



# NOVEL HIGH-PERFORMANCE CVD COATINGS FOR MACHINING APPLICATIONS

R. Haubner, E. Rauchenwald, M. Lessiak, R. Pitonak, R. Weissenbacher

## Abstract

*Investigations of hard and wear resistant materials have a long tradition to increase the performance and profitability of machining applications. The evolution started with WC-Co hardmetal alloys, which were produced by PM technology, followed by CVD coatings on hardmetal tools. The first CVD coatings applied were TiC, TiN and  $Al_2O_3$ . The properties of these coatings could be optimized by varying the crystal size, crystal orientation but also combination of the materials in multilayer systems. Nowadays, about 85% of all hardmetal tools are coated. During the last years, driven by PVD coatings showing good performance (e.g. TiAlN), the search for new CVD coatings was intensified. Medium temperature (MT) CVD processes for TiCN allowed the deposition of TiCN crystals with different composition side by side. Due to this microstructure the adhesion between single layers in new multilayer coatings like TiN/MT-TiCN/ $Al_2O_3$ /TiN could be increased. Novel (Ti,Al)N coatings were developed, showing a nanolamellae microstructure consisting of self-assembled (Ti,Al)N with different composition.*

*For the future there is still plenty to investigate. The already existing coatings and coating systems have to be optimized for the various machining applications. To find new types of CVD coatings, we look for chemical reactions practicable for its use in CVD equipment.*

**Keywords:** CVD, hardmetal, coatings, nanostructures.

## INTRODUCTION

Chemical Vapour Deposition (CVD) for hard materials started in the 1930s, when Moers [1] investigated the deposition of TiC. About twenty years later Pollard, Woodward [2] and Münster, Ruppert [3] deposited the first TiC coatings on steel. After further 20 years Krupp Widia launched the first commercial TiC coating on hardmetal tools. Prof. Richard Kieffer started in the 1970s at the “Technische Hochschule Wien” with CVD of TiN [4]. The next important invention was the CVD process for  $\alpha-Al_2O_3$ , by Benno Lux’s group at Battelle Geneva, Switzerland. Sandvik Coromant took over these patents in 1971 [5]. The further progress was rapid and many different coatings and combinations of coatings called multilayers were developed [6, 7].

## THE CVD PROCESS

The CVD processes are relatively simple regarding the reactor equipment, gas supply and power supply. Compared to PVD (Physical Vapour Deposition) the throughput of samples in CVD processes is much higher, due to the larger reactor volume [8, 9]. In Fig.1a the production reactor at Boehlerit is shown.

A disadvantage of CVD for hard coatings is the rather high process temperature needed to activate the chemical reactions, and deposit the hard coatings [10]. In Fig.1b the temperature ranges of CVD and PVD processes are summarized. Conventional HT-CVD (high-temperature) works around 1000°C. If precursors with a higher reactivity are used the temperatures can be decreased to about 800°C for MT-CVD (medium temperature), or LT-CVD (low temperature) at around 700°C.

Additionally the chemical reactions cannot be individually influenced in the large reactors. For each coating the chemical reactions have to be designed specifically to guarantee similar coating properties all over the reactor. Once the coating process is optimized, CVD coatings are much cheaper compared to PVD.

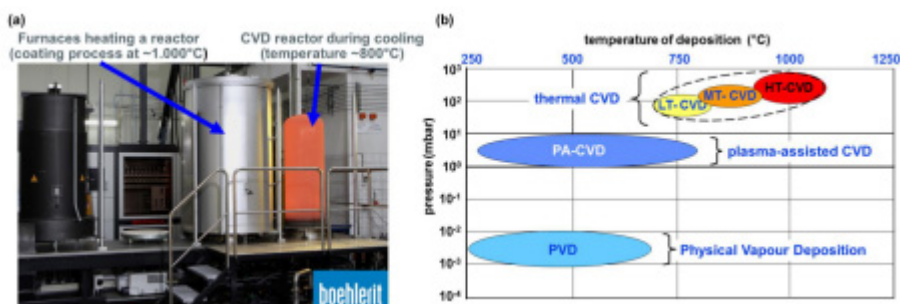


Fig.1. CVD equipment (a); substrate temperature ranges for the deposition processes (b).

