Effect of nanostructured multilayer coatings on functional properties of tools

Wpływ nanostrukturalnych powłok wielowarstwowych na właściwości użytkowe narzędzi

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State of the art of deposition of wear resistant coatings on cutting and cold forming tools is briefly reported. Some the PVD arc coatings developed and deposited at the Institute of Advanced Manufacturing Technology (IAMT) are discussed. The coatings' structures are presented and the multilayer architecture in micro and nano-scale is revealed. Some results of PVD arc coatings developed and deposited at the Institute are presented. These include nanostructured and multilayer coatings, which indicate the possibility of considerable increase in tool lives. The current trends in development of coatings are briefly discussed.

KEYWORDS: coatings, arc plasma PVD method, tools

The need for more and better tools in the manufacturing process is influenced by many factors, including the following:

- making parts of machines and other products of increasingly better quality (often associated with their difficult susceptibility to processing);
- striving for ever more economical technological processes (this involves the use of high-speed machining and high efficiency, which is of particular importance in mass production, such as in aeronautics and automotive industries, as well as medical technology);
- taking into account increasingly high ecological requirements (e.g. limiting the use of metalworking fluids).

The basic materials used for cutting tools are cemented carbides and high-speed steels (predominantly the former). Ceramic materials, including super hard (PCD, PCBN), are much less used. In turn, the working parts of machining tools for cold working are usually made of tool alloy steel or high-speed steel, and much less - cemented carbide. In the case of tool materials - both for machining and cold-working - very fine and fine-grained cemented carbides are used nowadays, while in the case of steel – PM steel grades.

Dynamically developing techniques of coatings' deposition on working parts of tools with high wear resistance exert very considerable effect on the economic efficiency of the production process. Coatings also lower friction coefficients and eliminate crack initiation, which is the main reason for using coatings in specific cases on ceramic materials of high and very high hardness.

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Coating deposition methods

Coatings intended for working parts of tools generally can be divided into CVD (*chemical vapour deposition*) and PVD (*physical vapour deposition*) methods.

The CVD method, which involves the chemical reaction of the gaseous atmosphere components, produces a thin, hard layer on the tool surface. This process can be carried out at atmospheric pressure at a temperature of 900-1100 °C (APCVD - *atmospheric pressure*). When using reagents, the process temperature can be lowered to 800-850 °C (MTCVD - *medium temperature*) or pressure to 1-5 kPa (LPCVD - *low pressure*). By electrical activation of gaseous reagents applying glow discharge or high frequency currents, the process temperature can be reduced to 400-600 °C (PACVD - *plasma assisted*) [1].

The PVD method involves depositing thin layers by physical deposition from the gaseous phase, which typically takes place at a significantly reduced pressure of the order of 0.1-1 Pa at temperatures around 300-700 °C. Existing variants of the PVD method in simple cases differ in the way of supplying the heat required to evaporate the deposited material (resistive, inductive or laser heating, or electron beam bombardment), and in more complex cases in the method of obtaining an ionized gaseous phase, i.e. plasma (PAPVD), unlike the processes of depositing layers from the non-ionized gas phase, i.e. vacuum evaporation. One technique to obtain plasma is thermal evaporation (ion plating methods). Plasma can also be obtained by evaporating the metal and ionizing its vapour by cathodic arc at the site of its formation (PVD arc-plasma method - *arc deposition*). Another way to obtain a plasma is to knock out particles of deposited material from the cathode by bombarding with high energy ions (*sputter deposition*), e.g. by producing a properly formed magnetic field (*magnetron sputtering*). There are also various combinations of basic PVD coating methods [1].

In the PVD arc-plasma method, cathode material evaporation is effected by high-current arc discharge: continuous (as in the modernized NNW-6.6 equipment owned by IAMT – Fig. 1) or pulse. Plasma with a high degree of ionization (about 90%) is produced. The anode is the walls of the vacuum chamber.

Targeting and increasing the kinetic energy of ions is achieved by polarizing with a negative voltage of the substrate on which the coating is applied [1-3].

The high degree of plasma ionization in arc processes distinguishes them significantly from magnetron sputtering and ion plating methods, in which materials forming the coating are composed, among others, of molecules. High-energy ions produced in the arc-cathode process lead to higher density coatings at a relatively lower application temperature, as compared to other PVD processes [4].

