

## Carbon effect in the sintered high-speed steels matrix composites - HSSMC

**G. Matula\***

Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland

\* Corresponding e-mail address: grzegorz.matula@polsl.pl

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### Manufacturing and processing

#### ABSTRACT

**Goal:** The goal of this monograph is development of the tool materials being the outcome of the concept of merging the surface engineering as the domain of knowledge with technology which is the powder metallurgy. The result are the fabricated materials with the gradient, high-speed steels matrix composites (HSSMC) surface layers on steel substrate, combining the mutually exclusive mechanical properties like the high surface hardness and ductility of a tool.

**Project/methodology/approach:** Modern powder forming technologies were used for fabrication of the developed tool materials, e.g., powder injection moulding, pressureless forming, and classic compacting. Sintering was carried out in the vacuum or protective atmosphere conditions, which makes direct material hardening possible from the sintering temperature. Testing of mechanical properties encompassed hardness testing, bending strength testing, and determining the abrasion wear resistance. Detailed structural examinations were carried out to determine the effect of temperature and atmosphere during sintering on type and size of the carbide- and carbonitride precipitations. Moreover, retained austenite portion was determined after hardening and tempering.

**Achievements:** The original achievement is development of the method of the polymer-powder slurry moulding for fabrication of coatings which, because of the binding agent degradation and sintering, form the homogeneous or gradient HSSMC surface layers on the steel substrate - completed or fabricated in the same technological process. Tool materials fabricated with this method are characteristic of high ductility of the steel core and high hardness of the surface layer.

**Limitations of research/applications:** The assumption of the powder injection moulding technique is forming of the small elements with complex shapes and, therefore, this technology is not designed for fabrication of tools with the big overall dimensions. In case of the pressureless forming of the surface layers from HSSMC on the steel core or in case of regeneration of the tool worn out, the limitations come only from the heating device chamber size and the necessity to heat up the entire treated element.

**Practical applications:** It is anticipated that the worked out and fabricated tool materials of the new generation will fill a gap in respect of the mechanical properties between the relatively ductile high-speed steels and the brittle sintered carbides. The newly developed method may be used in the mass- or piece production conditions making, e.g., regeneration possible of the costly tools' surfaces.

**Originality/value:** Employment of the modern powders forming techniques, and especially of the pressureless forming and sintering in the flowing nitrogen-hydrogen mixture atmosphere, makes it possible to fabricate tool materials with the layered or gradient structure with the multidirectional growing portion of the hard carbide- or carbonitride phases.

**Keywords:** Powder injection moulding; Pressureless forming; Sintering; Heat treatment; Tool materials; Gradient materials; High-speed steels matrix composites; Cermets

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## 1. Introduction

This monograph has been worked out based on the selected and attached own work published in scientific journals [1-25], carried out in the last years, pertaining to the manufacturing technologies of high-speed steels and cermets consisting in forming and sintering of powders. These methods make fabrication possible of tool materials with the homogeneous or gradient structures and have been described in three chapters, each presenting different powders forming technique, and the fourth one presenting their mechanical properties:

- powder injection moulding [1-10],
- pressureless forming [11-15],
- classic compacting in a rigid die [16-23],
- mechanical properties of the fabricated tool materials [24-25].

Results of the own research in the area have been presented also at scientific conferences [26-35], and also in the Author's book [36].

Because of the powder injection moulding method complexity, this chapter describes in detail results of research connected with: the rheological properties of the polymer-powder mixtures, their moulding and binding agent degradation [1-5, 7, 27, 30, 32, 36], injection moulding modelling [6, 34, 36], structure and properties after sintering and heat treatment [3, 4, 7-9, 25-33, 36].

Development of the sintered tool materials fabrication techniques offers the possibility for working out and fabricating the all-purpose tools, whose properties, like high hardness and surface wear resistance along with the relatively high core ductility, may be combined thanks to the modern powders forming and consolidation methods. These methods allow partial- or total elimination of machining and plastic working, and significantly affect progress of the "near-net-shape" or "additive manufacturing" technologies, which is connected with the production cost reduction opportunity. Moreover, powder metallurgy makes fabrication possible of materials with the layered or gradient structure, which results in improvement of their properties in respect to the homogeneous materials.

The best known and dynamically evolving powder forming method employing binding agents is the powder injection moulding PIM. This technology is consistent with the modern trends of the "ready-made" materials fabrication and has more and more widespread applications, also in the tool materials production [62-64]. The scope of PIM technology applications and also other technologies, depending on production scale and product complexity, is presented in Figure 1.

This method is used most often for fabrication of products in the mass scale, which – in addition – are characteristic of high complexity. Several powders forming techniques using binding agents are known apart from the PIM method, which may be counted, in general, to the pressureless forming, as high pressure characteristic for the injection moulding machines is not used in them. Regardless of the forming methods presented in article "Alternative to PIM: variant on almost the same theme" by R.M. German [39], i.e., pressureless forming, extrusion moulding, and injection moulding, the entire process is composed of mixing the powder with the binding agent, forming, debinding, and sintering.

Author of the article counts the following methods to the pressureless forming: immersion method in which the binding agent portion is about 50%, slip casting of the polymer-powder slurry into the rubber moulds, sprinkling consisting in covering

the surface with the binding agent and next dusting it with powder, electrophoresis, strip casting, laminating surfaces with thin layers fabricated in strip casting process, jet printing on element surface, laser stereolithography, extrusion of slurry through the capillary nozzles in the x-y coordinate system, surface spraying.

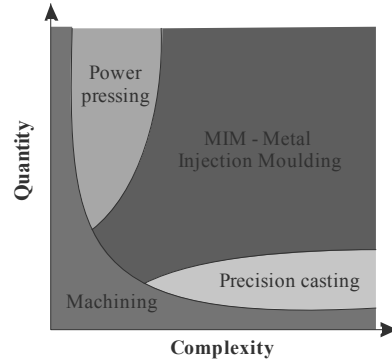


Fig. 1. Selection of manufacturing technology depending on production scale and product complexity [38]

Data presented in Figure 2 pertaining to sales of elements made using PIM technique from 1987 to 2007 unambiguously prove how considerable is development of this method. Metal Injection Moulding (MIM) is of special importance. Total sales of the ceramic, metal, and composite elements is represented by curve denoted as PIM.

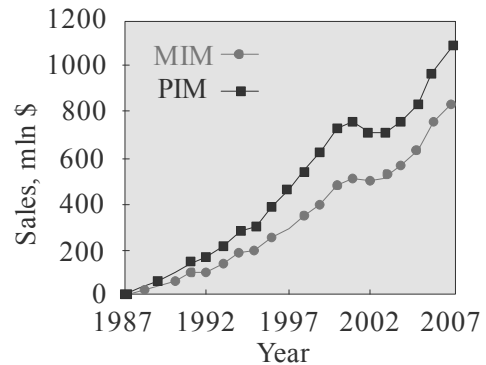


Fig. 2. Sales forecast for elements fabricated using the metal powder injection moulding method – MIM, and of metal and ceramic together – PIM [40]

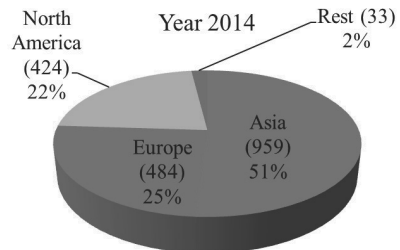


Fig. 3. Development forecast for world regions – figures in brackets are in US\$ millions [44]

Sales forecasts for 2014 (Fig. 3) pertain to the metal powder injection moulding split to various regions of the world, where the total value of the products manufactured will be US\$ 1.9 billion.

Sinters made with this method are mostly characteristic of the homogeneous structure and only the sintering process or sequential injection and spraying of coatings onto the substrate make it possible to obtain the layered structure [41,42].

## 2. Material and testing methods

The powders of HS6-5-2 steel, atomized by water or gas, marked as HS6-5-2 (H) and HS6-5-2 (O), respectively and the powder of HS12-1-5-5 steel were used for the production of sintered high-speed steels. For sintering the materials of high-speed steels matrix composites (HSSMC) structure, the said powders were used as matrix, TiC or WC carbide powders as well as the mixture of carbides marked MW, containing WC, TiC, TaC and NbC. The detailed information concerning the chemical composition of high-speed steels, density, shape and size of grain, oxidation extent of the powder surface, technological properties, carbide content in case of high-speed steels matrix composites production and the method of moulding and sintering were described in publications [1, 3-5, 7-12, 15-18, 26-33, 36]. Table 1 presents the marking of the mixtures tested, moulding methods and portion of the particular components. The stearic acid was only used for covering the surface of carbide powders in the powder injection moulding (PIM) method or powder extrusion moulding (PEM) method. The pressureless forming method PLF consists in the production of one or multi-layered coats from polymer-powder slurry on steels cast by classical methods and plastically worked or injection moulded green parts produced under the same technological process. The detailed information about cemented carbides were described in publications [19-23].

Table 1. Components and forming methods of investigated powder mixtures

Method of forming	Type of matrix	Type of carbide	Binder
PM	HS6-5-2 (H) produced by Höganäs AB	WC or TiC	Without binder (PW as a lubricant)
PIM, PEM	HS6-5-2 (O) produced by of Sandvik Osprey	MW mixture	PW, PP, HDPE, SA
PLF	HS6-5-2 (O) and HS12-1-5-5 produced by Sandvik Osprey	WC or MW mixture	PW, 50%PP/50%PW, cellulosic laquer, thermosetting resin

The materials used as substrate are high-speed steel type HS6-5-2, C70U unalloyed tool steel and 41Cr4 steel used for toughening. The pressureless forming method applied consists in

laying a coating with a brush, immersing in the polymer-powder slurry or powder coating. The slurry containing paraffin or lacquer as binder was prepared using a blade mixer within 30 minutes. While being mixed, the paraffin was heated to the temperature 70°C. The total thickness of the coatings applied shall not exceed 1.5 mm [9, 12, 13, 35, 36].