## HARD COATINGS AND POSSIBILITIES FOR THEIR IMPROVEMENT

For hard coatings on cutting tools several factors have to be considered starting with the tool substrate, the interface to the coating, the properties of the coating itself and the interactions of the coating with the work piece (Fig.2). The properties of the most important materials used for hard coatings are summarized in Tab. 1.

Due to the absence of property changes during the coating process, CVD coated tools are mostly made out of hardmetal alloys (WC-Co). In contrast the microstructure and properties of steel substrates are destroyed at high temperatures.

The interface between substrate and coating is important for the coating adhesion. Differences between thermal expansion coefficients lead to stress at the interface, which can reduce adhesion. Additionally the interface of coatings and its properties are determined during the nucleation phase of the crystal growth, respectively the layer formation. Therefore diffusion and the formation of interlayers have effects too.

The microstructure of coatings is influenced by the deposition parameters, e.g. deposition temperature, concentrations of precursors, gas pressure and gas flow. Additionally the coating performance can be increased by changing the crystal size, the chemical composition and the phase composition of the coatings. Three options to increase wear properties of hard materials can be distinguished.

- Crystalline phases representing solid solutions of two individual phases (solid solution mixed crystals – ss-mixed crystals) [11, 12].
- A decrease in crystallite size increases hardness, because the grain boundaries inhibit the deformation of crystals and crystallographic cracking is reduced.
- Composite mixtures of different phases in one coating. If this mixture is within one layer, the grain size of the crystals is of interest and nano-composites are aspired.

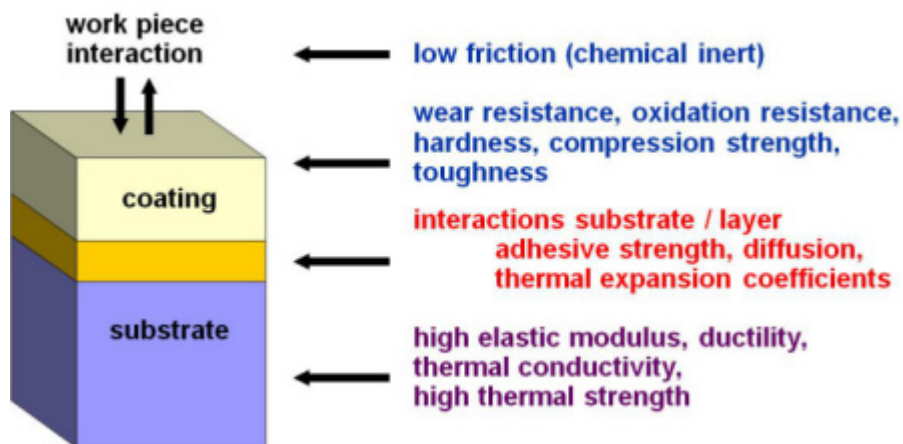


Fig.2. Criteria for the selection of CVD coatings.

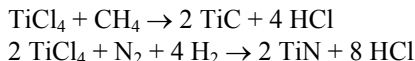
Tab.1. Properties and applications of conventional hard coatings.

