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Fabrication, Structure, Properties and Application of Gradient Sintered Carbide-Steels with HS6-5-2 Matrix

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Additional information is available at the end of the chapter

Abstract

This chapter presents essential information concerning sintered tool materials containing carbides, i.e. high-speed steels and metal matrix composites, including sintered carbides and carbide steels. Gradient materials, whose properties change gradually according to their volume, are characterised. The results of investigations are presented in the final part into the structure and properties of newly developed sintered graded tool materials fabricated by the conventional metallurgy method from a mixture of high-speed HS6-5-2 steel powder and WC carbides. Investigations are described for four-layer materials, where the successive transition layers with a smaller and smaller volume fraction of tungsten carbide were constituted from the surface layer side, until a substrate layer containing high-speed HS6-5-2 steel only. The outcomes are described of structural examinations in a scanning and transmission electron microscope, an X-ray microanalysis and the results of density, porosity and hardness examinations of sintered gradient materials and the results of structure and hardness examinations of heat-treated materials.

Keywords: gradient tool materials, uniaxial pressing, sintering, high-speed steel, tungsten carbide, vanadium carbide

1. General characteristics of carbide-reinforced sintered tool materials

Technical progress in tools manufacturing is manifested, most of all, by endeavours to produce tools with better properties, and powder metallurgy plays a key role in such activities. Methods permitting to improve production quality and effectiveness have been sought for continuously. The main directions of development are centred on creating new and improving the existing methods of manufacturing; on preparing and compressing powders from which sintered tool

materials are produced; on optimising the chemical composition of materials and improving the techniques of tool surface deposition with hard antiwear layers and the techniques of surface layer constitution. The fundamental direction of development should be the optimisation of chemical composition of the existing tool materials possessing good functional properties [1, 2]. The common characteristic of various materials is that, as hardness is rising, they become more brittle. Where high cracking resistance is required, material hardness is decreasing (**Figure 1a**). Efforts are hence being made to raise the ductility of materials with higher hardness.
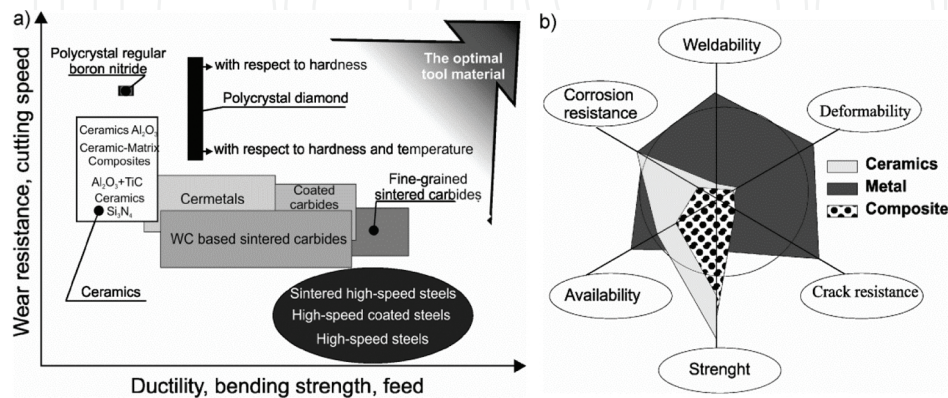

Figure 1. The schema of: (a) comparison of tool materials' properties by range and (b) selected properties of metallic, ceramic and composite materials.

Cutting tool edges are subject to various wear mechanisms in service, thus the quality of tool materials should satisfy specific requirements [1–5]. Tool materials should be characterised by:

- high hardness and possibly high ductility and high rigidity and fatigue strength to dynamic loads occurring during tool work;

- high abrasive wear;

- high resistance to the annealing activity of elevated temperature;

- good thermal fatigue resistance;

- good machining and cutting properties;

- high dimensional stability, especially important for gauges and measuring tools;

- good resistance to the harmful activity of grinding;

- good resistance to corrosive factors.

It is difficult to produce a material satisfying all the desired properties at the same time, as some of them are mutually exclusive. The application range of specific material groups has therefore been established, for which minimised wear, and consequently, service life, are the fundamental criteria for selection of the particular material type.

Tool material selection is always a compromise solution between high abrasive resistance and mechanical properties. Significant progress in production efficiency has been achieved by

applying advanced tool materials enabling machining with high cutting rates with the increased section of the layer being cut and with different geometrical characteristics of the edge. Their use as tool cutting parts is limited, though, due to a high price of such materials. For this reason, for example, sintered tool inserts are mounted on shanks or holders made of cheaper materials whose job is to transfer cutting forces. The best solution would be to combine the properties of metallic materials with the properties of ceramic materials, namely to produce metallic-ceramic composites (**Figure 1b**).

Hardness is the key criterion in tool material selection. It should be at least 30 HRC higher than hardness of the worked material. It is important because it is possible these days to work materials whose hardness is much higher than the hardness of many tool materials (e.g. steels hardened to 70 HRC). The hardness of tool materials can be substantially increased by changing their chemical composition. One of the directions may be an attempt to change the relative volume of hard reinforcing phases and a matrix in tool materials with a binding matrix. Furthermore, if such a change is controlled and takes place in the direction defined, a graded material is achievable with high hardness in the surface layer, while maintaining considerable continuity in its remaining part. The chemical composition, structure and properties can be freely customised in such materials using the powder metallurgy methods generally described in one of the previous chapters. High-speed steels (HSS) are an important group of sintered tool materials with a much more uniform structure as compared to conventional steel grades. The usable properties of the cutting edges manufactured from such materials have been enhanced by eliminating the basic drawbacks of conventional high-speed steels such as uneven distribution of components and carbide banding [2–5]. The technological and service properties of high-speed steels are largely dependent on the powder fabrication method and its granulation degree. It may therefore be misleading to compare the properties of steels with the same chemical composition without knowing the factors mentioned. High-speed steels are fabricated from powders obtained by sputtering liquid steel, with appropriate chemical composition, by means with water or insert gases, mainly argon, helium or nitride. Steel melting takes place usually in a medium-frequency induction furnace. Liquid metal is poured into a melting pot placed on the top of a chamber which is more than ten metres high. Afterwards, the liquid metal flows through a centric orifice into a chamber into which gas or water is supplied simultaneously, atomising the flowing metal stream into very fine droplets. The droplets, while falling onto the chamber bottom, are cooled with gas and solidify in the form of ball-like grains collecting on the chamber bottom. The so-obtained powder is sifted to remove oversized grains. The composition and size of powder grains is adjustable by selecting suitable atomisation conditions, i.e. temperature and a fraction of liquid metal and by changing the pressure and gas flow rate [2, 5, 6]. High-speed steel powders atomised with water feature a frayed shape and good compressibility. In respect of gas-atomised powders, they are more oxidised (have a 20–50 times higher concentration of O_2). Water-atomised powders are oftentimes additionally crushed mechanically (in vibration or ball mills) and powdered to the diameter of 0.001–0.002 mm. Finished mouldings can be moulded from such powders by the uniaxial cold pressing method and sintered until a moulding is fully compressed, or additional hot isostatic pressing can be applied [2, 4–7]. The shape of the sintered mouldings is similar to the shape of a ready product and have the relative density of over 65%. Approximately 10%