For the production of laminar or gradient materials through classical pressing of powders the die was filled with 1 to 2 mm thick layers of powder mixtures and increasing portion of hard carbide phases towards the surface of the tool material or cobalt. Detailed information is presented in papers [16-23].

The wide range of testing the polymer-powder slurry used in the PIM method, the selection of type and share of binder, the impact of powder share on the mixture viscosity and the effect of application of surfactants were described in papers [1-5, 7, 10, 26, 27, 36, 37]. A simulation of injection moulding of selected polymer-powder mixtures was carried out using Cadmold commercial software mainly intended for modelling of thermoplastic polymer injection moulding. The simulation results confirmed the possibility to use selected polymer-powder mixtures for injection moulding [6, 34, 36]. Further a thermogravimetric analysis was carried out for injection moulded materials, representing a foundation for selection of appropriate thermal debinding cycle. Solvent debinding was also applied in order to reduce the thermal debinding time [3, 5, 7, 10, 11, 14, 15, 27, 30, 36].

Disregarding the powder formation method, the samples were sintered in a tubular furnace, under the atmosphere of flowing gas mixture N<sub>2</sub>-10%H<sub>2</sub> or in Carbolite Tubular vacuum tubular furnace. The further thermal processing was made for the samples that presented the best microstructure and mechanical properties after sintering. The thermal processing included classical quenching from austenitising temperature or direct quenching from sintering temperature defined as „sinterhardening” [54, 67]. Directly after hardening the samples in oil, they were tempered at the same temperature three times, 540, 570, 600 respectively 630°C, within 1 h.

The tribological tests were carried out with the use of equipment for „pin-on-plate” and „pin-on-disc” tests. The „pin-on-plate” test was made on Tribometer CSM and the pin-on-disc test – on a device from Microtest. The wear tracks were tested with the use of Sutronic 25 profilometer from Taylor Hobson and on a confocal microscope. Disregarding the type of device, the replaceable pin in the form of a small ball made with Al<sub>2</sub>O<sub>3</sub>, loaded with 10 N force is slid on the flat surface of the sample tested. It must be emphasised here that the ball surface wear is negligibly low.

The testing methods of the structure and properties of sintered and heat treated materials and the testing devices used have been described in detail in the publications enclosed.

## 3. Test results and related discussion

### 3.1. Test results of injection moulded materials

For powder injection moulding the spherical powder, average particle size below 20 µm and appropriate size distribution is the best [49, 50]. The test results of the torque of mixtures, depending

on the powders used, their portions and binder components and testing results of the rheological properties of polymer-powder slurry were presented in detail in numerous publications [1-5, 7, 10, 27, 32, 36]. The mixtures prepared are characterized with low viscosity. The viscosity of the mixtures prepared is often lower than that of the polymers applied, which is presented in Figure 4, where mixture A (described in Table 2), is characterised with lower viscosity than polypropylene. Based on the analysis of rheological tests and torque tests, six different polymer-powder mixtures were prepared for moulding and further tests. The detailed portions of the components of the mixtures have been presented in Table 2. The application of finite elements methods for modelling powder injection moulding is not so commonly used as it is for the simulation of thermoplastic material injection moulding process [58, 59]. This is related to the necessity to carry out tests on the polymer-powder mixture properties. The data concerning thermoplastics so popular as polypropylene (PP) or high density polyethylene (HDPE) are generally available, however, upon analysis of the rheological tests, the introduction of solid particles or additional binder in the form of paraffin, increases or reduces the viscosity of the slurry, correspondingly. In case of composite injection moulding modelling, its viscosity needs to be tested first, depending on the shear rate.

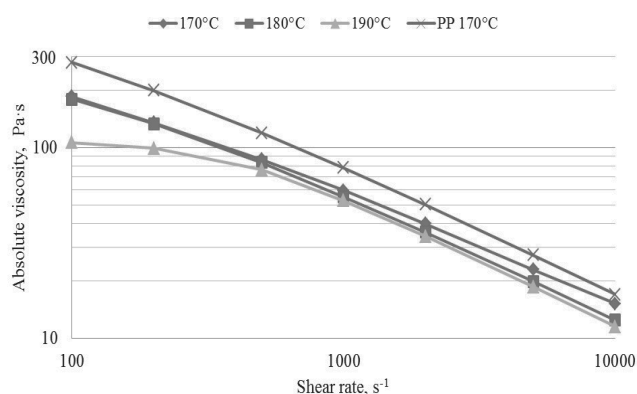


Fig. 4. Viscosity versus shear rate and temperature of the polypropylene and A composition mixture (presented in Table 2)

Table 2.  
Types of injection moulded polymer-powder mixtures

Designation of feedstock	Component in volume, %						
	HS6-5-2 (O)	HS12-1-5-5	MW	PP	HDPE	PW	SA
A	58	-	10	14	0	14	4
B	58	-	10	16	0	16	-
C	70	-	-	15	0	15	-
D	68	-	-	-	16	16	-
E	-	68	-	-	16	16	-
F	-	58	10	14	-	14	4
G	-	58	10	16	-	16	-

Cadmold commercial software, based on the Carreau-WLF (William-Lendel-Ferry) mathematical model, was used for injection moulding simulation. The Carreau parameters and temperature should be determined from diagrams presenting the dependency between viscosity and cutting speed. The Carreau parameters P1, P2 and P3 correspond to: viscosity for shear rate of  $0 \text{ s}^{-1}$ , shear rate at which refraction of curve occurs, i.e. transfer from the shear rate range, where the fluid is Newtonian, into the pseudoplastic range and coefficient determining viscosity drop along with the shear rate growth, respectively.

The results of injection moulding simulation process are described in detail in publications [6, 34, 36]. Injection pressure and injection moulding machine clamping force necessary for moulding of the polymer-powder mixtures tested are comparable to the values corresponding to commercial polymers, which confirms the thesis that the polymer-powder mixtures tested are appropriate for injection moulding.

The results of modelling of the injection moulding of polymer-powder slurry are comparable to the real injection conditions. This applies mainly to the mould cavity filling time being ca. 0.4 s both for factual injection moulding and in the model process. Therefore, the conclusion is that the model applied and injection conditions have been selected correctly.

The testing results of debinding conditions selection and their effect on the rate of removing, the mould properties and carbon concentration were published in papers [3, 4, 7, 10, 27, 30, 36]. Figure 5 presents the structure of steel made of composite D after debinding at temperature  $475^\circ\text{C}$  and sintering at  $1240^\circ\text{C}$ , characterised with high dispersion of carbides (Fig. 5c). The reduction of degradation temperature to  $450$  and further to  $400^\circ\text{C}$  causes coarsening and coagulation of carbides at the same temperature  $1240^\circ\text{C}$ , which is the consequence of higher concentration of carbon reducing the solidus temperature (Fig. 5a). As a result of testing of density of HS6-5-2 (O) steel sintered at  $1240^\circ\text{C}$ , depending on the debinding temperature ranging between  $400$  and  $500^\circ\text{C}$  it was observed that the highest density (ca. 98% of theoretical density) was achieved by HS6-5-2 (O) steel with the highest carbon concentration, i.e. (1.06%), obtained as a result of thermal debinding at the lowest temperature  $400^\circ\text{C}$ . The density and concentration of carbon testing results, depending on debinding temperature of steels produced by the PIM method are presented in Figure 5d.

The results of testing composite A in which polypropylene, HS6-5-2 and MW powders were applied, confirm that the debinding conditions strongly affect the concentration and structure of carbon after sintering. Forming with the use of binder causing the growth of carbon concentration also causes the expansion of sintering temperature range in comparison to the powder pressed in the mould and sintered. The addition of MW carbides to the high-speed steel mixture causes further expansion of sintering temperature range and totally eliminates the precipitation of eutectic carbides having a „fishbone” or „Chinese script”. Figure 6 presents high-speed and high-speed steels matrix composites sintered at  $1300^\circ\text{C}$ . The structure and size of precipitations in the comparable materials are by far different (Fig. 6).

In low temperature of sintering carbide steels, the occurrence of bright colour WC secondary carbides (Fig. 7) was observed. The grey colour phase rich with W, Fe, V and Mo was produced from alloy additions contained in high-speed steel or from elements derived from dissolved carbides introduced in the steel.



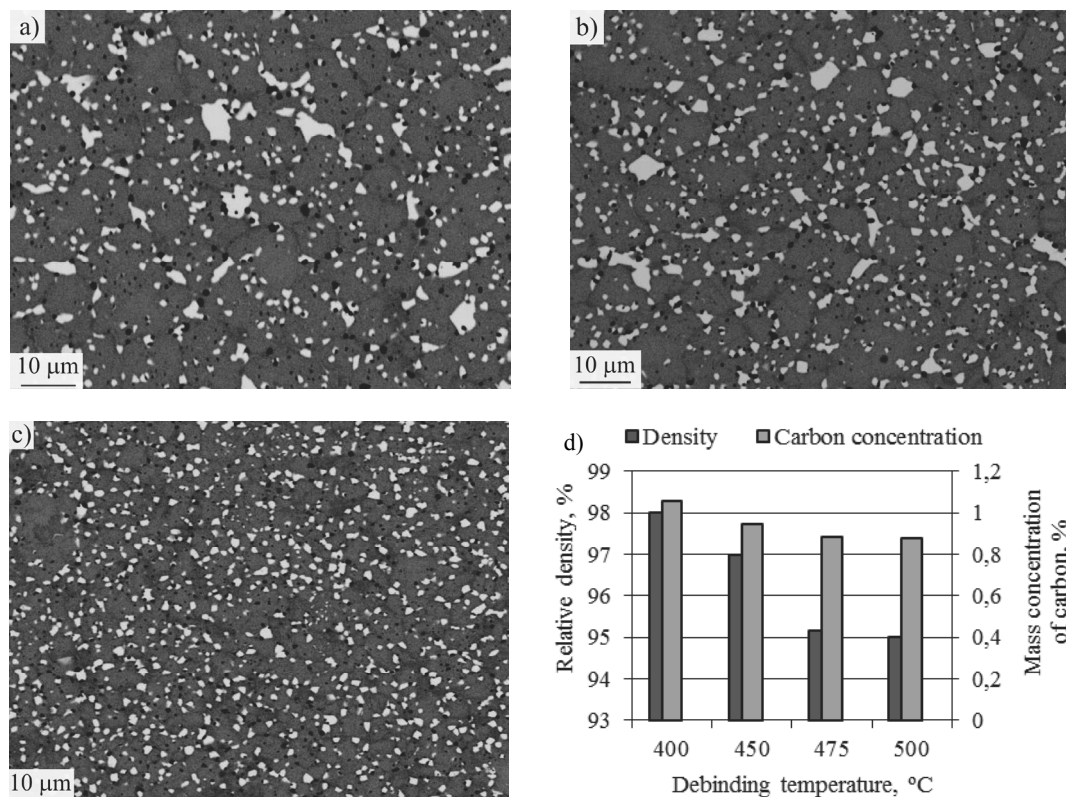


Fig. 5. Structure of material D sintered at 1240°C depending on debinding temperature: a) 400, b) 450, c) 475°C and d) effect of debinding temperature on density and carbon concentration in HS6-5-2 (O) steel