| coating                   | TiC  | TiN   | TiCN   | $\alpha\text{-Al}_2\text{O}_3$                                 |
|---------------------------|--|---|--|--|
|                           | first CVD coating for wear applications                      |   |  | low thermal conductivity                                       |
| structure                 | cubic  | cubic   | cubic  | trigonal   |
| hardness HV               | 2800 - 3200  | 2200 - 2400   | 2500 - 2800  | 2400 - 2600  |
| colour                    | gray – black   | gold – yellow   | gray – red – yellow  | colourless, transparent  |
| max.ox.res.               | 600°C  | 800°C   | 700°C  | 1900°C   |
| production                | CVD and PVD  | CVD and PVD   | CVD and PVD  | CVD  |
| areas of wear application | combined with other hard coatings<br><br>decorative coatings | single layers for drilling with cooling<br>intermediate layer to increase adhesion<br>decorative coatings | low flank wear during cutting and milling<br><br>decorative coatings | cutting and milling of steel<br>best thermal isolation >1000°C |

max.ox.res. = maximal oxidation resistance; HV = Vickers hardness

Ti based coatings – TiC, TiN, Ti(C,N)

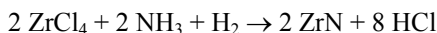
For carbides and nitrides the chemical reactions are simple and by controlling the precursor concentrations homogeneous deposition is possible even in large industrial reactors. As carrier gases hydrogen or argon can be used.



These reactions can also be used for hard coatings containing Zr, Hf and Ta. The differences in the deposition processes are mainly determined by the chemical properties and the vapor pressure of the used precursors [13 - 17].

By adding carbon and nitrogen compounds simultaneously, various TiCN mixtures can easily be deposited (Fig.3). It is also possible to use organic compounds containing both elements (e.g. acetonitrile [18]) as precursors to set the C:N ratio and to allow deposition at medium temperature (MT). In Fig.3 the influence of the deposition conditions on various surface morphologies of coatings is shown. Fig.4 shows the effect of deposition time on the coating surface. It is evident that the surface morphology of coatings influences the interface between different coatings in case of multilayers.

As an additional example in Fig.5 ZrN coatings are shown deposited at 900°C using NH<sub>3</sub> as nitrogen source [19].



The various microstructures of the coatings are caused by the different amounts of ammonia added. Different colors are caused by the sample position in the reactor due to slight inhomogeneities in the deposition parameters. Other Zr containing coatings were shown by several researchers [20, 21].

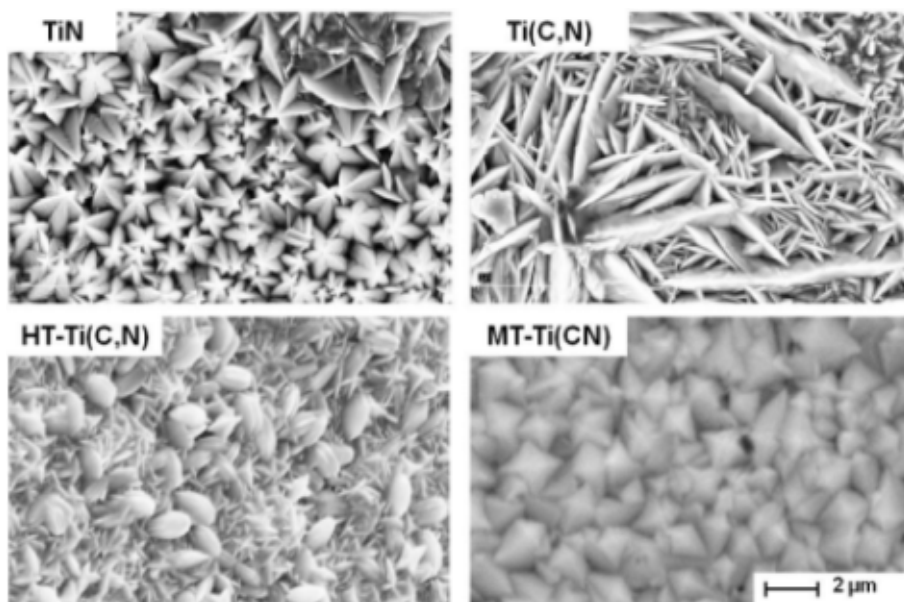


Fig.3. Various surface morphologies of TiN respectively TiCN coatings (Boehlerit GmbH).