linear contraction in sintering has to be taken account of in designing moulding dimensions. Inert gas-atomised powders are ball-shaped with the diameter of 0.01–1 mm and a lower concentration of O_2, good liquidity, but poor compressibility. The most often used method of high-speed steel making is a Swedish ASP method, by ASEA-STORA company. Powder undergoes cold isostatic pressing in this method in a cylindrical container for pre-compression. Pressing pressure is about 400 MPa. Next, the moulded block undergoes hot isostatic pressing in the atmosphere of argon, at the temperature of 1150°C and under the pressure of 100–150 MPa in specially constructed Quintus presses. Bars are made from the so-manufactured semi-product by plastic working, the same as for conventional high-speed steels cast as ingots weighing several hundred kilos, and tools are produced from such bars in a plastic working and machining process [2, 4]. The method has been modified differently over time, including in STAMP and MICROCLEAN processes [5]. Powder injection moulding (PIM) and low-pressure moulding processes are employed more and more often to produce high-speed steels [8–11]. Metal powder in both cases is mixed with a binding agent to produce powder mass suitable for moulding. In injection moulding, a mixture of powders is additionally plasticised in a heated injection moulder cylinder and then injected into a mould via a nozzle. The moulded preforms are degraded thermally, as a result of which the binder is removed and then they are sintered. It was concluded based on the examinations of the structure and properties of HS6-5-2 high-speed steel fabricated by powder injection moulding, low-pressure moulding, pressing and sintering, that a common advantage of injection moulded and low-pressure moulded steels is a broader sintering temperature range in relation to steels produced by a conventional powder metallurgy method, for which it is approximately 5°C [8–10, 12, 13]. Injection moulded steels possess the lowest sintering temperature and the highest density as compared to pressed and sintered steels, resulting from a high concentration of carbon coming from binder degradation. Powder injection moulding also enables to produce ready-made tools, i.e. without plastic working and machining. Cutting tools made of sintered high-speed steels are heat treated to achieve an optimum structure consisting of fine matrix grains with identical size and carbides uniformly distributed in it. In the softened condition, the structure of sintered high-speed steels contains alloy ferrite with uniformly arranged MC, M_6C and $M_{23}C_6$ carbides and also contains M_2C carbides in steels with a high concentration of molybdenum and M_7C_3-type carbides in steels with a high concentration of silicon, and in steels containing $M_{23}C_6$-type carbides with a higher concentration of carbon [2, 4, 14–17]. Heating to the austenitisation temperature is usually performed in salt baths with indirect heating at the temperature of approximately 550 and 850°C, for 15 min. Austenitisation temperature for particular grades of sintered steels is lower by approximately 230–250°C compared to the austenitisation temperature of conventional steels with the analogous chemical composition. This is caused by the initial sizes of carbides. Fine carbides in sintered steels are dissolving faster than larger ones in conventional steels. With gradual heating, the time of austenitisation depends on the austenitisation temperature and is going down as the temperature is rising. Cooling from the austenitisation temperature is usually done in salt bath. Cooling in oil bath or in vacuum is also allowed [2, 4]. The same transformations take place in sintered steels as in conventional steels during cooling. The steel structure after hardening contains martensite, retained austenite (approximately 25%) and M_6C and MC carbides

unsolved during austenitisation, whose fraction in the structure depends on the steel grade and accounts for 20–25%. High-speed sintered steels are annealed twice or thrice, in the temperature range ensuring the maximum secondary hardness (550–560°C). The secondary hardness effect attained is caused by the precipitation of coherent M_4C_3 carbides in a martensitic matrix and by the transformation of retained austenite into martensite during cooling from the tempering temperature [4, 14–19]. The secondary hardness range in sintered steels is shifted to a slightly lower temperature than in convention steels with a similar chemical composition. The maximum hardness achieved depends on the applied austenitisation temperature [2, 4, 14–19]. The fabrication costs of sintered high-speed steels are higher than manufacturing costs of conventional steels, but the tools made of sintered steels are much more durable than those made of conventional steels. A homogenous structure of sintered steels and a sintering technology enabling to produce materials with a higher concentration of carbon and alloy elements than for conventional steels have an effect on that. Higher hardness of such materials can be attained whilst maintaining comparable ductility, and, consequently, higher abrasive resistance. Moreover, sintered high-speed steels allow for much better hot plastic forming and machining and are more susceptible to heat treatment than conventional steels. The dimensional changes taking place in such steels as a consequence of a martensitic transformation and release processes during tempering can be anticipated and considered in grinding allowances. Sintered high-speed steels are also distinct for very good grindability, whereas the steels made by isostatic hot pressing exhibit better susceptibility to grinding than those sintered in a vacuum [2, 4–6]. The tools made of sintered high-speed steels usually have better cutting properties than conventional steels with the same chemical composition. This is especially true for the treatment of steels that are hard to cut, at higher cutting rates. The indicators showing an increase in tool service life depend on the tool type and treatment conditions (including mainly the strength of the worked material) and may span between several dozen to several hundred per cents as cutting speed is rising. Additionally, it is apparent by analysing the relationship between manufacturing costs of cast and sintered high-speed steels over the last years that the manufacturing costs of sintered high-speed steels are decreasing and are approximating the manufacturing costs of conventional high-speed steels and coincide for some grades of such steels.