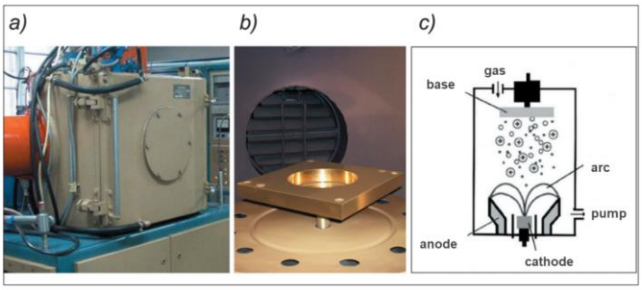

Fig. 1. View of the chamber (*a*) of the PVD arc-plasma device owned by IAMT; inside the chamber - a part with deposited coating (*b*) and the principle of the device operation (*c*)

Table I. Basic types of modern cutting tools [1]

Coating type (most commonly applied deposition method)	Coating structure	Hardness HV0.05 (dry friction coefficient of steel)	Maximum operating temperature °C	Advantages	Exemplary application of the coating to the cutting edges of tools for machining
TiN (PVD)	Monolayer	2300 (0,4)	600	General purpose	High-speed steel tools for the machining of carbon and alloysteels and cemented carbides for machining of these steels and copper - especially for threading tools
AlCrN (PVD)	Monolayer	3200 (0,35)	1100	High resistance to oxidation and good hot hardness	Tools of high-speed steels and carbides for milling steel and cast iron and of nickel and titanium alloys (including for machining gears wheels); this coating can also be used on PCBN tool blades for machining high strength steels and hardness (> 52 HRC)
AlCrN (PVD)	Multilayer	3200 (0,3)	1100	High resistance to oxidation and high hot hardness	Tools of high-speed steels and cemented carbides for drilling or reaming of steel (including stainless steel), cast iron,aluminum and titanium alloys, bronze, brass and copper
TiCN (PVD)	Gradient	3000 (0,4)	400	High hardness and good mechanical strength	Tools of high-speed steels and carbides for steel threading (<52 HRC, including stainless steel), nickel alloys, brass and bronze; coating for milling with cooling, e.g. steel gears
TiAlN (PVD)	Nano-layer	3300 (0,3–0,35)	900	Very high hardness and very high oxidation resistance	Tools of high-speed steels and cemented carbides for milling, boring and threading of carbon steels with hardness up to 52 HRC, stainless steel, cast iron, nickel, titanium and aluminum, brass, bronze and copper; tools for machining toothed wheels of steel hardness up to 52 HRC (including stainless steel), cast iron, brass and bronze
AlTiN (PVD)	Monolayer	3300 (0,4)	900	Very high hardness and very high oxidation resistance	Cemented carbide tools for turning and milling high strength steel and hardness >52 HRC and stainless steel as well as titanium and nickel alloys; For mainly drilling nickel alloys and for threading primarily steel >>52 HRC; high-speed steel and carbide tools used in machining gears for carbon and alloy steel with a hardness up to 52 HRC
TiAlN + WC/C (PVD)	Multilayer	3000 (0,15–0,2)	800	High hardness and high resistance to high temperature and favorable lubrication and sliding properties	Cemented carbide tools for turning aluminum and its alloys, brass, copper and bronze; high-speed steel tools for milling and threading of aluminum, brass and bronze alloys; thiscoating can be used in machining brass and bronze gears
WC/C (PVD)	Lamellar	1000–1500 (0,1–0,2)	300	With relatively low hardness - very low coefficient of friction (good sliding properties)	Tools of high-speed steels and cemented carbides for the machining of aluminum and its alloys with silicon content of less than 6%
Diamond (CVD)	Monolayer	8000–10 000	600	With super high hardness - high chemical stability	Cemented carbide tools for turning, milling, drilling and threading graphite; micro-machining tools (e.g. milling)
Diamond (CVD)	Nano-crystalline	8000–10 000	600	With super high hardness - high chemical stability	Cemented carbide tools for the machining of composite materials reinforced with carbon or glass fiber and aluminum and its alloys containing silicon