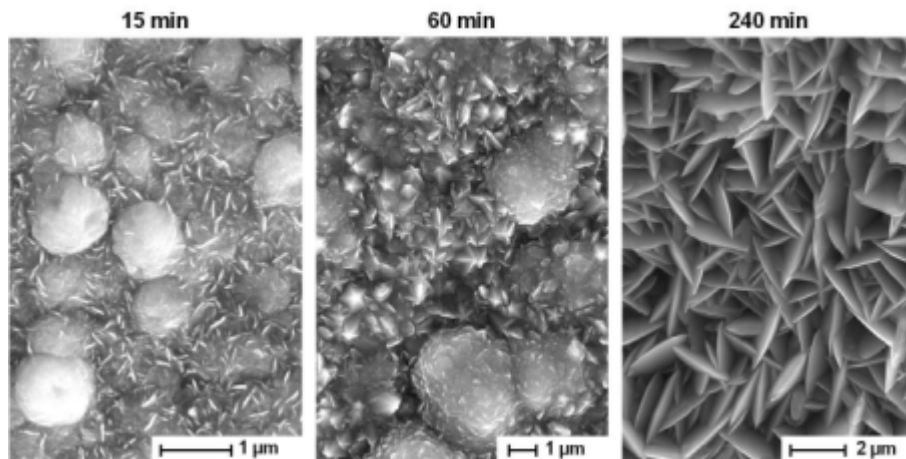


Fig.4. Influence of deposition time on the morphology of HT-TiCN coatings (Boehlerit GmbH).

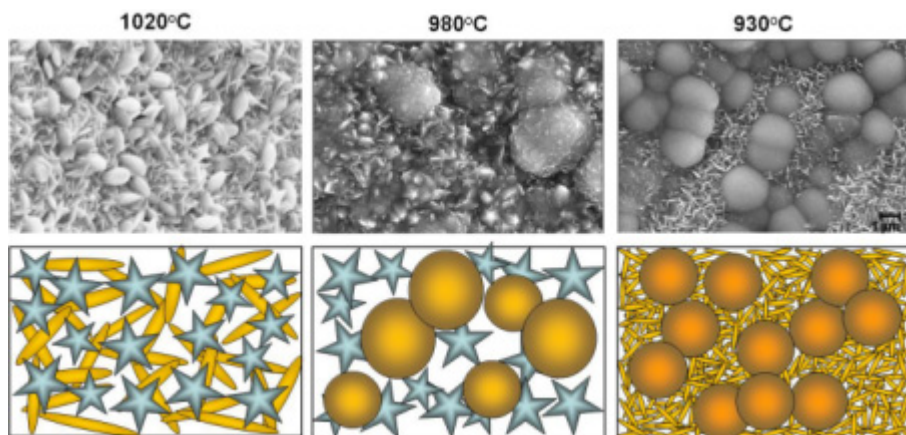


Fig.5. Influence of the deposition temperature on the morphology respectively microstructure of HT-TiCN. Basis of the nanolock coating from Boehlerit.

### Simultaneous deposition of two phases by CVD

First investigations for simultaneous deposition of hard materials were executed with  $\text{Al}_2\text{O}_3$  and TiC [31]. Due to the rather different chemical reactions for  $\text{Al}_2\text{O}_3$  and TiC by CVD it was not possible to deposit mixed layers of high quality and up-scaling for industrial production was impossible. Later the simultaneous deposition of TiC and  $\text{TiB}_2$  was successful on laboratory scale but again these coatings were not realized for industrial applications [21].

### The TiCN based Boehlerit coating „NANOLOCK“

A breakthrough for mixed layers was reached by reducing the crystal size of both phases to the range of nanometers. By changing the CVD deposition parameters it was possible to influence nucleation and growth of TiCN crystals with different composition.