Tool materials with a binding matrix represent another important group of sintered tool materials. These include particulate-reinforced sintered metal matrix composites in which sintered carbides are the basic group [2, 5, 20]. Sintered carbides are also considered to be, apart from high-speed steel and carbide steels, a group of materials based on carbides of transition metals. Such classification derives from the volume fraction of carbides in the material structure [2, 4, 20]. The main components of conventional sintered steels are tungsten carbide WC and cobalt, used as a binder metal. The sinters of hard carbides of high-melting metals such as VC, TiC, TaC, NbC are also considered to be sintered carbides and nickel or iron can also be a metal matrix apart from cobalt. The carbides mentioned are distinct for their high hardness (1900–2500 HV), critical for good abrasive wear resistance of sintered carbides. However, as such carbides are highly brittle, this is limiting their application as the materials exposed to the acting dynamic external loads, e.g. in the use of cutting tools [2, 4]. As the relative volume of carbides is growing, so is growing hardness and resistance of sintered carbides to

wear in cutting, bending strength is declining, though. A higher relative volume of a metal matrix raises bending strength and reduces hardness and wear resistance in cutting [4, 5, 20]. TiC carbide improves hardness and wear resistance in cutting, but at the same time decreases the bending strength of sintered carbides. NbC and TaC carbides raise hardness at ambient and at elevated temperature, and also the bending strength of sintered carbides [2, 4]. Various aspects of fabrication and technical applications of sintered carbides are discussed in a few chapters of the book, hence only certain related aspects are touched upon in this chapter.

The manufacture of products from sintered carbides is a complex technological process. The first step in the process is to produce carbide powder by the numerous methods of: melting, carburising of powders of pristine metals, metal oxides or hydrocarbons in the solid state by sintering, carburising of powders of pristine metals, metal oxides or hydrocarbons with gases containing carbon, precipitates of gas phase, carbide precipitations from melted metals or electrolysis. Next, carbides are usually cleaned and crushed. Carbide products are manufactured by powder metallurgy methods by pressing and sintering and hot pressing [4–7, 20]. The following technologies can also be employed: pressure sintering technologies with induction heating, extrusion of bars and sleeves from powders with plasticisers added, and casting in a suspension. Such methods enable to form large-size, high-density products and such with untypical shape for sinters, e.g. rods or plates [2, 4–7, 20]. The sintered carbide grades most commonly produced are characterised by a conventional structure with carbides sized several micrometres or with carbides with their size smaller than 1 μm. The properties of sintered carbides are principally dictated by the chemical composition of carbides, by the shape and size of their grains and by the volume fraction of carbides in the structure. The most significant property of sintered carbides is their hardness in high temperature, allowing cutting at high rates.

Sintered carbides are finding their applications most of all as materials for cutting iron alloys, non-ferrous metal alloys, non-metal materials and rocks and for plastic working tools. Some grades of sintered carbides featuring a high concentration of cobalt are utilised as constructional materials of machine parts from which good abrasive resistance is required, especially at elevated temperature, e.g. slide and roller bearing parts, nozzles, guides, blades in heat machines and hydraulic plungers [2, 4–7, 20].

Carbide steels with indirect properties between tool steels and sintered carbides also belong to the group of particulate-reinforced metal matrix sintered composites. Their wear resistance versus high-speed steels is 10–20 times higher. The chemical composition of a matrix in traditional carbide steels corresponds to structural steel for quenching and tempering, stainless austenitic steel or precipitation-reinforced maraging steel. A carbide phase consists of titanium carbides TiC, which are practically insoluble in a steel matrix in heat treatment. A relative volume of a matrix in a sinter is much higher than in sintered carbides and accounts for over 50% [2, 4, 20]. Carbide steels have, therefore, higher ductility than sintered carbides, and also much higher abrasive wear resistance than tool steels. The tools made of carbide steels after sintering undergo mechanical and heat treatment (quenching and tempering). One of the chapters also describes special carbide steels with a matrix of high-speed steels with carbides of transition metals, including WC, VC, TiC, NbC and their unique manufacturing technology.

An advantage of carbide steels is the fact that their mechanical properties may vary over a broad range depending on the matrix material and the condition of heat treatment. The pressing and sintering of a mixture of carbide and steel powders or saturation of a pre-sintered porous carbide skeleton with steel are classified as carbide steel manufacturing methods [2, 4–7, 20]. Variations in the properties of a particulate-reinforced composite enables to combine reinforcement properties with matrix properties. The effective properties of a composite are thus dependent upon the properties and relative volume of the components forming it.

2. General concept of sintered gradient materials

Gradient materials are one of newer generations of engineering materials in which properties change gradually in the material volume as chemical composition, grain size, structure or atomic order are changing [2, 21–23]. Such materials are not a technically separate group of materials, but rather represent an engineering approach to chemical material structure and/or chemical composition formation. Such an approach is most advantageous when one material may ensure a diverse combination of properties which is hard to achieve, as in the case of the required high hardness, and also high ductility of tool materials [23]. The manufacture of such materials is hard, tough. A graded structure can be obtained by, among others, reinforcing a matrix with precipitates or particles having diverse properties, size and shape, and also by changing the function of the reinforcing phase and matrix. A material structure can then be achieved with properties changing continuously or discreetly. The examples of gradient structures are also observable in nature, for instance in plant and animal tissues, bones, teeth and shells [21]. A representative example of a graded structure is a bamboo stalk. It has a very strong outer surface and an elastic core. Fibre distribution changes on the stalk section, ensuring its high flexibility and strength.

The potential benefits resulting from the use of graded materials were considered theoretically already in 1972 [24]. It was not sooner than in 1984–1985 in Japan when a concept of functionally graded materials (FGM) was developed in aeronautics [25]. The use of graded materials as heat barriers in space shutters was considered. Systematic researches over the fabrication of such materials were initiated in 1987 under a research project [22, 26], and the Research Society for Functionally Graded Materials publishing the *FGM News* was set up a year later. An international conference on functionally graded materials, stimulating rapid advancements in materials production, has been regularly held in Sendai, Japan, since 1990 [27]. Many of the researches on graded materials are addressed to modernise and improve their manufacturing technologies already known and to search new low-input technologies with high reproducibility and performance. As growing interest in graded materials has been observed, it becomes necessary to carry out research on optimising the chemical and phase composition of such materials and their manufacturing technology.

