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Evolution of conventional hard coatings for its use on cutting tools

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ABSTRACT

The investigation of hard materials started already in the 1930s by depositing TiC, although it took until the 1950s that coatings were deposited on steel substrates and further 20 years till the first commercial TiC coatings on hardmetal tools were available. The development of coatings was deemed necessary because conventional hardmetal tools were no longer cost-effective for its use in the new generation of metal working machines. However it was not until the introduction of TiN and Ti(CN) that the machines could be used to their full capability. Further progress for hard coatings was the development of CVD processes for industrial deposition of other compounds like Al_2O_3 , ZrN, Zr(C,N), Ti-Zr-C, TiB₂, various Ta_xC_y - and Cr_xC_y -layers. Parallel to CVD the development of PVD coatings started in the 1980s. The next step was to control the microstructure of the hard coatings. The crystal size could be varied by changing the deposition temperature and adding impurities. Medium temperature (MT) and Plasma CVD processes were developed. For improving cutting tool performances various coatings were combined to multilayers like TiN/MT-TiCN/Al₂O₃/TiN. The newest investigations are interested in nanostructured coatings mixing two phases within one layer. (Al,Ti)N-coatings with high Al-content show great potential and are one example developed during the last years.

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1. History of hard CVD coatings

Chemical Vapor Deposition (CVD) started in the 19th century using the Mond process for nickel production and with the production of lamp filaments. In the early 20th century metals for applications in the lamp industry were deposited from the gas phase by Van Arkel [1].

In the 1930s, Moers [2] started to investigate hard materials by depositing TiC.

The first TiC coatings were deposited on steel substrates by Pollard, Woodward [3] and Münster, Ruppert [4] in the 1950s. It took further 20 years till Krupp Widia launched the first commercial TiC coating on hardmetal tools.

In 1960 the term CVD was introduced to distinguish "chemical vapor deposition" from "physical vapor deposition" (PVD) [5].

In the 1970s at the "Technische Hochschule Wien"; Prof. Richard Kieffer started with TiN deposition by CVD [6]. D. Fister (1970) [7] described a TiN coating in his doctoral thesis. The typical concept of his CVD apparatus and a TiN coating are shown in Fig. 1. Based on this work various Ti(C,N) coatings were developed [8].

The next large step was done by Benno Lux's group at Battelle Geneva, Switzerland by inventing the CVD process for α -Al₂O₃. In 1971 [9] Sandvik Coromant took over these patents.

In the 1970s the progress was rapid and many different coatings and combinations of coatings called multilayers were developed [10,11].

Development of PVD coatings for tools started in the 1980s and at first TiN on steel was commercially available. An early presentation of the variety of PVD processes was given by Rother and Vetter [12].

The following compilation concentrates on CVD coatings with examples from Technische Universität Wien and Boehlerit GnbH.

2. CVD deposition of hard coatings

Due to the chemical reactions involved in CVD the deposition process had to be optimized separately for every hard material. The precursors and deposition conditions which allow layer growth without powder formation had to be found [13].

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.

$$TiCl_4 + CH_4 \rightarrow 2TiC + 4HCl$$

 $2TiCl_4 + N_2 + 4H_2 {\rightarrow} 2TiN + 8HCl$

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R. Haubner et al. / Int. Journal of Refractory Metals and Hard Materials xxx (2016) xxx-xxx

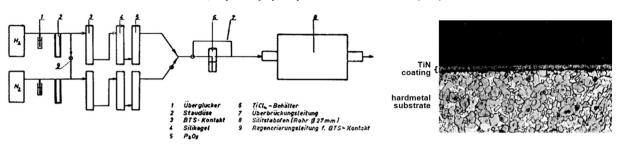


Fig. 1. First CVD arrangement for deposition of TiN coatings from 1970 and cross section of a TiN coated hardmetal substrate [7].

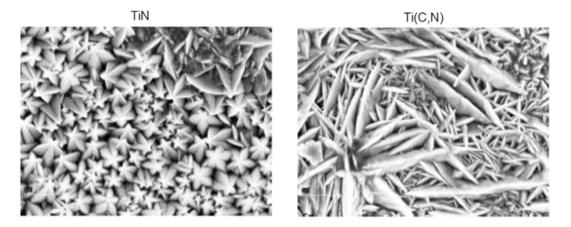


Fig. 2. Surface morphologies of TiN and Ti(C,N) coatings (Boehlerit GmbH).

These reactions can also be used for elements like Zr, Hf, Cr and Ta. The differences are mainly in the properties of the corresponding precursors [14,15,16]. Especially the vapor pressure of the precursors is important for introducing the compounds into the reactor. For example to

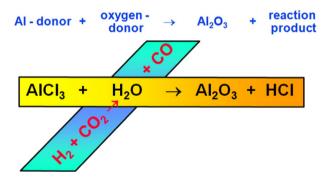


Fig. 3. CVD reaction for deposition of Al_2O_3 and water formation from the hydrogen shift reaction.

add Cr to Al based coatings the complex compound Cr(AlCl₄)₂ was investigated [17,18].

By adding carbon and nitrogen simultaneously Ti(C,N) can easily be deposited (Fig. 2). Instead of methane and nitrogen it is also possible to use organic compounds containing both elements (e.g. acetonitrile) [19]. The use of acetonitrile also allowed a decrease in deposition temperature and medium temperature (MT) deposition was introduced [20].

In case of the α -Al₂O₃ deposition process, the situation was much more sophisticated because the necessary compounds for layer growth (AlCl₃ and H₂O) cannot be mixed and introduced in the reactor primarily. The hydrogen shift reaction (CO₂ + H₂ \rightarrow H₂O + CO) is used to slowly produce water inside the reactor and thus powder formation can be prevented (Fig. 3) [10,21,22,23].

In further works nucleation and growth of α -Al₂O₃ on different substrates (Fig. 4) [24,25] and the use of various precursors was studied [26]. In addition the conditions and parameters for Al₂O₃ deposition were optimized for industrial processes. [27]. During this phase of research the use of halides (AlCl₃, AlBr₃ and AlJ₃) and alternative gas phases was investigated (Fig. 5) [26]. Several years later it was found

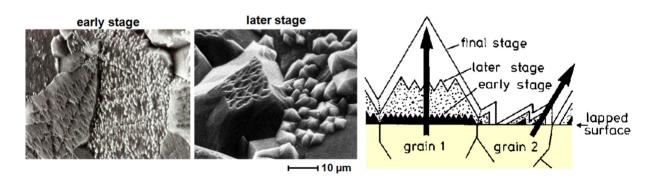


Fig. 4. Al₂O₃ CVD deposition on Al₂O₃ ceramic substrates showing the crystal growth during CVD deposition [24].

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