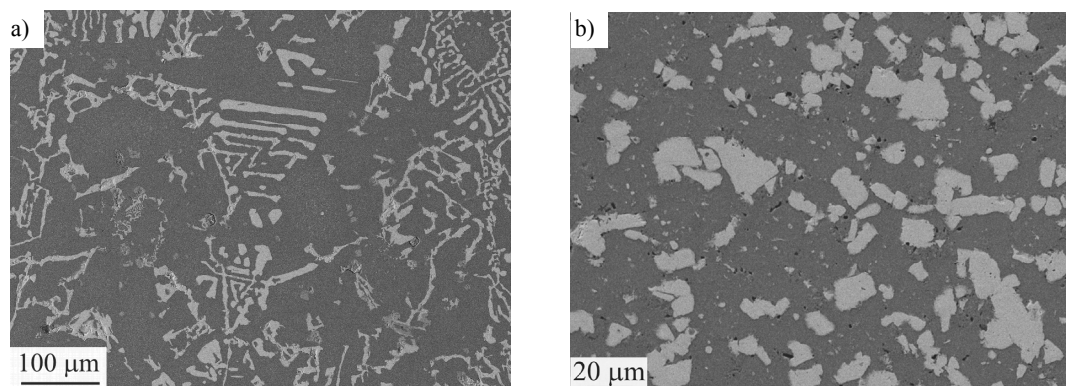


Fig. 6. Structure of materials sintered at 1300°C a) HS6-5-2 (O) high-speed steel, b) HS6-5-2 (O)/MW HSSMC

No WC carbide presence was found at higher sintering temperature, which is confirmed by X-ray phase analysis test results. However  $M_6C$  and MC carbides, typical for high-speed steel have been identified. The growth of bright carbides appearing on the secondary electron image, rich with W, Mo and Fe is restricted by grey, spherical precipitations, rich with Ti and V, whose size does not exceed 1 μm. During the observation of HSSMC in scanning microscope no presence

was found of  $M_2C$  carbides, typical for high-speed steel rich with molybdenum, in the form rod-like carbides that are precipitated at high sintering temperature and significantly decrease the mechanical properties [47]. The test results on electrolytically carbides sediments did not show the presence of other precipitations than  $M_6C$  and MX (Fig. 8). The test results after heat treatment were presented in papers [7, 24, 25-32, 36].

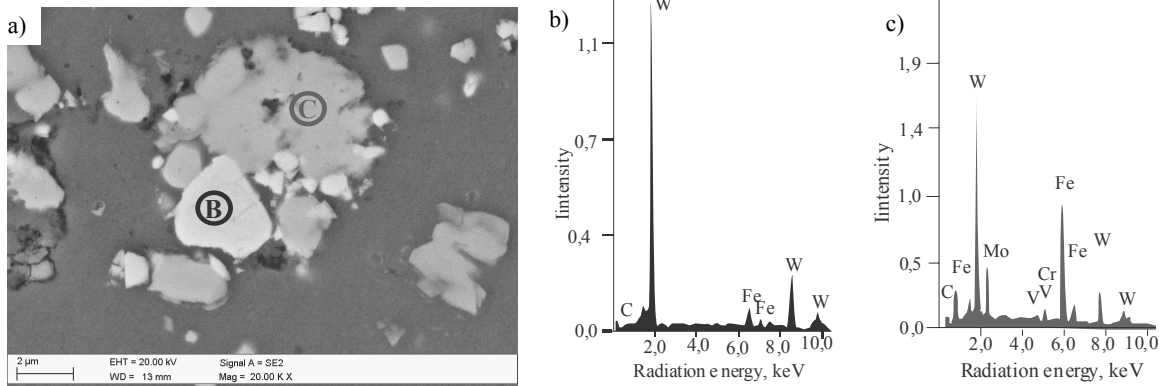


Fig. 7. a) Structure of HS6-5-2 (O)/MW composite sintered at temperature 1200°C, b), c) plots of the X-ray dispersive energy phases of indicate areas

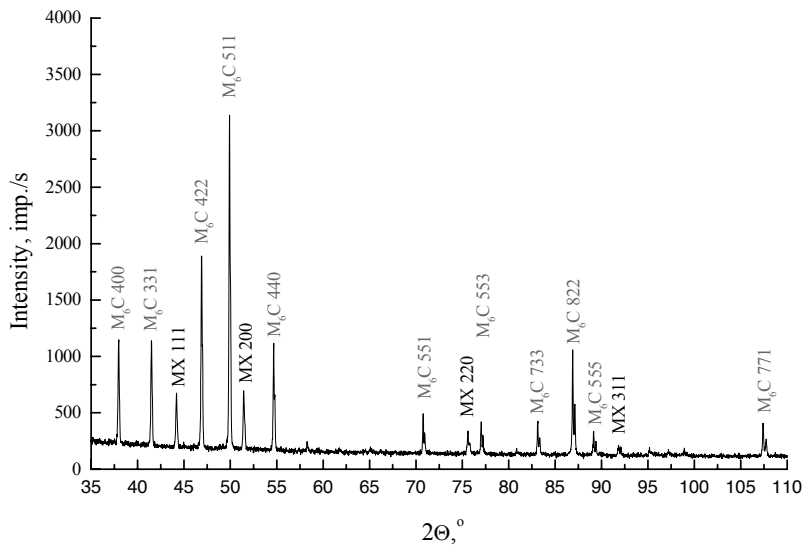


Fig. 8. X ray diffraction pattern of electrolytically isolated precipitations from quenched and tempered at 540°C HSSMC

### 3.2. Test results of pressurelessly formed materials

The results of the author’s tests on high-speed steels, high-speed steels matrix composites and steel-based surface layers by the method of pressureless powder formation have been presented in papers [11-15, 24, 26, 35, 36]. The tests of pressurelessly formed high-speed steels [11, 14, 15, 24] were the foundation for developing a proprietary method of producing homogeneous or gradient surface layers on steel substrate [9, 12, 13, 35, 36]. The pressureless forming method, like the injection moulding method of HS6-5-2 and HS12-15-5 high-speed steels enables the reduction of sintering temperature in comparison to the same sorts of compacted and sintered steels, which is related to the growth of carbon concentration. The carbon concentration measuring results,

depending on the debinding temperature of thermosetting resin, have been presented in Table 3. The heating rate during resin debinding should not exceed 0.3°C/min, otherwise numerous cracks occur [11, 14]. In case of coats up to 1 mm thick, the debinding may be ca. 1°C/min [12].

Table 3. The effect on thermal debinding temperature on carbon concentration in pressureless formed steels

Type of powder	Thermal debinding temperature, °C			
	300	350	400	450
Mass concentration of C, %				
HS6-5-2 (O)	4.15	2.11	2.01	1.75
HS12-1-5-5	4.42	2.35	2.09	1.86

The binder and its removal conditions should be selected so as to enable technologically easy application of polymer-powder coats and fast thermal debinding. Based on the experimental tests it was found that the best effects of pressureless forming of the surface layers were achieved when using paraffin as the binder of the polymer-powder slurry that tightly covers the substrate surface and can be applied easily with a brush or through immersion of the coated element [12, 13, 35, 36].

Paraffin as a binder enables direct heating to the sintering temperature at the rate of 5°/min, which causes incomplete debinding, concentration growth of carbon as the activator of the sintering process and guarantees adhesion of the surface coat with the substrate. The layers containing thermosetting resin should be heated to the sintering temperature with an isothermal hold. After coating the resin it should be heated at 95°C temperature, in order to be polymerised.

The test results in the scanning microscope confirmed that, disregarding the type of binder used, the appropriately selected conditions of thermal debinding and sintering enable to obtain surface layers tightly covering the substrate material. The type of carbides and their size and structure porosity, depend on the concentration of carbon as activator of sintering, atmosphere, time and sintering temperature. The joint of the polymer-powder coat with the substrate after the formation is of adhesive nature. As a result of sintering accompanied by mutual diffusion between the coat powder and the substrate, we obtain a material with steel core and surface coat with the structure of high-speed steel or high-speed steel matrix composite [12, 13, 35, 36].

Disregarding the sintering temperature in the surface layer structure of HS6-5-2(O) examined in the scanning microscope with EDS unit, the presence of carbides rich with W, Fe and Mo and carbonitrides rich with V was found and observed in the image of secondary electrons as a bright and dark precipitations. The occurrence of such phases was confirmed by the method of X-ray phase analysis. The surface layer presented in Figure 9, sintered at 1260°C, consists of upper and lower layer, containing HS6-5-2(O) and 20 and 10% WC carbide, respectively. In Figure 9b presenting the lower layer, minor particles of WC carbide of size below 1µm, totally dissolved in the matrix, further producing large bright precipitations in the shape of polyhedrons. It is accompanied by the growth of voluminous portion of carbide phases. The average size of such precipitations is 12 µm. The precipitations of  $M_6C$  carbides rich with W and Fe is a frequent phenomenon occurring in cermetals, in which Fe is applied instead of Co or Ni matrix, which increases their fragility [68]. In the upper layer with higher portion of WC, not all the carbides are dissolved, which is confirmed by X-ray phase analysis (Fig. 10).