Graded materials can be classified according to different criteria, usually in terms of structural criteria, manufacturing methods and application. With regard to their application, such materials can be divided into, notably, functionally graded materials [22, 26], tool gradient

materials (TGM) [28–36], gradient biomaterials and functionally graded piezoelectric materials (FGPM). Gradient materials, according to the type of combined materials, can be grouped into, particularly [37]: metal material-ceramic material, metal material-metal material, ceramic material-ceramic material, polymer material-ceramic material. Gradient materials are also grouped by their manufacturing methods. For example, for the powder metallurgy method, which is often used, materials can be produced with porosity gradient or porosity size, chemical composition in a single-phase material, volume fraction of phases or grain size in a material with two or many phases [22, 27]. Gradient materials can also be grouped according to gradient distribution (one-, two- or three-dimensional) or gradient range (gradient situated in a particular area, or extending in the whole section).

Different physical and chemical methods can be used for manufacturing gradient materials. It is hard to say which one of them best fulfils its task and technical requirements resulting from a complicated structure of materials. The combination of different manufacturing methods may solve problems with production of gradient materials. The combinations of such methods depend on the state of the input material and its properties. Apart from the cases where an input material is in the gaseous or liquid state and by concentrating on the solid state, the use of different powder methods should be listed, allowing easily to select the input composition of a moulding [22, 37, 38]. Several key methods of gradient material manufacturing have been developed until now, such as powder metallurgy methods, and also coating deposition methods and diffusion-based methods [1, 21, 27]. The main advantage of powder metallurgy methods is that the selection of output composition of a moulding can be controlled, which allows to obtain a sinter with variable chemical composition of phases in the material volume. Gradient materials in a conventional powder metallurgy method can be produced by filling a matrix with subsequent layers of powder mixtures differing in their chemical composition, and then the mixtures are pressed and sintered. The composition of powders depends on the required properties of the fabricated material. For instance, materials can be achieved with porosity gradient, by filling a mixture of powder with various particle size or by changing compression conditions, and with pore size gradient, by differentiating the size of powder particles. A chemical composition gradient is also attainable. If a phase balance chart indicates potential solubility above the selected range of chemical composition of a gradient material, a single phase material with a mild variation of concentration is created when sintering a mixture of powders with continuous chemical composition variation. In order to achieve a gradient material structure, a condition has to be satisfied saying that the diffusion range of the differing atoms must be higher than the average size of particles [23]. Layer thickness can to be taken into account if filling is done in successive steps. The most popular group of graded materials are those with the gradient of the volume fraction of phases or grain size in a multi-phase material. Multi-component systems of phase balance are usually distinct for the limited solubility of components. The growth of soluble phase grains in heat treatment has to be considered, especially in sintering with the presence of the liquid phase. As a result, the structure of the material obtained consists of two or more phases with a gradient in the volume of the material or grain size. Although powder moulding by filling and pressing a large number of powder layers (over 5) in a die is an uneconomical process in industrial terms, it is widespread in laboratory tests [11, 27, 36, 39].

Gradient materials manufactured by powder metallurgy methods are most often characterised by a gradient step of chemical composition. Automated systems of component dosing or centrifugal force are applied to avoid uneven transition between layers. The consolidation method of input materials is largely impacting the content of the structure and the character of the chemical composition change, especially in the region of layers' boundary. A liquid phase emerges very frequently when sintering multi-phase mixtures or a chemical reaction takes place [40]. Sintering with the presence of the liquid phase usually occurs at a temperature higher than the lowest melting point of one of mixture components. A sintering process is inherent to the presence of the liquid phase. A disadvantage of the process is a difficulty to maintain a concentration gradient, which sometimes tends to disappear due to component homogenisation processes [41, 42]. This can be solved by shortening the time needed to consolidate components to avoid their homogenisation. A high-temperature synthesis is used where the heat necessary for sintering comes from a chemical reaction. Self-propagating high-temperature synthesis (SHS) is a method of synthesising chemical compounds utilising mainly the heat of exothermic reactions taking place in the system. In this method, powders are heated to the adequate temperature, after exceeding which the reaction is running by itself. The method is especially effective for a synthesis of such compounds as carbides, but also oxides, nitrides and borides. The compounds are highly refractory, for this reason, to synthesise their powders, processes are necessary most often, which are occurring at measureable speed only in high temperature of 1000–2000°C. When chemical compounds are synthesised conventionally, e.g. by a mixture of constant reagents in an oven, high heat losses to the surrounding occur and heat has to be supplied constantly from external energy sources to maintain a high temperature and the reaction running. The processes are energy- and time-consuming [1, 21, 37, 43].

Different coating deposition techniques are utilised to produce graded coatings [8, 44–47]. The most widespread ones include vacuum deposition (PVD, CVD). A non-gradual change in properties occurs between the coating and the substrate, causing a concentration of stresses in the boundary region during material production and usage. Fast degradation, consisting of coating cracking and delamination, takes place in this region as a consequence. PVD and CVD methods create an opportunity to set off unfavourable phenomena and to obtain a relatively thin layer which is between several to more than ten micrometres thick. A graded coating can be produced by dosing components which are critical for the properties of the materials and by changing residual pressure or reactive gas in the deposition chamber [1, 21, 23]. Graded coatings have broad applications due to their specific properties, such as resistance to high temperature oxidisation, erosion and abrasive wear resistance. Depending on the usage, they can be grouped into, in particular, wear-resistant coatings (WRC) and thermal barrier coatings (TBC).

Nanocrystalline functionally graded materials represent a promising direction of development in modern coatings. Advanced PVD methods, in particular pulsed laser deposition (PLD), are applied to produce mono- or multilayer coatings with a nanocrystalline structure [48]. The method has been employed successfully for producing biocompatible coatings based on TiN

and hydroxyapatite, designed for use in production of bone implants and hemocompatible materials.

Own works cover numerous investigations of graded coatings deposited onto tools produced by a PM method. Graded coatings are applied in a PVD process by reactive magnetron sputtering (RMS), by Cathodic arc evaporation (CAE), Thermionic arc evaporation (TAE), Reactive ion plating (RIP) methods and by CVD method [44–46, 49–51]. The aspects of this method are detailed in one of the chapters.