This yielded in a specific microstructures and surface morphologies (Fig.5.) [32]. A core-shell structure was formed with higher Nitrogen concentrations in the core and higher Carbon concentrations in the shell respectively [33]. These types of coatings show best results for tube deburring and continuous turning of steel [34]. Due to its good adhesion to subsequent coatings it was named “nanolock”.

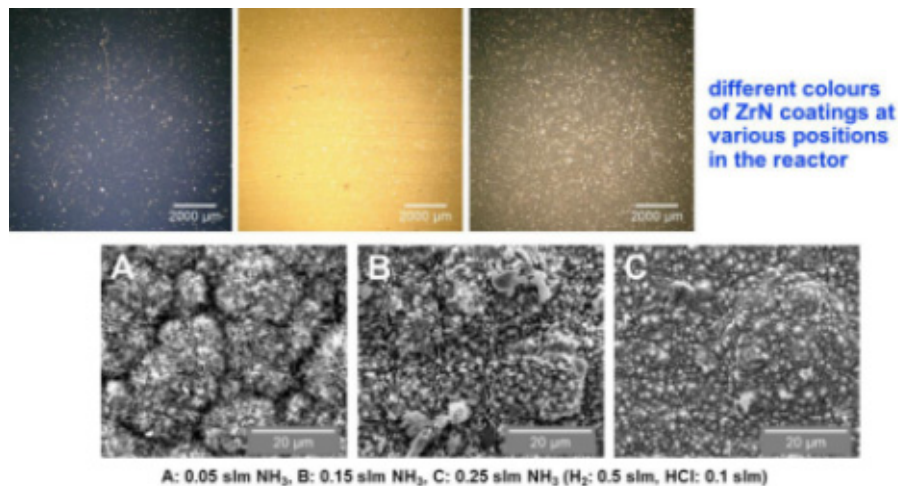


Fig.6. ZrN coatings deposited at 900°C.

### Corundum, $\alpha$ - $\text{Al}_2\text{O}_3$ coating

The corundum coating is most important for machining steel, due to its low thermal conductivity and high oxidation resistance. The  $\alpha$ - $\text{Al}_2\text{O}_3$  deposition process has to be performed above 1000°C to achieve the corundum phase. For the coating formation it is not possible to introduce the precursors ( $\text{AlCl}_3$  and  $\text{H}_2\text{O}$ ) directly in the reactor, because of powder formation. To permit the slowly formation of  $\text{H}_2\text{O}$  the reverse watergas shift reaction ( $\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$ ) is used (Fig.3) [22, 23, 24].

In various works nucleation and growth of  $\alpha$ - $\text{Al}_2\text{O}_3$  on different substrates [25] and the use of different precursors was studied [26]. In addition the conditions and parameters for  $\text{Al}_2\text{O}_3$  deposition were optimized for industrial processes [27]. During this research it was found that  $\text{H}_2\text{S}$  addition to the process results in more homogeneous coatings. This can be explained by influences on the reaction kinetic of the reverse watergas shift reaction [28]. To modify the microstructure of the  $\alpha$ - $\text{Al}_2\text{O}_3$  coatings also the effect of impurities was investigated [29, 30].

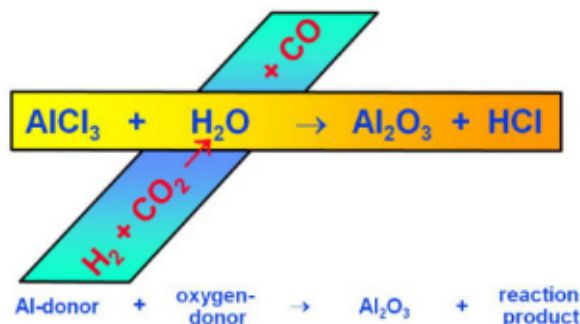
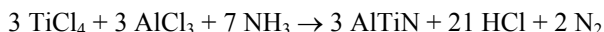


Fig.7. Chemical reactions involved in the deposition of  $\alpha$ - $\text{Al}_2\text{O}_3$  coatings by CVD.