Types of coatings

Due to the structure of coatings deposited on the working parts of tools, they can be divided into single-layer (monolithic, composite, gradient) and multilayer (microscale, nanoscale, superlattice). These coatings can take the form of nitrides, carbides, carbo-nitrides, oxides and be multi-component. Multilayered coatings can consist of several, dozens, and even several thousand layers (in the latter case a few nm thick). Many layers of the coating give more favourable stress distribution and better fracture toughness, because the crack energy is dispersed by deflection and branching [1]. Multilayered coatings on the microscale, applied by the PVD technique, consist of several functional layers. They may be (in order from the substrate) e.g.: metallic adhesive layer (e.g. Ti, Cr, Mo, Zr), basic layer of high hardness and possibly low stress levels (e.g. TiN, CrN, ZrN, TiCN), heat blocking layer (e.g. TiAlN, TiZrN) and (on the surface) layer with low friction coefficient (e.g. Cr, CrN, TiN) [5]. PVD coatings are increasingly being developed as multilayer nanostructured coatings, which provides to tools, among others [1]: optimum hardness to internal stresses ratio (high tool geometry stability and its uniform wear), higher thermal and chemical resistance (dry machining capability with higher cutting speeds, less groove wear), better sliding properties (improved chip formation, higher quality of processed surface) or greater wear resistance (reduction of tool costs).

Phase formation and their separation in multiphase and multilayer coatings during the coating application process results in extraordinary coating properties, such as high hardness, much higher than that of the coatings or layers, especially for nanostructured ones [6-8].

Substances that are part of multilayer coatings are crystalline or amorphous; the coating is also a mixture of amorphous and crystalline components. Depositing hard PVD coatings is accompanied by the formation of phases, between which different relationships occur, namely:

- total mutual solubility (e.g. TiN-TiC, TiC-WC),
- total lack of miscibility (e.g. TiC/Ag, WC/Ag),
- coexistence of crystalline phases with amorphous phases (e.g. nanocrystalline grains (nc) of TiN with amorphous a-SiNx phase),
- coexistence of crystalline and amorphous phases and the presence of several different amorphous phases (e.g. thin WC-SiC films showing a significant diversification of degree of amorphous and crystallinity, depending on the SiC content) [9].

By selecting the appropriate structure and the specific phase composition of multiphase coatings, their properties can be modified, for example, to increase hardness and reduce friction coefficient [5].

Table 1 shows a list of basic types of modern cutting tools. Most of the presented coatings are deposited as PVD thin films. CVD and hybrid methods are also used. Diamond coatings are generally deposited by CVD, although research is under way to obtain these coatings by the PVD method. Coating depositing companies attribute unique and proprietary trade names to them.

In addition to universal TiN coatings for plastic forming, used are also the following coatings: TiCN, Al-TiN, TiAlN, CrN and CrC. Furthermore, coatings with very low friction coefficient (of the order of 0.10-0.15), such as diamond-like carbon coatings (DLC) and hard coatings containing sulphides – e.g. molybdenum disulphide, which acts as a solid lubricant, are worth mentioning. Based on information materials [1], it can be thought that TiCN and TiN coatings are the best solution for all types of metalworking tools; the same type of coating is recommended for brass and magnesium alloys, while CrN coatings for plastic forming of copper, for titanium alloys - ZrN coatings, and for aluminum alloys - ZrN and DLC. The AlCrN coating can be used for tools for cutting and stamping various types of steel and brass [10].

In the coatings intended for both machining and cold working, different layer systems are possible, the sequence of which is determined according to the role to be played in the machining.

Examples of multilayer coatings developed and implemented at IAMT

In IAMT, micro and nano multilayer coatings are developed mainly for cutting tools (including special gear cutting hobs made of high speed steels and cemented carbides, end milling cutters and ball nose endmills made of cemented carbides and indexable inserts for turning and milling, made of cemented carbides and ceramic materials), as well as working parts of tools for cold working (e.g. punches and tools made of high speed and tool steels).