The other, commonly applied graded coating manufacturing technologies include remelting, alloying and laser cladding technologies [2, 52]. They ensure good properties of a surface layer and good substrate attachment. Due to differing substrate and surface layer properties, layer cracks in the substrate heat affected zone and in the area of surface layers occur during laser production of surface layers. Cracking can be limited or totally eliminated by applying a graded fraction of hard ceramic phases or a graded fraction of an alloying component in the surface layer. If an indirect layer is used between a surface layer and a substrate, good attachment is ensured along with high corrosive resistance, wear resistance, high hardness, ductility, plasticity and fatigue strength of a coating [53, 54]. These issues are discussed in one of the first chapters of the book. Own research into laser surface engineering using a high performance diode laser [49–52, 55, 56] have shown that alloying/laser cladding technologies ensure the highest quality, 0.1–1.5 mm thick surface layers and a very high quality of the substrate attachment. The materials achieved possess enhanced abrasive wear resistance as well as good mechanical and tribological properties. Very high resistance to thermal fatigue of materials is achieved by alloying with NbC, TaC, TiC, VC and WC carbide particles.

Thermal spraying, known for many decades, offers broad opportunities to produce graded layers. Plasma spraying (PS) was patented already in 1960 and 1962. In this method, a material constituting a layer is melted in a stream of plasma and the melted particles are directed at high velocity by a stream of plasma gas onto an appropriately prepared surface [2, 57, 58]. Plasma spraying can take place in two variants. In the first of them, a coating forming the material is supplied by one burner. In the other, a system of burners with different powders is used, allowing to produce coatings easily and efficiently. Layers with specific heat parameters can be obtained with this method, e.g. thermally insulating TBC coatings [2, 47, 59, 60] and other coatings, e.g. biocompatible ones (hydroxyapatite). The methods are also generally characterised in one of the previous chapters of the book.

Materials with a graded structure can also be constituted with heat treatment processes known for thousands of years, e.g. by hardening or thermochemical treatment processes, such as carburising and nitriding [2]. Only part of the scientific environment shares a view that a material, in which surface treatment is carried out only, without combining two different materials, should be considered a gradient material. It is true, however, that a gradient of chemical composition and properties exist in the volume of such a material. Moreover, such methods, for long, were dominant as a fabrication technique of materials with a structure changing on their surface.

There are many gradient material manufacturing processes. Modernised or innovative manufacturing methods are often found in publications concerning gradient materials. Gradient materials offer extensive application possibilities. About 200 potential uses were proposed in 1990 in a survey made by *FGM Forum*, among others in machine, car, optic and power industry and even in nuclear physics and medicine [61]. Gradient materials are broadly used for producing parts where, in the conditions of use, a high temperature gradient exists, in particular in the space and aviation industry [1, 21, 23, 37]. They are used for producing heat barriers, shell plating or rocket engine parts most often [1, 43, 59]. Gradient materials can be used in a combustion chamber of jet turbine engines where very aggressive conditions prevail for the materials used. An innovative solution is a construction of segmented semiconductor heat sensors. The sensor is built of several modules differing in a thermal and electrical conductivity coefficient. The so-produced element has its resultant characteristic almost independent from its working temperature; any changes in electrical conductivity result only from the sensor surface layer profile being formed. It is thus easy to monitor temperature by measuring voltage on the sensor electrodes. An additional advantage is sensor construction, owing to which the sensor can have dimensions of several tenths of millimetre. It is thus possible to incorporate a sensor inside the element which is diagnosed and thus protects the sensor against an aggressive environment or mechanical damage, e.g. in a jet engine combustion chamber. Gradient materials are also used for producing solid oxide fuel cells (SOFCs), where the problem is to maintain the suitable cell durability at high working temperature of about 950°C due to various thermal expansion coefficients of its particular parts. Such a cell incorporates a cathode made of $(La, Sr)MnO_3$ and a cermetal Ni/ZrO_2 anode, with permanent electrolyte in between (ZrO_2 stabilised with yttrium oxide). The application of gradient materials allows to achieve cell efficiency of even 40% higher compared to a traditionally made fuel cell. Works are in progress over gradient piezoelectric excitation elements [62]. Traditional excitation elements are highly unreliable due to materials with different piezoelectric properties. At low temperature, the connecting layer, usually made of epoxy resin, is cracking and at higher temperature is excessively creeping. Hence, efforts are made to develop gradient piezoelectric excitation elements in the system of PZT $(Pb(Zr, Ti)O_3)$/PNN $(PbNi_{1/3}Nb_{2/3}O_3)$ materials, connected diffusively [63]. Intensive studies are also held over gradient optic fibres ensuring the same light wave propagation velocity along the conductor for different modes. A core of a gradient optic fibre is made of many thousands of layers. This is aimed at simulating a smooth change of the light refractive indexes. The maximum light refractive index value is assumed on the core axis and the minimum on the boundary with the jacket. This is eliminating signal blurring to the same level as the waves propagated in larger distance from the centre are moving in the layers with a lower refractive index, hence have higher linear speed. The shape of a single mode is similar to the sinusoidal waveform. Bandwidth was consequently increased by the order of magnitude compared to a step optic fibre.

The biomedical branch is the next area of potential applications of materials with a property gradient [61, 64]. In bone surgery, ceramic materials with a porosity gradient can be used for fabrication of orthopaedic gradients, which are designed just like a living bone tissue [65–70]. The works [71, 72] describe orthopaedic implants made of hydroxyapatite and titanium. Bioactive hydroxyapatite is responsible for a strong connection with an organic tissue in such

implants, whereas titanium is used in the parts of the implant requiring high mechanical stability. Gradient and porous materials are studied in the works [66–70], applied for implants, implant-scaffolds and scaffolds manufactured by selective laser sintering, what is detailed in the respective chapters of this book.

Gradient materials may also play an important role in the machine industry, for example in a toothed gear manufacturing technology, where a body of an element should be resistant to dynamic loads, while its surface should be hard and abrasive resistant. The differing core and surface layer properties are now achieved by carburising the surface of steel toothed gears. A state-of-the-art solution can be the production of toothed gears with the inner layers made of metal, while the outer layers would consist of hard ceramics attached to metal with indirect layers. Tool gradient materials are usually designed in such a way as to ensure high abrasive resistance of tools in the working layer, while maintaining a ductile core which ensures that high dynamic loads are transferred. Sintered carbides, sintered carbide steels and sintered high-speed steels can be used as the material of a working part [1, 73–75]. An example of a tool gradient material can be a gradient sintered carbide. Such a material consists of sintered carbides WC-Co, cermetal TiCN-Ni and a thin ceramic layer made of sintered carbides [1, 74].