### Coatings containing nano-crystalline lamellae of different (TiAl)N phases

At first coatings containing mixtures of Al and Ti were realized by the invention of (TiAl)N PVD-coatings [35, 36]. These coatings are composed of homogeneous mixed crystals which pass through a spinodal decomposition, into TiN and AlN at increased temperatures [37]. This is responsible for the so called age hardening effect of (TiAl)N and the high performance in milling operations.

To realize the advantages of CVD for industrial mass production, a process for the deposition of (TiAl)N was investigated and realized [38, 39]. This special coating is deposited by MT-CVD at temperatures  $<850^\circ\text{C}$  and pressures  $<50$  mbar. The overall reaction for the deposition of AlTiN is:



Due to higher Al concentrations in these coatings the material is called (AlTi)N. Intense TEM investigations pointed out that not a single phase was deposited but a nano lamellar composite (Fig.8.) [40]. Different phases (w-AlN, c-(TiAl)N or h-(TiAl)N) with a spacing between 6 and 8 nm were measured. The detailed chemistry of the CVD mechanism requires further investigation; however the coating shows high performance in milling of cast iron and steel to which point two milling grades have already been launched on the market.

### Multilayer coatings to optimize the wear resistance

Wear resistance and tool life are strongly influenced by the machining conditions and the correlations are complex. New coating sequences are created to increase the performance of tools for selected applications [41, 42].

At first multilayers were deposited to increase the adhesion between substrate and coating.  $\alpha$ - $\text{Al}_2\text{O}_3$  layers deposited directly on hardmetal tools exhibit a low adhesion, therefore an intermediate TiC layer was deposited [43].

Another reason for the use of multilayers is the reduction of the crystal size within the coatings. During every change in the material new nucleation of crystals is promoted, resulting in a smoother surface or rather smaller roughness [44]. Furthermore the internal stresses caused by different thermal expansion coefficients of substrate and coating materials can be balanced [45].

In praxis it is hard to distinguish which reason is dominant for the good performance of a multilayer coating. In Fig.9 a typical multilayer coating for cutting operations is shown. The nanolock coating described above is located below the  $\alpha$ - $\text{Al}_2\text{O}_3$  layers. Fig.10 shows the evolution of industrial multilayer coatings with time for cutting operations of steel.