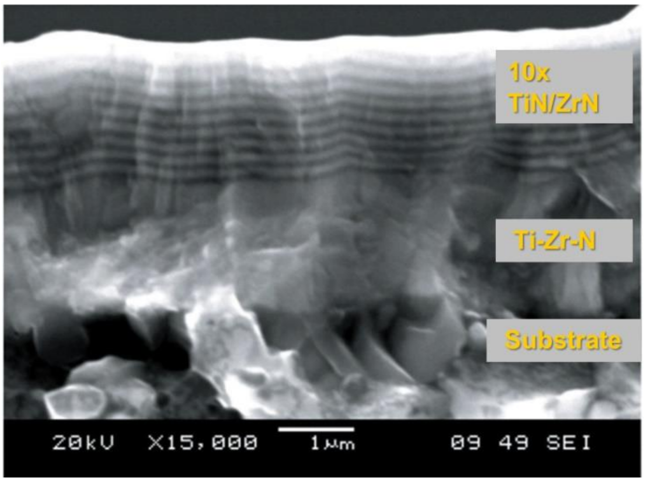

Fig. 2. Example of structure of multilayer PVD coating of Ti-Zr-N/10x(TiN/ZrN) type developed in IAMT, deposited on the cutting edge - electron micrograph.

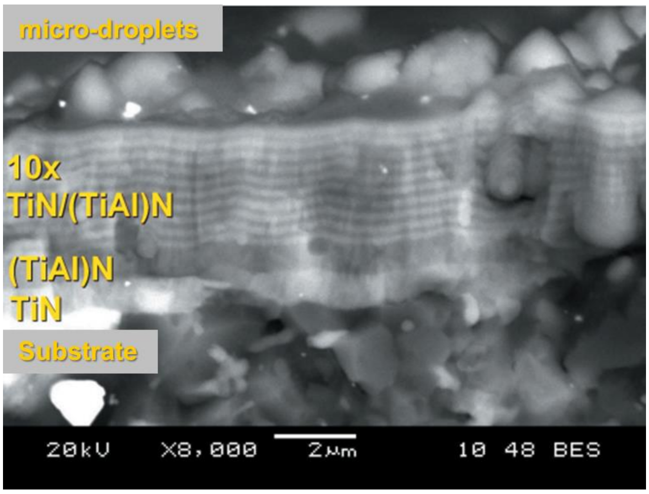

Fig. 3. Example of structure of multilayer PVD coating of TiN/(TiAl)N/10x(TiN/(TiAl)N) type developed in IAMT deposited on the cutting edge - electron micrograph.

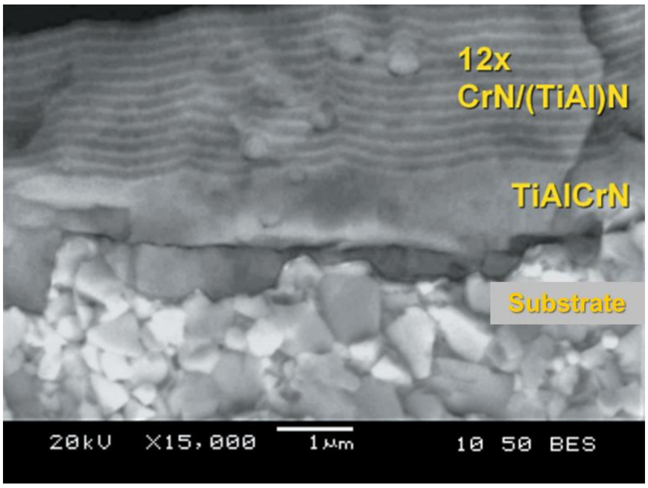

Fig. 4. Example of structure of multilayer PVD coating of TiAlCr-N/12x(CrN/(TiAl)N) type developed in IAMT, deposited on the cutting edge - electron micrograph.

Anti-wear multilayer coatings developed in IAMT, deposited by arc-plasma PVD method, consist of micro- and nanolayer coatings (listed below, from the substrate, to which Ti layer was deposited each time to obtain better adhesion - with a thickness of tens of nm):