3. The results of own investigations into sintered gradient tool materials

Gradient material technologies have gained special importance in tool production. Cutting tool edges are subject to various wear mechanisms in service, and for this reason, special properties are required for them. The best solution would be to develop a material which, on one hand, would be characterised by high hardness, on the other, relatively high ductility. It is hard, however, to manufacture a material satisfying at the same time such contradictory properties, because as their material hardness is rising, they become more brittle. A solution to this problem may be to produce gradient materials representing a special group of composite materials. It is being endeavoured to fabricate materials with a varying fraction of hard reinforcing phases and matrix in their volume. If such a change is controlled and takes place in the direction defined (e.g. perpendicular to the surface), a graded material is achievable with high hardness in the surface layer while maintaining considerable continuity in its remaining part. A graded structure can be obtained by, among others, reinforcing a matrix with precipitates or particles having diverse properties, size and shape. The chemical composition, structure and properties of materials can be freely tailored using the powder metallurgy methods. Graded materials in the conventional powder metallurgy method can be produced by filling a matrix with the subsequent layers of powder mixtures. The mixtures differ in their chemical composition depending on the required properties of the material produced, and then the mixtures are pressed and sintered. The most popular group of graded materials are those with the gradient of the volume fraction of phases or grain size in a multi-phase material. Particulate-reinforced metal matrix composites are an important group of sintered tool materials. Reinforcement properties can be combined with matrix properties by forming the properties of composites. The effective properties of a composite are thus dependent upon the properties and relative volume of the components forming it. An example can be high-speed

steel having relatively high ductility applied onto a matrix material, and carbides with high hardness used onto reinforcing particles. The research now conducted by various research institutes is aimed at the fabrication of high-speed steel matrix composites with raised abrasive wear resistance. The works [1, 76–78] studied the effect of additives of WC, TiC, VC and NbC carbides on the structure and properties of high-speed steel matrix composites of HS6-5-2, HS6-5-4 and HS12-1-5-5 type. It was found that, as the relative volume of carbides is growing in the high-speed steel matrix, so is growing hardness and wear resistance of composites; their bending strength is declining, though.

Investigations were performed under own works [11, 28–36, 48, 79] to create a new group of gradient sintered carbide steels on a high-speed HS6-5-2 steel matrix, reinforced with hard WC carbide phases, to develop their manufacturing technology and identify their structure and properties.

The newly developed graded carbide steels were produced by uniaxial pressing and sintering in a vacuum furnace and in a furnace with the atmosphere of flowing nitrogen with the addition of hydrogen (N_2 + 5% H_2), at temperature of 1210–1270°C, for 30 and 60 min. The steels consisted of four layers, and the successive layers were constituted by decreasing a fraction volume of the reinforcing phase, until a substrate layer was obtained containing high-speed HS6-5-2 steel only. Its surface layer and transition layers contained, respectively, 25, 15 and 5% and 10, 7 and 4% of WC carbide. The powders were mixed for an hour, and powder mixtures were next filled successively into the matrix, thus producing layers with a gradually changing volume fraction of carbides in high-speed steel. The next transition layers containing, respectively, 15 and 5% of such carbides, were constituted—for the volume fraction in the surface layer of 25% of WC—and then they were pressed (**Figure 2**) and sintered, followed by heat treatment.
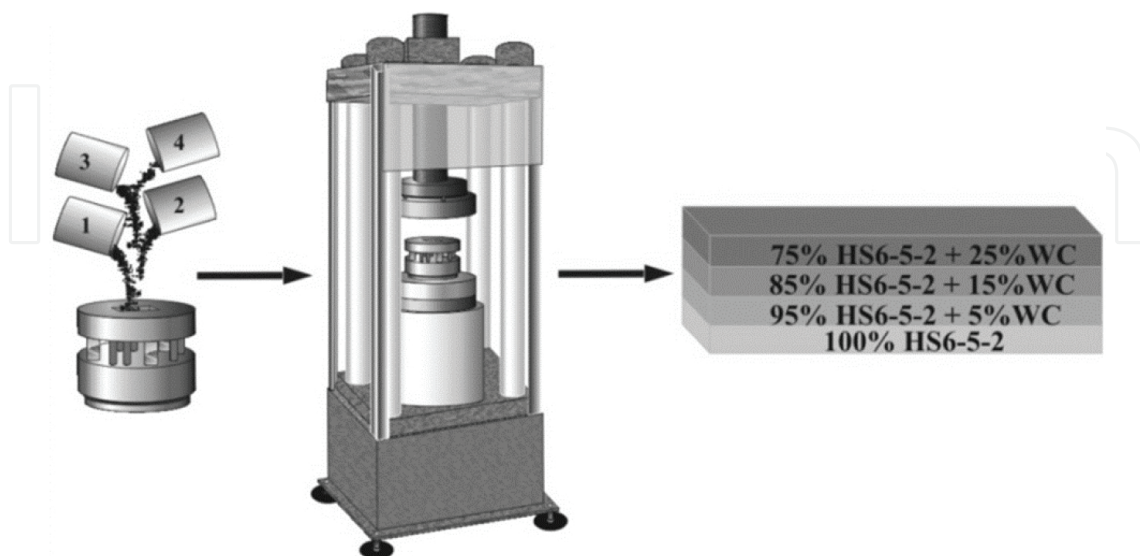

Figure 2. Moulding production scheme.