Comparing the high-speed steels matrix composites surface layer to the WC addition and the coat without this phase, the clear effect of the carbide is visible, even under small magnification, due to the voluminous portion of hard phases amounting to 68% after sintering.

The portion of carbides so high causes that the high-speed steels matrix composites surface layer's structure resembles cermetals or sintered carbides, due to the morphology of carbide precipitations. The test results of carbide grain size and porosity of the steel structure of the surface layer proved that the maximum sintering temperature should not exceed 1240°C. This applies in particular to surface layers on HS6-5-2 steels, because

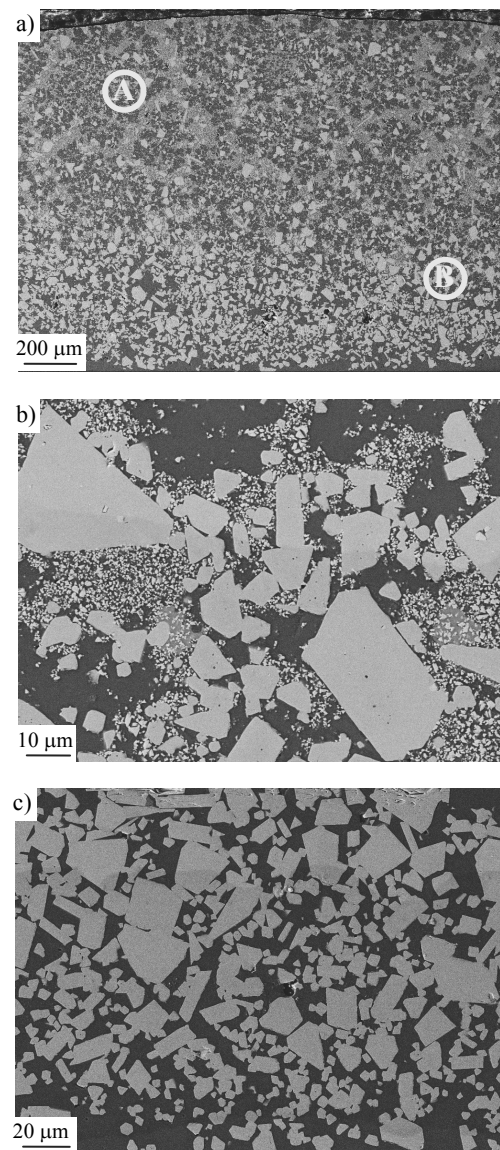


Fig. 9. a) surface layer structure of HS6-5-2(O)/WC on 41Cr4 steel sintered at 1260°C, b) enlargement of marked area A (upper layer), c) enlargement of marked area B (lower layer)

the substrate structure held at a temperature above 1240°C is characterised with large carbides on the boundaries of primary austenite (Fig. 11c) eutectic carbides occurring locally in the form of “fishbone”. The structure of the surface layer of HS12-1-5-5 steel is characterised with high homogeneity with minor carbide precipitations and clearly differs from the substrate structure (Fig. 11b). The surface layer tightly covers the substrate, but a clear boundary between them is noticeable (Fig. 11a). The growth of sintering temperature above 1240°C is not dangerous for the high-speed steels matrix composites of the surface layer, because the  $M_6C$  identified with the X-ray phase analysis method, visible as clear precipitations in the scanning microscope on the image of inverse scattered electrons scarcely expand and do not



exceed 10  $\mu\text{m}$  and the layer structure is still homogeneous. The growth of bright carbides  $\text{M}_6\text{C}$  is blocked by dark minor precipitations rich with V and N, which was tested with EDS and WDS methods. The phases were identified with the method of X-ray

phase analysis as carbonitrides MX (Fig. 12). The creation of such phases in high-speed steels during sintering is extensively described in references [57, 70], and the selection of appropriate sintering conditions may lead to creation of nitrides VN [51].

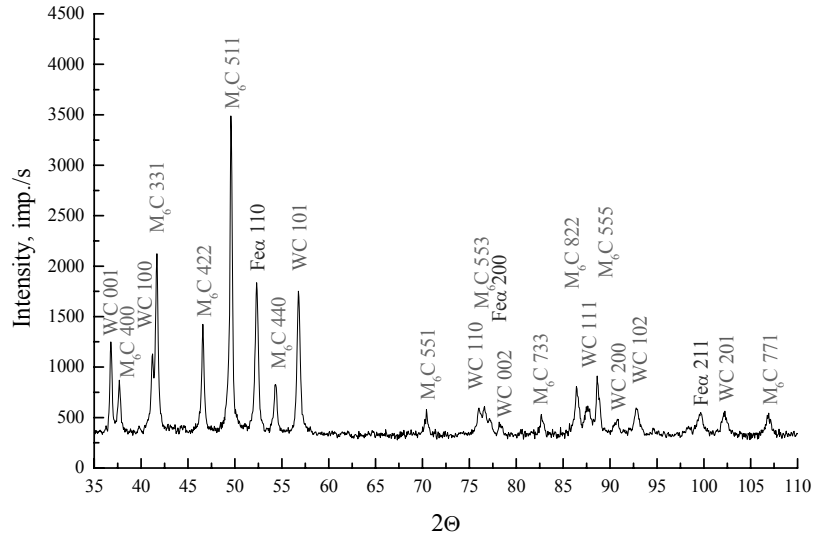


Fig. 10. X ray diffraction pattern of gradient tool material TGM (41Cr4 with surface layer HS6-5-2(O)/WC) sintered at 1260°C

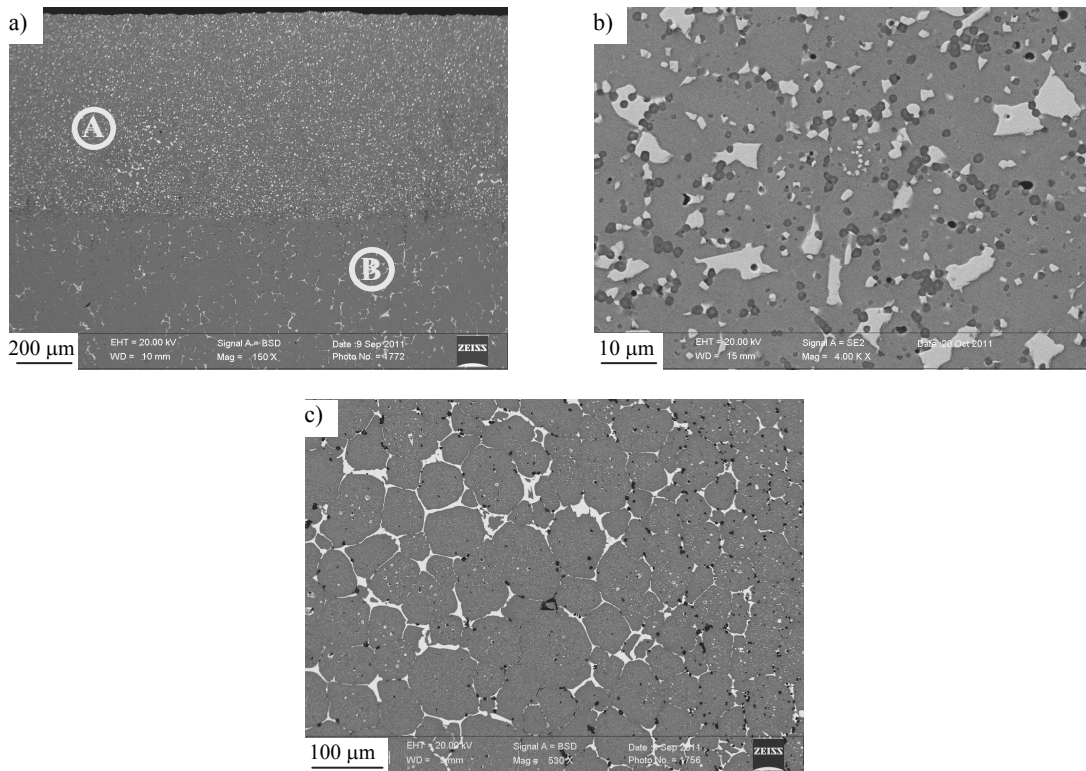


Fig. 11. The structure of high-speed steel HS6-5-2 with surface layer of HS12-1-5-5 sintered at 1280°C a) substrate and surface layer, b) enlargement of marked area A (the upper layer), c) enlargement of marked area B (the lower layer)



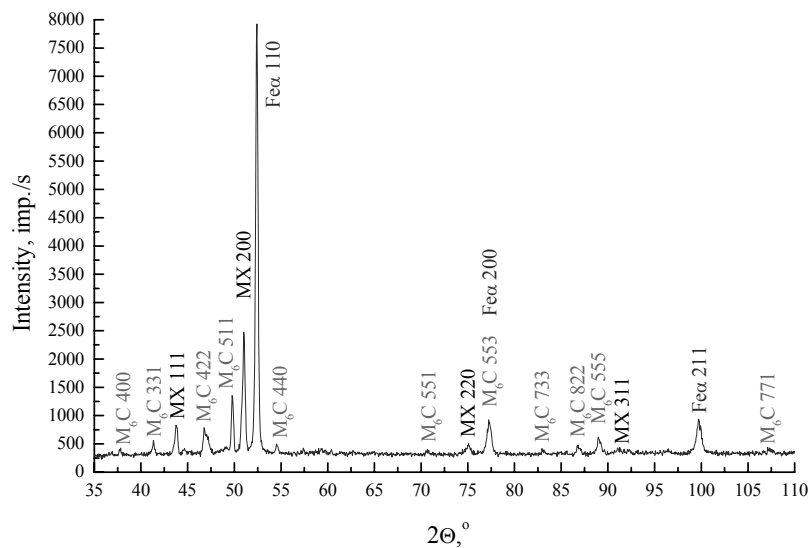


Fig. 12. X-ray diffraction patterns for the surface layer HS12-1-5-5 on substrate of HS6-5-2 steel

In the materials tested carbonitrides are precipitated in the surface layer and in the substrate, i.e. high-speed steel. Figure 13 presents the structure of HS6-5-2 steel and distribution of N, V and Fe analysed in the marked area along the line, with the method of scattered X-ray radiation energy. The results confirm that carbides rich with N and V are also created in high-speed steel. The presence of Ti was observed in carbonitrides being precipitated during sintering of the surface layer HS12-1-5-5/MW, Ti was introduced together with other elements in the form of carbides.

