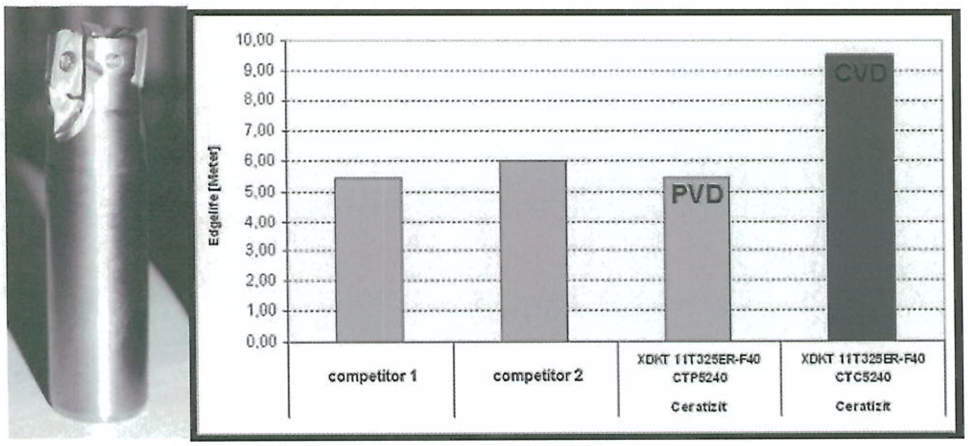


Fig. 19: Cutting results with edge milling system C211

As shown in Fig. 19 the CVD TiB_2 coated version designated as CTC5240 exhibits more than 50% more life time compared to competitors and the PVD TiB_2 version. The increase in life time was found to be controlled by the higher edge stability and reduced wear during the experiment.

In Fig. 20 the flank wear pattern of the PVD TiB_2 coated version (left) and of the CVD TiB_2 version (right) are shown after 10 minutes of application.

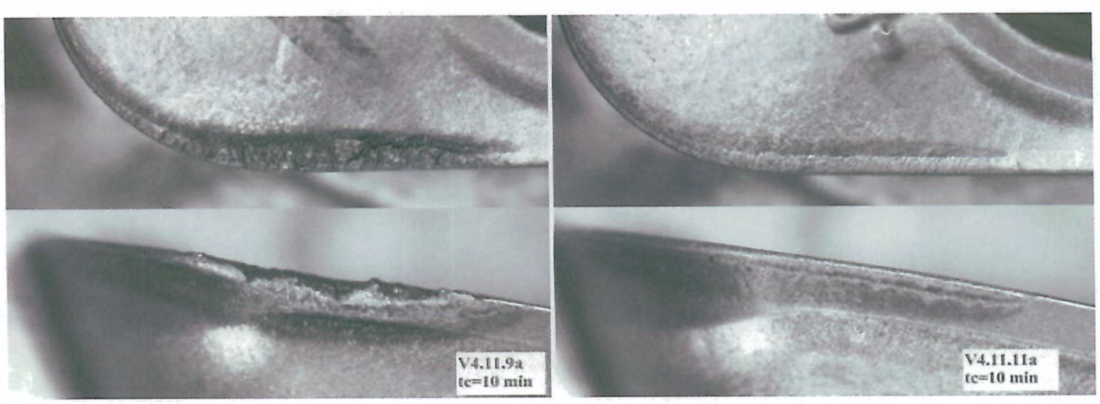


Fig. 20: Flank wear pattern of PVD TiB_2 (left) and the new developed CVD TiB_2 (right) after 10 minutes of application, cutting parameters mentioned above

The higher wear resistance and lower tendency to edge chipping during the cutting process for the new developed CVD TiB_2 development can be easily seen.

Conclusion

A new approach of depositing TiB_2 coatings by using a CVD process leads to improved structure and behaviour in cutting applications especially for the machining of titanium alloys.

The hardness of the coating was increased by 60%, the roughness of the coating surface was decreased by 60% compared to PVD TiB_2 coatings. This fact in combination with a fine grained structure which shows grain sizes smaller than 50 nm without texture and good adhesion properties on the substrate surface leads to a cutting grade system with extraordinary properties for high performance applications.

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