It was confirmed that a conventional powder metallurgy method—consisting of the uniaxial pressing of powder in a closed matrix and then sintering it—allows to produce graded carbide steels with the desired structure and properties. It is performed by dosing and mixing high-speed steel matrix material powders with hard carbide phases. This ensures a step-like change in the fraction of reinforcing phases in the matrix in the direction perpendicular to the surface. In addition, the newly created materials do not exhibit any cracks and delamination in the boundary zone between the layers. They are also characterised by smooth transition between the layers and show a linear variation in properties (**Figure 3**).
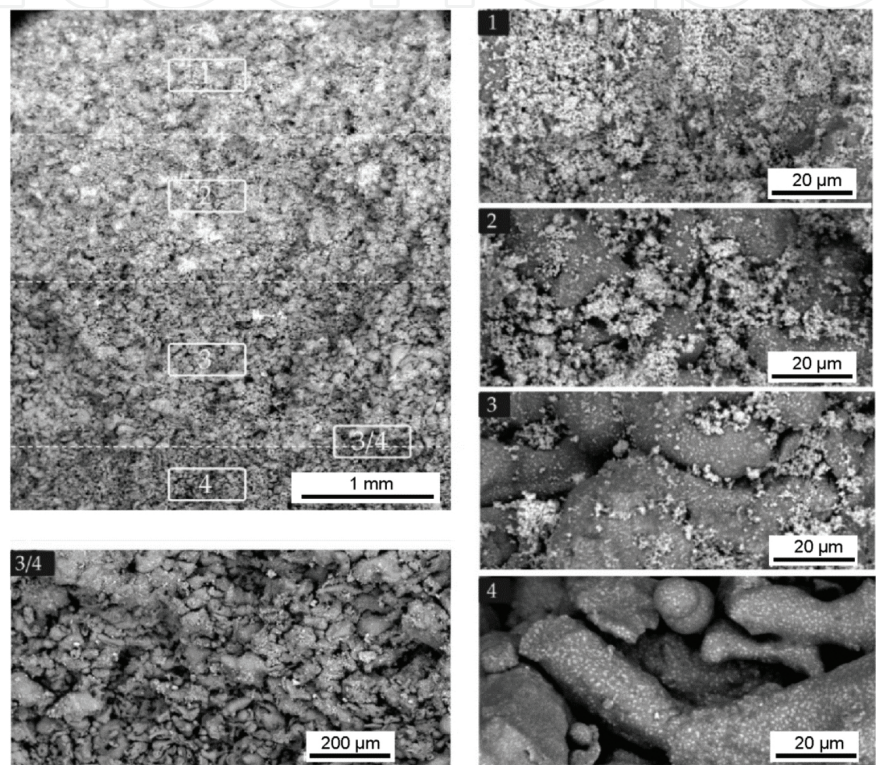

Figure 3. Moulding structure with particular layers: (1) 25%WC +75% high-speed steel, (2) 15%WC + 85% high-speed steel, (3) 5%WC + 95% high-speed steel, (4) 100% high-speed steel.
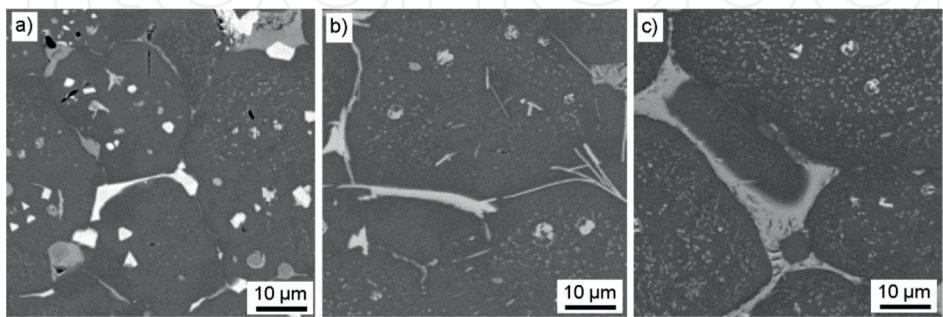

Figure 4. Structure of the high-speed steel layer of the gradient material, sintered in vacuum furnace at temperatures of: (a) 1210°C for 60 min, (b) 1230°C for 30 min, (c) 1230°C for 60 min.

The newly developed sintered graded carbide steels are characterised by a multi-phase structure composed of ferrite, primary high-speed steel carbides such as MC, M_2C and M_6C and WC tungsten carbide, introduced into carbide steels as powder. MC and M_6C carbides, depending on the sintering conditions, are distributed uniformly in the matrix or undergo coagulation and create large precipitates (approximately 2 μm) on the boundaries of primary austenite grains of high-speed steel (**Figures 4** and **5**).
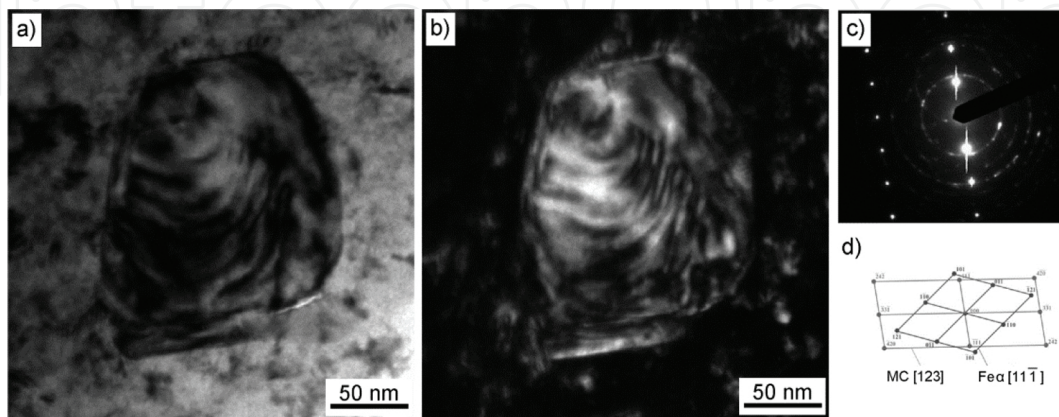

Figure 5. Structure of thin foil from the surface layer of the gradient material, sintered in vacuum furnace at temperature of 1250°C for 60 min; (a) image in the bright field, (b) image in the dark field from reflex ″\11{$\overline{1}$ MC, (c) diffraction pattern from the area as in figure (a), (d) solution of the diffraction pattern from figure (c).

Gradient carbide steels should be sintered in vacuum, at 1210°C for 30 min at a heating and cooling rate to/from the sintering temperature of 5°C/min, ensuring the material density of approximately 8.6 g/cm³ (**Figure 6a**), surface layer hardness of approximately 81 HRA (**Figure 6b**), porosity of approximately 2% (**Figure 7a**) and the substrate layer structure exhibiting no signs of remelting (**Figure 7b**).
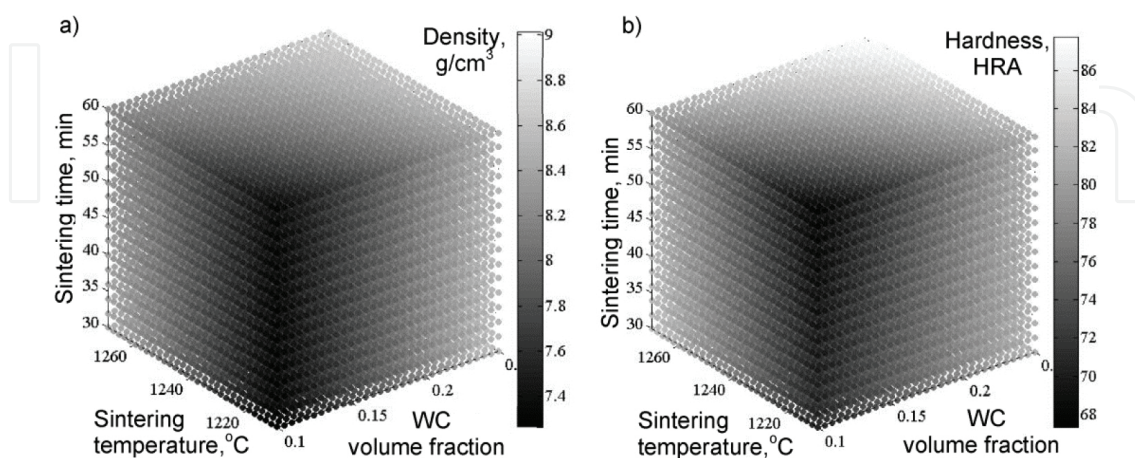