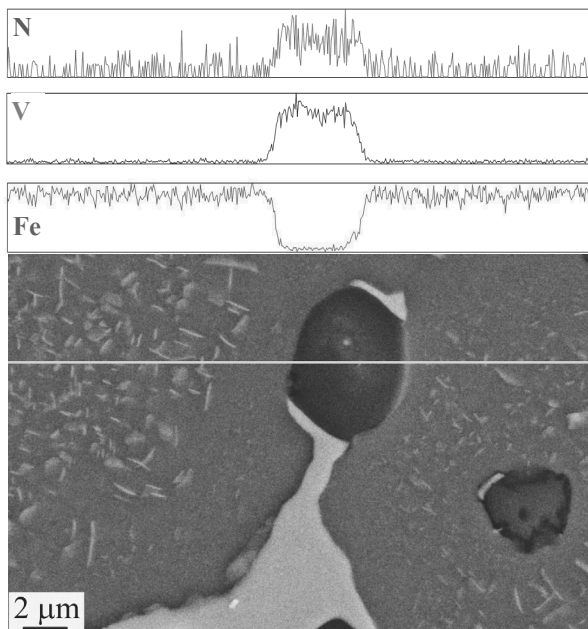


Fig. 13. The structure of HS6-5-2 steel annealed at 1280°C under atmosphere N<sub>2</sub>-10%H<sub>2</sub> and the linear distribution of N, V, and Fe elements

Disregarding the location of the carbonitride precipitation, i.e. either in the surface layer or in the substrate material, their form is spherical, where the size of precipitations in the surface layer most frequently does not exceed 1 μm. The size of carbonitrides being precipitated in the substrate reaches 6 μm. The results of testing the high-speed steels matrix composites structure of the surface layer after heat treatment and the analysis of crystalline materials with phase identification using electron backscattered diffraction technique EBSD, carried out in the scanning electron microscope, confirm the presence M<sub>6</sub>C, carbides and MX phases. Martensite and residual austenite compose matrix. Figure 14 presents the structure of high-speed steels matrix composites sintered at 1260°C and quenched and then tempered at 600°C. The results of crystallographic orientation analysis in the form of Kikuchi line for areas marked in Figure 11 were presented in Figure 15.

The phases identified in virtue of diffraction images corresponding to A, B, C, D areas are: martensite, residual austenite, M<sub>6</sub>C carbide and agglomeration of carbonitrides MX, respectively.

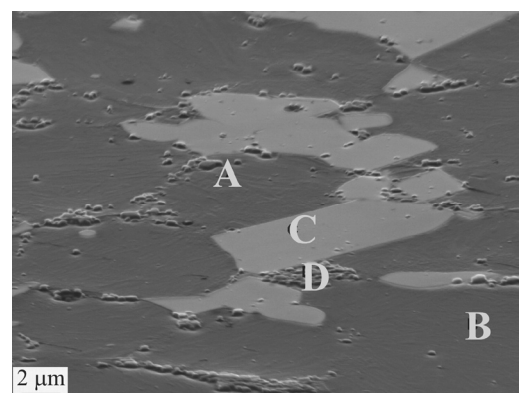


Fig. 14. Surface layer structure (HS6-5-2(O)/MW HSSMC), topography of surface inclined at the angle of 70° with marked areas of diffraction tests

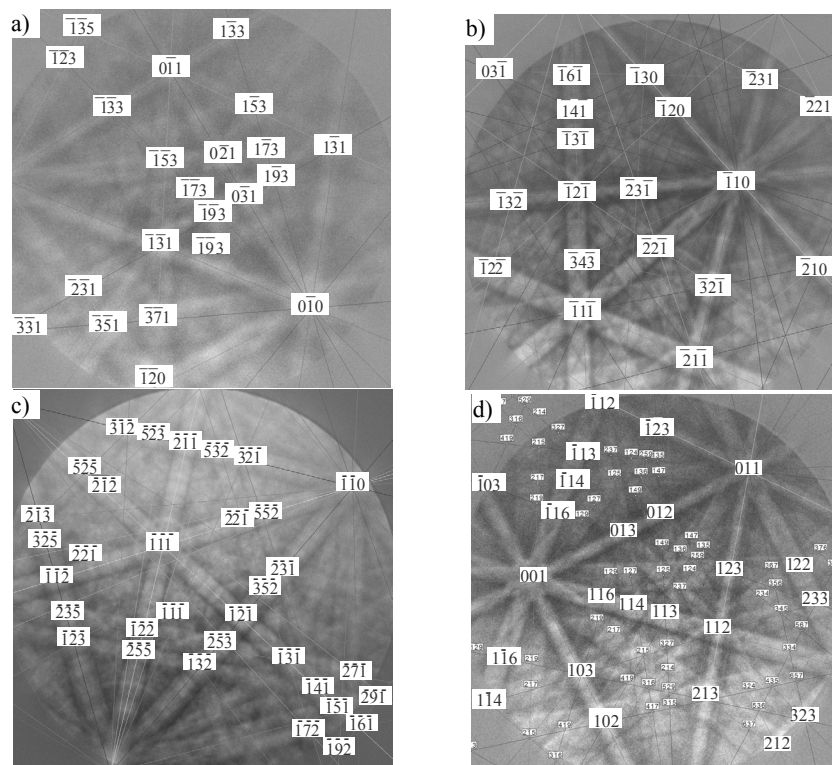


Fig. 15. Diffraction images (Kikuchi lines) of phases identified respectively: a) martensite from area A in figure 14, b) residual austenite from area B in figure 14, c) carbide  $\text{Fe}_3\text{W}_3\text{C}$  from area C, in figure 14 and d) VN nitride of area D in figure 14

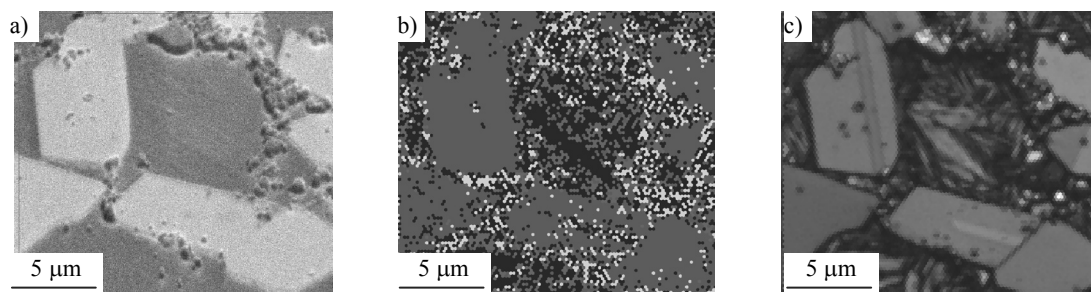


Fig. 16. a) the structure of HSSMC surface layer HS6-5-2(O)/MW sintered at  $1260^\circ\text{C}$ , quenched and tempered at  $600^\circ\text{C}$ , b) the grain distribution map of varied crystallographic orientation ( $\text{M}_6\text{C}$ , martensite, MX and austenite), c) EBSD quality distribution map

Figure 16b presents the map of distribution of grains of varied crystallographic orientation of high-speed steels matrix composites sintered at  $1260^\circ\text{C}$  and hardened and tempered at  $600^\circ\text{C}$ . The areas marked red, green, yellow and blue are  $\text{M}_6\text{C}$  carbides, martensite, carbonitrides MX and residual austenite, respectively. The  $\text{M}_6\text{C}$  and MX phases were identified based on charts of respective numbers 0411351 and 0021064 available in the file base [72]. The said charts concern  $\text{W}_3\text{Fe}_3\text{C}$  and VN phases, respectively, however, due to other elements present in high-speed steel matrix composite, contained in the chemical composition of the precipitations, the marking of  $\text{M}_6\text{C}$  and MX, respectively, presented before, are more appropriate. In case of carbonitrides

MX the nodal positions may be occupied by V, included in the chemical composition of HS6-5-2(O) or Ti, Nb and Ta that have been introduced in the form of carbides.

All the elements produce interstitial carbides with B1 lattice. The octahedral gaps may be filled with carbon or nitrogen. Due to shorter atom radius in comparison to carbon, the octahedral gaps of the nitrides are more filled in comparison to the octahedral gaps of carbides [69, 73]. The Gibbs free energy necessary for the precipitation of VN and TiN nitrides is lower in comparison to the energy necessary for the precipitation of VC and TiC carbides, therefore, with equal concentration of C and N, the portion of nitrogen atoms in the octahedral gaps is higher [45, 73].

The interesting test results of the two-layer coat HS6-5-2 (O)/WC with lacquer used as the binder, gave rise for the production of multi-layer coats and gradient layers, which was described in publications [12, 35, 36]. Tests were also made on the single-layer polymer-powder coat applied on HS6-5-2 steel, on which a groove was cut mapping the worn surface of the tool and the test results obtained prove the existence of possibility to apply pressureless forming in tools' surface regeneration [13].

The effect of the carbon concentration growth after debinding in comparison to the concentration of this element in the input powders used is the growth of residual austenite portion after hardening. This phenomenon occurs in pressureless formed materials and injection moulded materials, which was presented in publications [3, 7, 11, 14, 24, 26, 27, 30, 36].