- **Ti-Zr-N/10x(TiN/ZrN)** – Fig. 2 – coating, in which Ti-Zr-N microlayers have a thickness of about 1.5-2.5 μm, blocks the heat flow to the substrate, and due to 10 alternating very thin layers of TiN and ZrN (each with a thickness of 100-150 nm), it prevents crack propagation. The Ti-Zr-N microlayer part of the coating is nanostructured, resulting from its production technology. Due to the application of two opposite Ti and Zr cathodes and a rotary planetary table and corresponding tooling to provide cyclic shielding, Ti-Zr-N microlayer is made up of very thin TiN and ZrN nanolayers whose thickness depends on the PVD process conditions and is so small (even of the order of several nm) that these layers are not visible in the fracture images obtained with a scanning electron microscope;
- **11x(TiN/ZrN)** - 11 super-thin alternating TiN and ZrN layers (each with a thickness of 150 nm) are in this coating. Also in this case (due to the described coating technology), these layers are nanostructured;
- **TiN/(TiAl)N/10x(TiN/(TiAl)N)** – Fig. 3 – in this case, after basic microlayer (TiAl) of about 0.8 μm thickness, the (TiAl)N microlayer was deposited, which blocks the heat transfer to the substrate, followed by 10 very thin layers of TiN and (TiAl) N - each with a thickness of about 150 nm - which counteract crack propagation. Due to the coating technology, these layers - like before – are nanostructured;
- **TiAlCrN/12x(CrN/(TiAl)N)** – Fig. 4 – after basic microlayer of TiAlCrN approximately 1.5 μm thick (preceded by a 30 nm thick Cr adhesive layer), there are 12 alternate very thin layers of CrN and (TiAl) N (each with a thickness of approximately 60 nm); these layers are nanostructured;
- **(TiAl)N/12x((TiAl)N/TiN)** – as a basic microlayer blocking heat flow to the substrate, (TiAl)N was used, followed by 12 alternatively distributed very thin layers (TiAl)N and TiN, each having a thickness of approximately 60 nm, that counteract crack propagation.

In order to reveal the structure of the coatings, transverse and tapered low angle (5-6°) metallographic sections were made, which were then observed with a JSM-6460LV scanning electron microscope (Japanese company Jeol). Thicknesses of multilayer coatings and of forming them micro- and nanolayers, were determined in fractured samples using this microscope. The method of grinding a spherical crater was also used to evaluate the total thickness of the coatings and then microscopic examination of the resulting crater (according to PN-EN 1071-2:2004). The hardness of coatings and the substrate was determined on tapered low angle metallographic sections by a Vickers-type digital FM-7 micro-hardness meter (Future-Tech Corp.) with a force of 0.2452 N. Surface roughness measurements were performed using a Hommel Tester T1000 profilograph.

The hardness of the coatings was 3000-3500 HV0.025, which translated into an increase in the lives of tools with these coatings.

The research conducted at IAMT confirmed the possibility of obtaining, during turning of a hardened tool steel of grade 145Cr6 (with a hardness of about 50 HRC), 1.7-1.8 times higher tool lives of tool cutting edges made of oxide-carbide ceramics after deposition of multilayer coatings on micro and nano scale: Ti-Zr-N/10x(TiN/ZrN) or TiN/(TiAl)N/10x(TiN/(TiAl)N). For comparison, the TiN coating increased 1.3-fold the tool life. In turn, in the same steel turned with blades of cemented carbides with TiAlCrN/12x(CrN/(TiAl)N) or (TiAl)N/12x((TiAl)N/TiN) coatings, 1.4 and 3.1-fold increases, respectively, were achieved in tool life.

Fig. 5. High-speed steel gear cutting hob with module m = 10 mm with multilayer coating 11x(TiN/ZrN) deposited by PVD arc-plasma method in IAMT

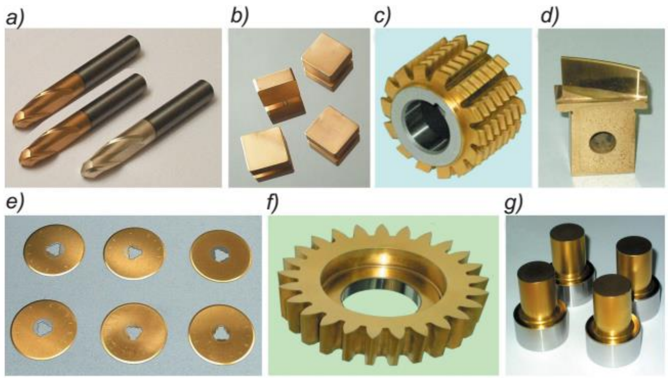

Fig. 6. Examples of tools with multilayered coatings deposited in IAMT: *a)* ball nose endmills, *b)* cutting inserts, *c)* gear cutting hob, *d)* blade for Gleason cutter head, *e)* circular cutting knives, *f)* Fellows gear shaper cutter, *g)* punches

Application of the 11x(TiN/ZrN) coatings, instead of TiN coatings, on milling cutters with module m = 10 mm (Fig. 5) resulted in lower – by about 15% - VB_{max} values than for TiN coated cutting edges. In this case, it was more difficult to demonstrate the variation in tool lives of hobs' cutting edges, due to multilayer coatings, since the differences were not sufficiently great that the number of gear wheels in one cutting hob position could be increased. Therefore, instead of cutting edges' lives, the VB_{max} flank wear land length values on their surfaces, obtained after the same cutting time, were compared. Due to the variation in the number of teeth on wheels and the machining parameters, the result of comparison was determined by relative values.