Figure 6. (a) RFP describing relationship between density and the WC volume fraction, temperature, and sintering time, for GM-HSS/WC sintered in a vacuum furnace, (b) RFP describing relationship between hardness and WC volume fraction, temperature, and sintering time, for GM-HSS/WC sintered in a vacuum furnace.
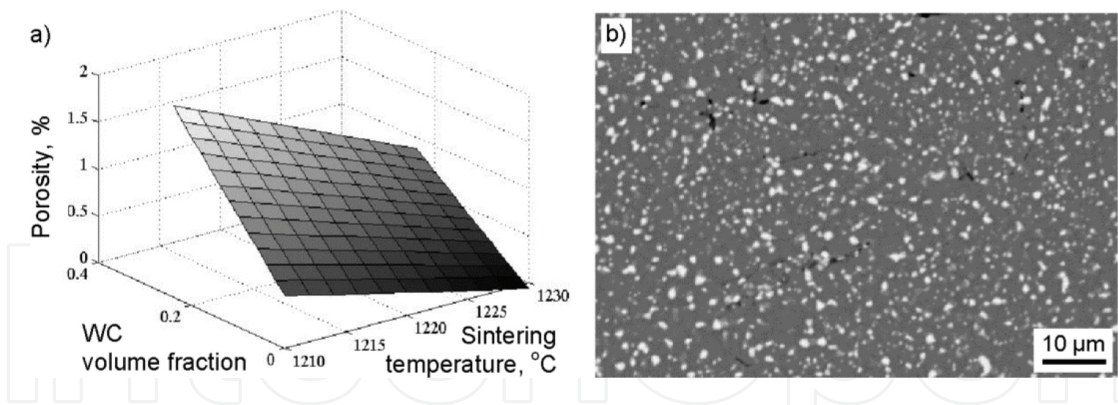
Figure 7. (a) RFP describing relationship between porosity and the volume fraction of the reinforcing phase and sintering temperature, for GM-HSS/WC sintered in a vacuum furnace for 30 min, (b) structure of the high-speed steel layer of the gradient material, sintered in vacuum furnace at temperatures of 1210°C for 30 min.

The heat treatment of the developed gradient carbide steels with a core corresponding to high-speed steel, encompassing quenching and tempering, produces a secondary hardness effect in the high-speed steel substrate layers by approximately 2–3 HRC higher than the hardness of the hardened material. The structure of graded carbide steels in the quenched condition represents martensite with residual austenite, M_6C and MC type carbides, both primary and secondary, unsolved in a solid solution during austenitising and WC carbides in the surface layer. The material austenitised at the temperature of 1120°C for 120 s, quenched and then tempered twice at the temperature of 530°C, shows the highest hardness of the surface layer of 71.2 HRC (**Figure 8**).
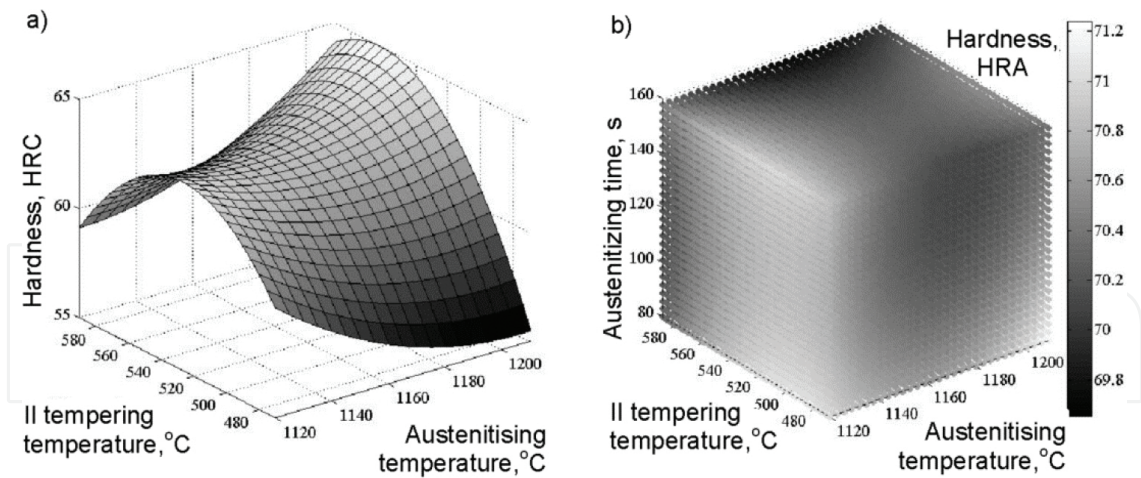

Figure 8. (a) RFP describing relationship between hardness and the second tempering temperature, and the austenitising temperature, for the high-speed steel layer of the gradient material austenitised for 120 s, (b) RFP describing relationship between hardness and the temperature, and austenitising time, and second tempering temperature for the surface layer of the gradient material.

The conventional powder metallurgy method, consisting of the uniaxial pressing of powder in a closed matrix and then sintering it, allows to produce graded carbide steels with the desired structure and properties, by dosing and mixing high-speed HS6-5-2 steel matrix material

powders with hard carbide phases, provided a linear change is ensured in the fraction of WC carbide reinforcing phase particles in the matrix in the direction perpendicular to the surface.

As the hardness of the surface layer of the newly developed graded HS6-5-2 high-speed steel matrix carbide steels reinforced with WC carbides can be formulated within a broad range according to their chemical composition and sintering conditions, this provides prospects for applying such materials for cutting tools.

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