### 3.3. Test results of materials compacted in die

The results of tests on materials compacted and sintered (PM) were published in the papers [4, 16-23]. An exemplary structure of the piece formed by pouring subsequent layers with powder mixtures with growing portion of WC towards the upper surface of the sample was presented in Figure 17a. No cracks or delaminations of the materials tested (HS-6-5-2/TiC) were found either in the compacted or sintered condition (Fig. 17b). Basing on the comparison of gradient materials' testing results reinforced with TiC carbide, sintered in vacuum and under atmosphere of flowing  $N_2$ -10% $H_2$  gas mixture, it was found that sintering in the nitrogen-hydrogen gas mixture enables the obtaining of better results. Figure 18 presents material sintered at 1260°C in vacuum, characterised with high porosity, particularly on the boundaries of high-speed steel particles that are additionally spaced by minor, grey particles of TiC phase. Sintering at higher temperature, in order to reduce the sinter porosity is not recommended, due to large, bright precipitation of carbides rich with W and Fe and occurring in high-speed steel grains. The further temperature growth may lead to local partial melts.

In case of materials sintered in atmosphere of flowing  $N_2$ -10% $H_2$  gas mixture, within the same temperature and time, the structure is more compact, with locally occurring pores only. Both TiC carbides, introduced in the steel, visible as grey precipitations in the image obtained through detection of secondary electrons in the scanning microscope, and the Fe and W rich carbides as visible as bright precipitation in the high-speed steel, create large conglomerates on the HS6-5-2 (H) powder particles' boundaries (Fig.19.).

The tests of oxygen concentration in HS6-5-2 (H) high-speed steel powder proved that its concentration is ca. 0.12%. In comparison to the HS6-5-2 (O) powders, the value is three-times higher. The portion of oxygen in the materials pressed and sintered is comparable, while the concentration of oxygen in the materials sintered in hydrogen rich atmosphere is ca. 0.06%. This is the result of reduction of oxides existing on the powder surface by hydrogen flowing during heating to sintering temperature, which facilitates sintering. Some elements undoubtedly have a positive effect on sintering, so-called activators, e.g. carbon. The creation of carbonitrides visible in Figure 20, rich with V, is caused by the growth of carbon concentration through partial precipitation of this

element, according to the  $MC + N \rightarrow M(X) + C$  mechanism [51, 66]. The atomic concentration of carbon, presented in Figure 20b, has been tested with EDS method. The result was confirmed with the use of the WDS detector. The growth of free carbon concentration in the matrix reduces the solidus temperature and the sintering temperature at the same time, thus activating the process [56, 66].

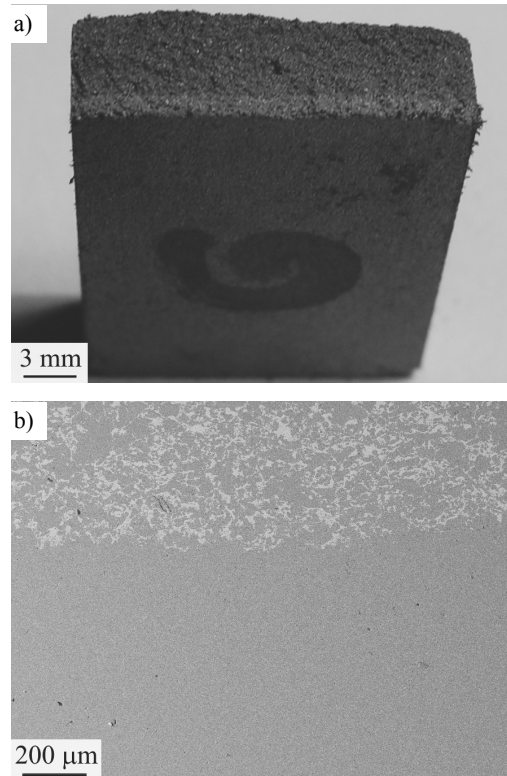


Fig. 17. a) the fracture of compacted sample of laminar structure and growing portion of WC powder towards the surface, b) HS6-5-2/WC gradient material structure sintered at 1260°C

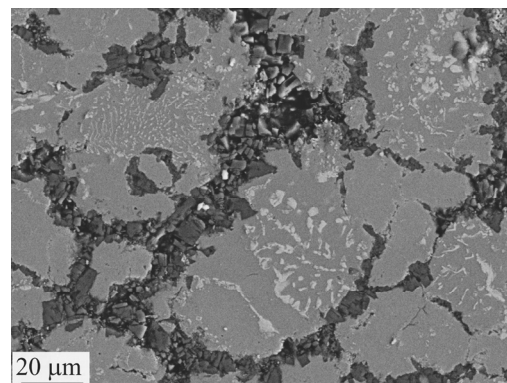


Fig. 18. The structure of HS6-5-2 (H)/TiC material sintered at 1260°C, in vacuum



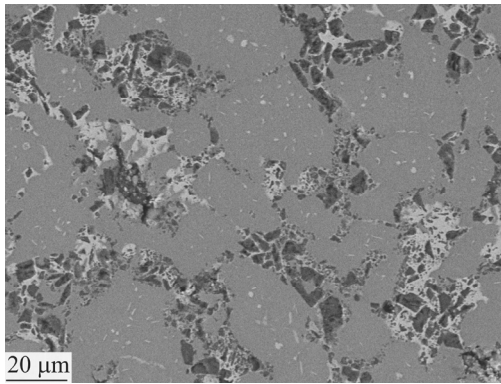


Fig. 19. The gradient material layer structure of HS6-5-2 (H)/TiC sintered at 1260°C under atmosphere N<sub>2</sub>-10%H<sub>2</sub>

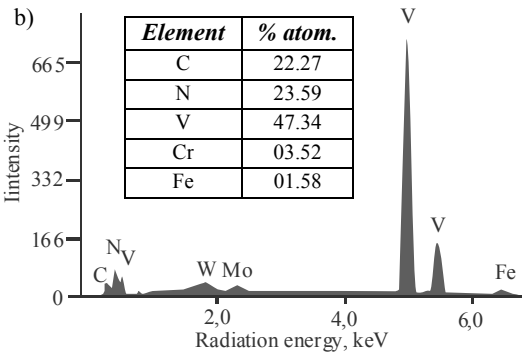
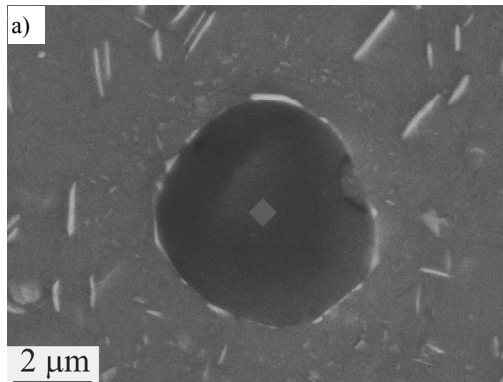
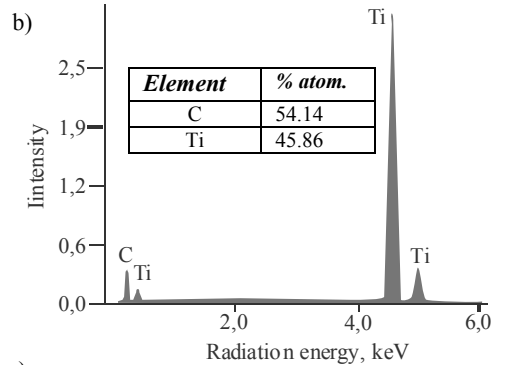
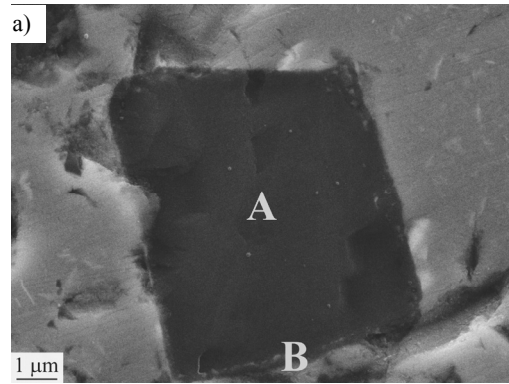


Fig. 20. a) the structure of HS6-5-2(H) as a substrate of HSSMC, sintered at 1280°C under N<sub>2</sub>-10%H<sub>2</sub> atmosphere, b) plot of the X-ray dispersive energy phases of indicate area and quantitative analysis results

The carbonitrides presented in Figure 20 most frequently occur in HS6-5-2 (H) high speed steel without addition of TiC or WC, representing the substrate for the gradient material. In the materials sintered in a vacuum furnace no phases of this type were observed. The phases are stable for high sintering or austenitisation temperature, which proves their low solubility. The results are confirmed by data of references [45, 71]. Moreover, the references



Element	% atom.	Element	% atom.
V	12.08	C	31.18
Fe	15.86	N	45.86
W	0.87	Ti	28.88

Fig. 21. a) surface layer structure of HS6-5-2 (H)/TiC material sintered at 1280°C, b) plot of the X-ray dispersive energy phases of area A and quantitative analysis results, c) plot of the X-ray dispersive energy phases of area B and quantitative analysis results

state that nitrogen beneficially affects the high-speed steel properties, because it reduces the steel inclination to adhesive combination with the chip during machining [47, 66]. Nitrogen also blocks the precipitation of M<sub>2</sub>C carbides of hexagonal structure that have a rod-like shape at high sintering temperature of high-speed steel, reducing the mechanical properties, while it stabilises the phases of regular lattice, such as M<sub>6</sub>C or MX [47].

In the TiC reinforced areas, no minor and spherical, V-rich MX carbonitrides were found. However, it was observed that a MX carbonitride layer, Ti and V rich is formed on TiC carbides.



The morphology of the phases differs from complex carbonitrides examined by S. Gimenez et al. [51, 71]. The difference in the mechanism of carbonitrides production is due to the fact that large TiC carbides, of average size 5  $\mu\text{m}$  no melt during sintering and become the base for the precipitation of a carbonitride layer (Fig. 21).