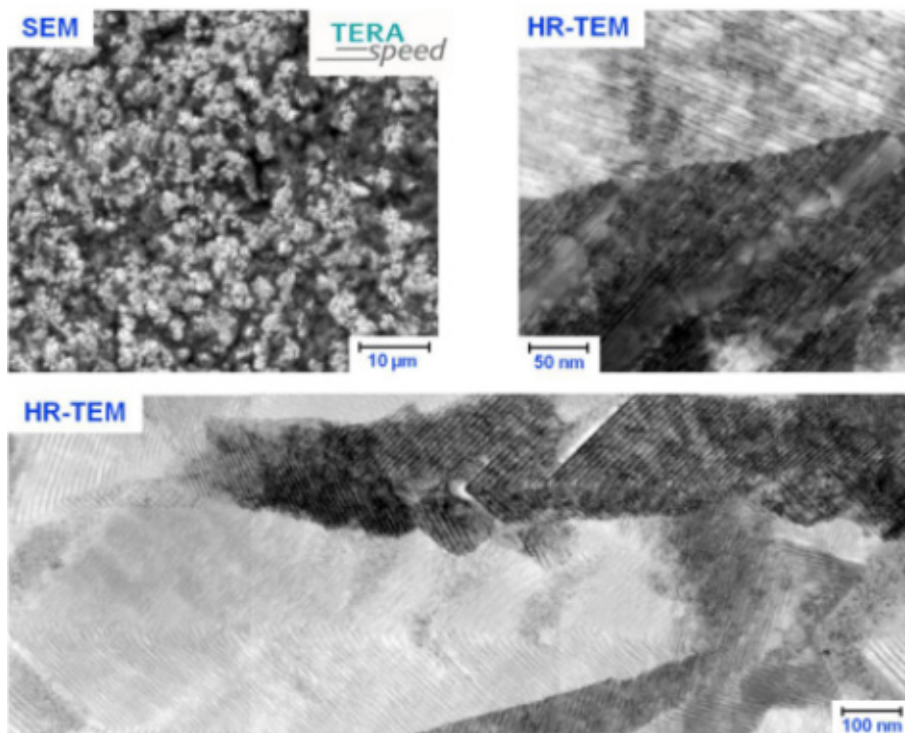


Fig.8. CVD (AlTi)N coating with nano-lamellar microstructure (Boehlerit GmbH).

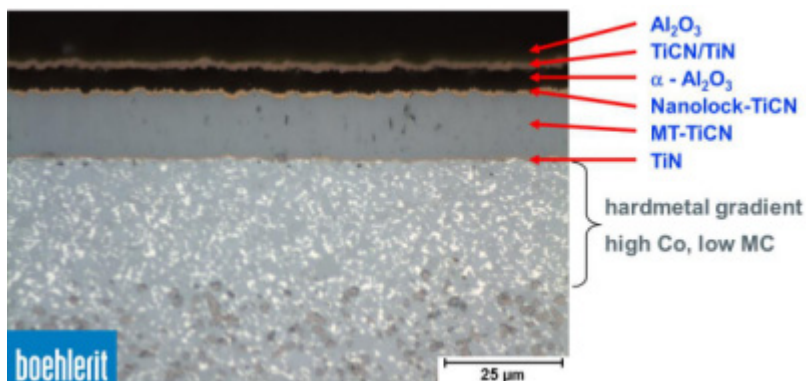


Fig.9. Typical CVD multilayer for cutting applications.



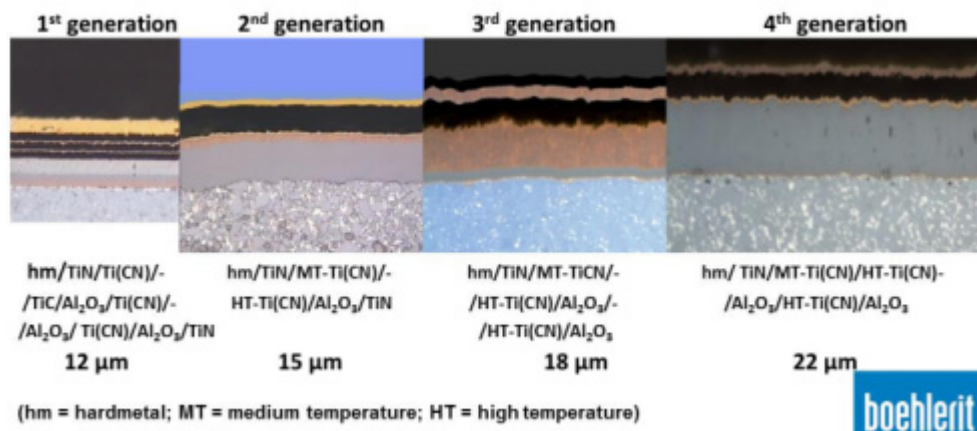


Fig.10. Evolution of CVD multilayer coatings on hardmetal substrates for cutting steel.

## CONCLUSION

In spite of the long history of CVD coatings there are still challenges for further research. The deposition of novel ss-mixed crystals, nano-crystalline materials or nano-crystalline mixtures of phases can result in interesting properties of coatings and open the door for new applications. For CVD coatings we have to consider, that for every change in the chemical reactions the deposition parameters have to be newly optimized. Therefore a good cooperation between research institutes and industry is helpfull to investigate novel and unique coatings respectively products.

## Acknowledgement

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