After applying the PVD arc-plasma coating, the surface roughness of the cutting edge was increased due to the presence of micro-droplets (marked in Fig. 3); their number and size depending to a large extent on the types of cathode materials and process conditions. The surface roughness index R_a increased 1.5-2 times, but this resulted in only a slight increase in R_a on the surface of the turned steel (from a few to less than 40%). The hardness of microdroplets, in which Ti, Zr, Cr, TiAl predominated in this case, were significantly lower than of the nitride coatings of these metals or their alloys - and therefore these droplets were quickly flattened or scratched off the surface of the coated cutting edge.

Examples of complex multilayer coatings developed in IAMT and based on TiN, ZrN, (TiAl)N and CrN thin films have been and still are used in the coatings described in the article and in other sequences - for coatings on tools for machining and cold working (Fig. 6).

The work on coatings carried out at IAMT is currently focused on complex nanostructured coatings deposited by PVD method, the multilayer nature and suitably selected layer sequences will result in very advantageous properties, including significantly higher wear resistance of cutting tools for machining and cold working, especially in difficult working conditions and for high quality surfaces.

Selected examples of new coatings developed in the world

Among coatings developed in recent years in the world, it is worth mentioning PVD coatings (examples are given in Table II), which are characterized by very high hardness and good adhesion.

Although high hardness is important for PVD nanostructured coatings, it is also important to minimize wear to obtain a coating with a sufficient degree of elasticity and deformation tolerance. Consequently, it is necessary to optimize both the hardness, which should normally be high enough, and Young's modulus, which in turn should have a relatively low value.

Table II. Examples of new PVD coatings developed in the world

Coating	Type of coating	Main advantages	References (year [pos.])
TiAlN/cBN ($TiAlN/B_4C/B$-C-N/cBN)	Multilayer	Super-hard (71-75 GPa), heat resistant (up to 1000 °C)	2011 [11]
CrTiAlN/cBN ($CrTiAlN/B_4C/B$-C-N/cBN)			
CrTiAlSiN/cBN ($CrTiAlSiN/B_4C/B$-C-N/cBN)			
TiAlN/VN	Multilayer superlattice	High hardness (42 GPa), roughness parameter Ra = 0.06 µm	2011 [12]
Al-Cr-O-N	Multi-component	Very high hardness (55 GPa), good adhesion	2012 [13]
Zr-O-N	Mono-layer	High hardness (44 GPa), good adhesion	
AlTiCrN (CrN/AlN/TiN)	Multilayer	High hardness (48 GPa), relativey low Young modulus (323 GPa)	2013 [14]
Ti-AlN/CrN-$Ti_{1-x-y}Cr_xAl_yN$; Zr-AlN/CrN-ZrCrAlN	Composite multilayer in nano scale	High hardness (32 GPa), good adhesion, long tool life in turning/milling	2014 [15]
(Ti,Al,Zr)N/(Ti,Al,Zr,Cr)N	Bi-layer	High hardness (41 GPa), very good adhesion	2014 [16]
(Ti,Al)N/γ-Al_2O_3	Bi-layer	Very high resistance to abrasion and adhesion wear in machining of austenitic steels	2014 [17]
TiN/CrN	Superlattice multilayer in nano scale	High fracture resistance (K1C ≈ 2 MPa · m1/2)	2016 [18]
CrN/TiN	Superlattice multilayer in nano scale	High hardness (36 GPa), high hardness coefficient and Young's modulus, low coefficient of friction, high abrasion and corrosion resistance	2016 [19]

Conclusions

Variety of commercially available tool materials, including with coatings, and continuous development in this field make it much easier to select the right tool material and coating for the process and to link more accurately the specific tool materials to groups and subgroups of processed materials.

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