The materials reinforced with TiC carbides, stable at high temperature, may be sintered applying atmosphere in the form of  $\text{N}_2$ -10% $\text{H}_2$  gas mixture, at temperature exceeding 1300°C even, which significantly contributes to obtainment of high-density sinters, without partial melts. Therefore, the addition of TiC carbides to steel and sintering such materials in nitrogen-hydrogen flowing atmosphere enables to expand the narrow sintering temperature range, so-called “sintering window” being just 5°C for HS6-5-2 high-speed [56]. This is particularly significant in case of using industrial furnaces in which the temperature control is more difficult than under laboratory conditions. In addition to the carbonitrides, W and Fe rich phases occur in the materials tested, their chemical composition resembling that of  $\text{M}_6\text{C}$  carbides that occur in high-speed steels, visible as bright precipitation in the image of secondary electrons (Fig. 22).

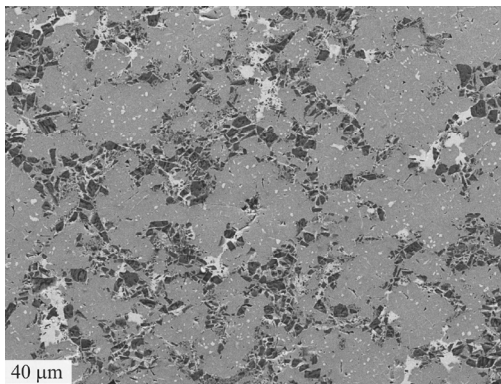


Fig. 22. The structure of HS6-5-2 (H) high-speed steel reinforced with TiC carbide and sintered at 1310°C under  $\text{N}_2$ -10% $\text{H}_2$  atmosphere

Based on tests of gradient tool materials reinforced with WC carbide, sintered under  $\text{N}_2$ -10% $\text{H}_2$  atmosphere it was found that in the high-speed steel structure as a substrate, like in the materials reinforced with TiC carbide, MX carbonitrides and  $\text{M}_6\text{C}$  carbides occur. In the layers reinforced with WC carbide, no MX carbonitrides or other nitrogen rich phases were found. The WC carbide dissolves at high sintering temperature and creates the  $\text{M}_6\text{C}$  phase, rich with tungsten deriving from the carbide and iron from the matrix. Testing the structure of materials with maximum portion of WC carbide in the surface layer, i.e. 12% proved that the WC carbide added in this area totally dissolves in the high-speed steel matrix under sintering temperature 1260°C, producing the  $\text{M}_6\text{C}$  carbide.

The precipitation of the  $\text{M}_6\text{C}$  carbide, at the cost of WC dissolved, is not beneficial due to the decrease of hardness. The hardness of the  $\text{M}_6\text{C}$  carbide is ca. 1600 HV, while that of WC is ca. 2350 HV [69]. The sintering temperature range for the gradient material reinforced with WC is narrow, because the substrate sintered below 1250°C is characterised with minor carbides, but

also with high portion of pores, being ca. 8%. The sintering temperature growth to 1270°C causes deformation of the surface layer, meaning that partial melting had occurred. Therefore, the sintering temperature should fit within the narrow range, around 1260°C. The maximum portion of the WC carbide should not exceed 12% in the surface layer. The further growth of the carbide share causes a decrease of the sintering temperature and distortion of the surface layer.

### 3.4. The mechanical properties of the tool materials developed

Based on the injection moulded HS6-5-2 (O) steel density test results where polyethylene and paraffin were applied as binder, subjected to thermal debinding under 450°C,  $\text{N}_2$ -10% $\text{H}_2$  atmosphere and sintered within 1210 to 1290°C temperature range, graded every 10°C, it was found that at temperature range between 1240 and 1260°C the steel reaches density close to the theoretical value, i.e. steel presenting no pores (Fig. 23). For the purposes of presenting the production method impact on the sintered steel density, Figure 23 also presents the results of testing density of the HS6-5-2 (O) steel, manufactured by pressureless forming method and the HS6-5-2 (H) steel, compacted and sintered. In pressurelessly formed steels large, spherical pores are noticeable, of ca. 0.5 mm diameter, being the residue of the gas cavities produced during mixing the powder and resin and moulding, such cavities cannot be eliminated in the sintering process, due to their size. The compacted steel HS6-5-2 (H) requires sintering at higher temperature and does not reach density as high as that of pressureless formed or injection moulded steels.

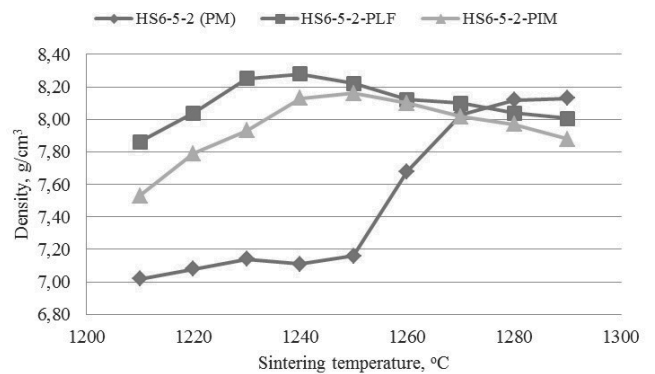


Fig. 23. Influence of powder forming method and sintering temperature on the HS6-5-2 steel density

The detailed information on the mechanical properties of the materials produced in sintered and heat treated condition were published in [4, 7, 24-26, 29, 31]. However, the tribological test results are worth presenting, the latter being published in the [36] monograph only. The tests, made with the use of the „pin-on-disc” on the HS12-1-5-5/MW high-speed steels matrix composites surface layer and sintered with the HIP method on the PMHS6-5-3 (ASP23) high-speed steel prove the reasonability of producing the surface layers using the method of pressureless forming and

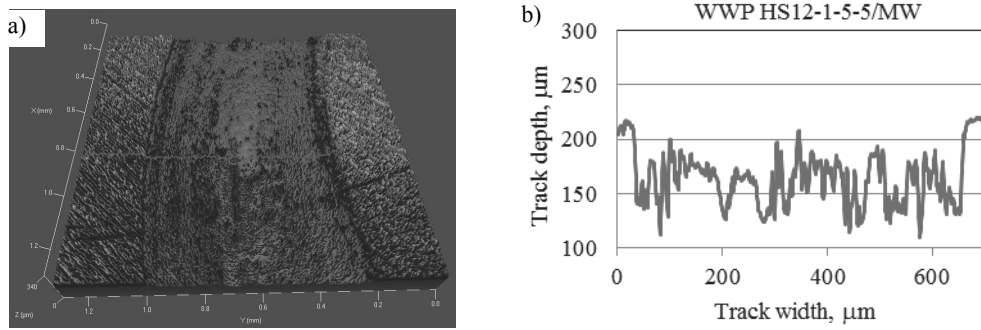


Fig. 24. Wear track of the surface layer of HS12-1-5-5/MW and its profile

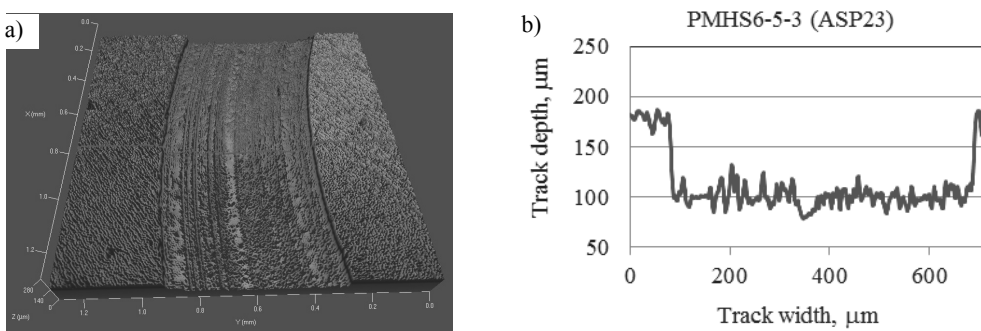


Fig. 25. Wear track of the PMHS6-5-3 and its profile

sintering. Such layers are characterised with higher resistance to wear than high-speed steel, with comparable friction coefficient. The kind of such wear should be defined as friction wear, due to various mechanisms occurring during the „pin-on-disc” or „pin-on-plate” test [48, 55]. Based on the measurement of the wear tracks produced during the „pin-on-disc” test of the HS12-1-5-5/MW surface layer and the PMHS6-5-3 (ASP23) high-speed steel, sintered with the HIP methods, it should be concluded that the depth of the wear track of the HS12-1-5-5/MW high-speed steels matrix composites presented in Figure 24 is lower than that of the wear track on the PMHS6-5-3 (ASP23) steel presented in Figure 25. The tests carried out on a confocal microscope proved that the average depth of wear track in the PMHS6-5-3 commercial steel is by ca. 10 µm higher. The results presented refer to friction path length of 600 m. Based on the friction track profiles produced during the „pin-on-plate” test, the areas of the cross-sections of wear were calculated (Fig. 26).

Analysing the wear test results of the HS12-1-5-5/MW high-speed steels matrix composites surface layer of gradient structure and the PMHS6-5-3-8 high-speed steel, sintered with the HIP method, covered with a TiN coat, 3.8 µm thick and of 2200 HV microhardness, it should be observed that the gradient material, produced with the pressureless forming method, shows slightly better properties. The HS6-5-2/MW high-speed steels matrix composites surface layer, injection moulded and sintered is characterised with a larger area of the wear track cross-section. The PMHS6-5-3 steel presents a comparable friction wear resistance, while the classically cast HS6-5-2 steel is characterised with the worst properties.

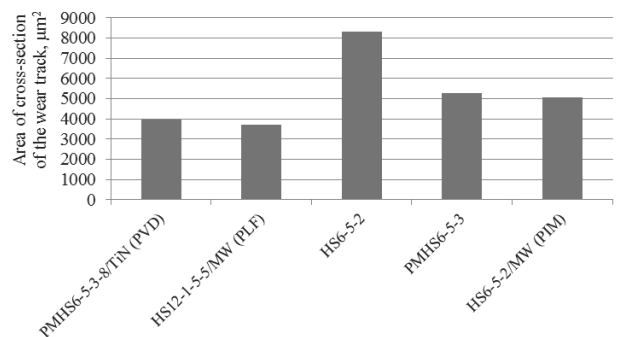


Fig. 26. Comparison of the area of cross-sections of the wear track produced during the „pin-on-plate” tests of investigated materials

#### 4. Summary and conclusions

The presented concept of combining surface engineering as a discipline of knowledge and technology of powder metallurgy is justified, the result being the tool materials with steel base and carbide steel surface layers. Thanks to the combination of high hardness and bending strength of the tool materials, provided in particular thanks to the pressureless powder forming, the usability of the tools produced is growing.

The author’s own test results indicate the reasonability of applying the powder forming and sintering techniques, in order to produce hard surface layers, particularly the pressureless forming process and sintering of carbide steel layers of gradient structure and

on a steel substrate. Selecting an appropriate binder, its proportion and controlling the technological process conditions, thanks to the increased concentration of carbon derived from the binder thermal degradation products, it is possible to produce carbide steel surface layers on steel substrate. Mainly, the high abrasion wear resistance of the surface layers, confirmed by tribological tests, exceeding even the resistance of tool steels, TiN coated in PVD processes, explicitly proves that the tool properties have improved and indicates the purposefulness of producing carbide steel surface layers. Analysing the test results on the tool materials produced, it needs to be pointed out that, disregarding the powder forming technique that all the materials comply with the assumption set and are characteristic of high hardness of the carbide steel surface layers. Unfortunately, the bending strength of the materials produced by pressing the powders in a mould or injection moulded carbide steel layers is lower in comparison to the classical high-speed steels. Moreover, the injection moulded surface layers should be sintered at 1240°C or above, in order to achieve low porosity. Such temperature is too high for the HS6-5-2 steel substrate applied.

The method presented of classical forming of layered structure moulds that upon sintering assume a gradient structure of rapid or linear growth of carbide proportion towards the surface, does not allow to obtain the expected high mechanical properties, particularly the high bending strength. The materials are not competitive to the widely used sintered carbides of homogeneous structure and by far better production technology. A. Simchi and M. Khakbiz obtained similar results, applying SiC as the phase reinforcing the HS6-5-2 steel matrix. The maximum bending resistance after sintering the materials was 850 MPa, while hardness was 250 HV [68]. High bending strength may be obtained by infiltrating the porous moulds, which was applied by J. Leżański and M. Madej in Poland, producing composites with HS6-5-2 steel matrix reinforced with WC carbide. However, the hardness of such composites is lower than that of the surface layers produced by pressing and presented in the paper. Undoubtedly, high hardness of composites with high-speed steel matrix may be obtained through mechanical synthesis of high-speed powders and carbides applied by J.M. Torralba, et al. [70]. However the high-speed steel powders, as a result of mechanical alloying with carbides are subject to refinement and reinforcement, which reduces their plasticity and compressibility while being pressed, while loose sintering does not assure high density and bending strength [70].

The author's own test results indicate that the carbide steel surface layers applied, injection moulded, sintered and thermally treated, are characteristic of higher hardness than carbide steels produced through the mechanical synthesis of powders, pressing and sintering where no soft infiltrating matrix is applied [52, 53]. Only the composites with high-speed steel matrix, reinforced with mixture of WC carbide and cobalt mixture with 44 and 6% proportion, respectively, are characterised with comparable hardness, compared to the injection moulded carbide steels [65]. The loose sintering of materials produced with the PIM methods assures higher strength to bending, compared to pressed materials. The structural test results confirmed the assumptions that the binder applied, in addition to its main function, i.e. enabling injection moulding or pressureless powder forming, is the source of carbon activating the sintering process. In case of high-speed steels or carbide steels produced with the PIM method, obtaining the high mechanical properties requires application of the final thermal treatment that is frequently ignored by research teams who focus on the powder forming, binder removal and sintering conditions

selection only [60-64]. Therefore, the tests taken up in order to explain the impact of binder and tool materials production conditions on the final structure and mechanical properties of the high-speed steel or carbide steel, thanks to which it was found that the growth of carbon concentration increases the proportion of residual austenite, which was proven by X-ray quantitative analysis tests after hardening, were justified. This causes the reduction of hardness of the steel matrix and causes the application of tempering in higher temperature in comparison to tempering the classical HS6-5-2 high-speed steel.

The pressureless powder forming method provides the possibility to produce a gradient, carbide steel surface layer on the HS6-5-2 steel base, of high hardness reaching the level of more than 1300 HV0.1 and the highest friction wear resistance among the materials tested (Figs. 24-26). The so high surface layer hardness was obtained after sintering and direct hardening from the 1230°C temperature and triple tempering at 570°C. Simultaneously, the bending strength depends on the steel substrate, its final thermal treatment after sintering and shape and size of pores in the sintered surface layer, such pores being the starting point of crack propagation. An interesting solution of the surface layer produced from the HS6-5-2 (O) high-speed steel powder, reinforced with WC carbide that melts under sintering and produces  $M_6C$ , of the voluminous proportion much higher than that of WC. In spite of the lower hardness of  $M_6C$  in comparison to WC, the coat hardness upon sintering is ca. 1050 HV0.1. An advantage of this material is the „natural” high hardness upon sintering, which required no further thermal treatment. The thermal treatment is recommended only in case of the low mechanical properties of the core upon sintering the surface layer. The application of this type of carbide steel surface layer on unalloyed steel substrate is more reasonable, because the sintering temperature of the layer may exceed 1230°C, i.e. the maximum HS6-5-2 steel austenitising temperature. Moreover, after sintering the thermal treatment of the unalloyed steel core may be done as it does not cause the coat hardness reduction.

The detailed tests of the carbide surface layers produced by powder injection moulding and pressureless powder forming indicate the synergic effect of the particular operations applied in the technological process. First of all, the following benefits should be specified here:

- application of a binder, its major purpose to apply a shape to the polymer-powder slurry, causes the growth of concentration of carbon activating the sintering process, increasing the sintering temperature range, preventing decarbonisation during soaking. In case of WWP on a steel substrate, the growth of carbon concentration in the boundary area between the coat and the base contributes to strong, diffusive combination with the substrate,
- use of the  $N_2-10\%H_2$  protective atmosphere enables an effective thermal degradation of the binder and at the same time to prevent oxidation of the surface, at the same time introducing the desired nitrogen to the sinter, which creates minor releases of the carbonitrides, restricting the growth of other carbide release grains and matrix grains,
- application of direct hardening from the sintering temperature, i.e. „sinterhardening”, excludes the necessity to reheat the material to the austenitising temperature, at the same time reducing the sinter cooling operation and enabling the saturation of the sinter matrix with the alloy elements, which causes the release of dispersion carbides reinforcing the matrix during high tempering,



- additional application of carbide mixture, particularly the internodular phases of regular lattice, stable in high sintering and austenitising temperature, inhibiting the growth of the primary austenite and also increases the carbide steel hardness.

Regardless of the type of binder applied, which affects the polymer-powder slurry forming method, and disregarding the sintering atmosphere and temperature in carbide steels reinforced with MW carbides, the release of large, eutectic carbides, typical for high-speed steels loosely sintered in the temperature exceeding the solidus line and sometimes also austenitised under such conditions, causing local melting, was totally eliminated. This is particularly significant due to the possibility to expand the sintering temperature range of carbide steel surface layers on steel base, which is restricted due to the loss of shape of the element sintered only, not due to the growth of carbides.

Based on the analysis of the test results obtained, the following final conclusions have been formulated:

1. The powder forming and sintering techniques applied enable the production of tool material of structure and properties changing in a continuous gradient or discrete ways, which enables to combine the high ductility of the steel core with the high hardness and abrasive wear resistance of the carbide steel surface layer of the tool. The best properties characterise the material produced by the proprietary method developed of pressureless forming of the polymer-powder slurry of the coats that upon sintering and thermal treatment represent a carbide surface layer of the base produced in a different technological process.
2. Analysis of test results enables the explanation of the impact of polymer-powder slurry formation on the properties of the sinters characterised with low porosity and homogeneous and fine-grained structure, in comparison to the sinters produced through classical pressing and sintering. Particular role is played by the binder used and its incomplete degradation, thanks to which the additionally introduced carbon activates sintering. The strict control of the binder degradation process is necessary, preceded by thermogravimetric tests and experiments, because of the excessive growth of carbon concentration in high-speed steel or high-speed steels matrix composites leads to partial melting and distortion of the sintered materials and growth of residual austenite upon thermal treatment.
3. The introduction of MW (WC, TiC, TaC, NbC) carbide mixture to the high-speed steel and sintering under the  $N_2$ -10% $H_2$  atmosphere prevents the occurrence of the eutectic structure being the result of partial melting during soaking in sintering temperature too high or austenitising of the high-speed steels. In spite of the partial melting and the liquid phase occurring during sintering of the carbide steels, proven by distortion of the samples sintered in 1290 and 1300°C, the structure is homogeneous and fine-grained with homogeneously distributed carbide releases, without any large carbide releases found, in the form of „fishbone” or „Chinese script”, typical for high-speed steels loosely sintered or austenitised under temperature exceeding the solidus line.
4. Based on the precise data concerning the properties of the polymer-powder mixture, it is possible to model the injection with the use of finite elements method and observe the process of filling the matrix with the polymer-powder slurry at the particular stages of the injection. The practical aspect of injection modelling needs to be particularly emphasised, because it may partly replace the costly technological tests.

The rheological testing results and computer simulation of the powder injection moulding using the CADMOULD software proved that the polymer-powder mixtures produced may be injection moulded, which was confirmed by carrying out injection moulding of the powder on typical injection moulders used in the industry. The injection moulding conditions, particularly the actual time of filling the cavity is comparable to the time presented in the computer simulation.

5. The pressureless powder forming method may be used for the production of high-speed steels matrix composites surface layers with gradient of structure and properties in order to produce tool or other materials operating under abrasive wear conditions. Sintering with the participation of the liquid phase of the powder representing the pressureless formed coat leads to the metallic fusion with the steel base. The production technology of high-speed steels matrix composites surface layers enables the increased abrasive wear resistance of commercial tool material, compared to its initial properties. Such technology may also be applied in the process of regeneration of worn surfaces of tools made from tool steels.

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