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Powder Injection Moulding of Tool Materials and Materials Containing One-Dimensional Nanostructural Elements

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Additional information is available at the end of the chapter

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Abstract

As modern manufacturing methods have been developing, the application methods of powders have changed, and they do not always have to be moulded prior to sintering. The powder injection moulding (PIM) method is suitable for large-lot and mass production; still, powder consumption is not too high. The metal injection moulding (MIM) is an advanced technology and not as developed as classical pressing and sintering but constantly and dynamically developing. The technology is developing towards micro-MIM, that is, production of very small parts for miniaturised devices. The chapter presents the overview of powder injection moulding as specialist powder metallurgy method and its application for fabrication of tool materials. Specially, the fabrication of high-speed steels and carbide-steels on their matrix by powder injection moulding is described. In last part of the chapter, the results of own investigations of the structure with nanostructural elements of high-speed steels and carbide-steels on their matrix fabricated by powder injection moulding are presented.

Keywords: powder injection moulding, debinding, sintering, tool materials
nanostructural elements

1. Introduction

As modern manufacturing methods have been developing, the application methods of powders have changed, and they do not always have to be moulded prior to sintering. This depends on the technological process applied, for example, hardfacing, thermal spraying, or selective laser sintering [1, 2] exclude the need of powder forming. Powder forming itself does

not have to be connected with pressing or with shaping the item being fabricated, as seen with the example of pressure-free moulding of coatings or foils using polymer-powder slips. Classical powder metallurgy is however based on pressing and at the same time forming the powder in such a way that the item has the dimensions and shape of a ready product or semi-product after sintering, requiring only minor final treatment [3, 4].

The introduction of atomisers into mass production of metallic powders allowed to reduce the production costs of sintered materials. For instance, the manufacturing cost of high speed conventionally cast and sintered steel at the end of the last century was comparable and dependent mainly on the price of alloy additives. The automotive industry is now estimated to be the key user of elements moulded and sintered using metallic powders [5]. Powder-pressed and sintered gears intended for gearboxes are characterised by very silent work, which is associated with the suppression of vibrations in porous materials. The teeth of such gears are burnished and heat treated, which ensure their high hardness and resistance to abrasive wear. Uniaxial pressing in closed dies is still most widespread and is dedicated to symmetric elements with relatively simple shapes. Products with a highly developed surface, small dimensions, and massively produced are manufactured by the injection moulding of powders witnessing very dynamic growth in the recent years. The moulding of ignition plugs' insulators was one of the first applications of this method in 1937 [6].

The method was employed in the 1970s of the last century for producing metals and ceramics used in electronics. The earlier limitations of this method were connected with binder removal, which is technologically difficult, time-consuming and is the source of defects in the form of cracks, gas bubbles, and distortions. In the majority of cases, binder removal is based on its thermal degradation, often without access of oxygen, that is, in the process of controlled pyrolysis. The growth of the technology in the recent years has been chiefly linked to a search for alternative solutions ensuring debinding, which is fast and safe for the products manufactured and for the environment. The methods of solvent degradation under heightened pressure in a vacuum and in supercritical pressure conditions were employed as a result of such investigations. The catalytic degradation method, adopted and developed by BASF, offering at that time ready granulates and binder removal devices, turned out to be a breakthrough method [7].

Although the powder injection moulding (PIM) method is suitable for large-lot and mass production; still, powder consumption is not too high. In general, the powders of metals and powders of metal alloys produced are principally designed for moulding and sintering products, and only a small fraction of powders is used in welding processes and in other processes, for example, in chemical industry. For instance, the United States have produced about 365 thousand tonnes of iron and steel powders in 2013, of which the powders used for other purposes than powder metallurgy account for only 10%. The remaining 90% include also powders used in the metal injection moulding (MIM) process. The MIM technology represents only 1% of all the metallic powders used in Europe in powder metallurgy. This signifies that this is an advanced technology and not as developed as classical pressing and sintering, but constantly and dynamically developing, which is confirmed by numerous Refs. [8–10]. It should be noted that the comparison of consumption in tonnes of powder for the MIM technology with other manufacturing methods is not the best indicator

of this method's popularity, because it is employed for producing small elements. The sales of parts manufactured by this method have grown very sharply in, for example, Europe and have gone up from less than 150 to over 250 mEUR between 2003 and 2013. The technology is developing towards micro-MIM, that is, production of very small parts for miniaturised devices [8, 11, 12].

2. Overview of powder injection moulding as specialist powder metallurgy method and its application for fabrication of tool materials

Powder forming and sintering technologies offer unlimited opportunities for selection of the chemical composition of the tool materials produced. Classical powder metallurgy, based on uniaxial pressing and sintering with potential isostatic pressing at a high sintering temperature, is used for the fabrication of the most popular tool materials such as sintered carbides produced as, for example, inserts for turning tools. Frequently, the simple shapes of such inserts do not require any other powder forming technique, whereas uniaxial pressing, especially one-sided pressing, is the easiest powder forming method, with no need to use a binder or a large inclusion of slipping agents, which ensures small shrinkage of the material after sintering. An uncomplicated technological process of fabrication of sintered carbides, introduced for the first time by a German company, Krupp, in 1926, is still enjoying great popularity, and sintered carbides themselves are the most often used tool material. For example, the annual growth rate for the market of sintered and superhard tool materials in 2007–2012 was 7.5% per annum, with the projected growth for the subsequent years of 11.3% [8, 13]. It is estimated that the global market of sintered carbides and superhard materials may reach the threshold of USD 20.2 billion in 2018 owing to the development of industry and production in developing countries and due to the resulting increased demand for highly efficient machining tools [14]. This method imposes, however, substantial constraints if carbide inserts with highly complex shapes are produced. An alternative, and actually an unrivalled method in such case, is powder injection moulding. It is injection moulding's strength that we can produce a complicated geometry or products in the final or nearly final form at once. We can come close to the final goal at once, and this is the crucial reason for choosing MIM [15]. The technology is dedicated to mass production solely, due to high investment costs necessitating the use of high class equipment. Metal injection moulding (MIM) is especially significant in metallic powder forming. **Table 1** lists the key advantages of the PIM method as compared to general disadvantages and advantages of other manufacturing techniques of elements with their shapes and dimensions similar to the final shapes and dimensions.

It is assumed that the powder injection moulding technology was introduced in 1849 by pressure casting of nonferrous metal alloys [8]. Further development was associated with proficiency in the polymer processing technology and with the first piston moulders constructed in the USA and Germany. PIM's history in Europe is relatively short and dates back 30 years ago. The first elements manufactured by this method are orthodontic hooks produced in Germany in the 1980s [17].

Selected characteristics	Technology			
	PIM	PM	Casting	Machining
Density	98%	90%	95–99%	100%
Strength versus solid material	100%	70%	98%	100%
Complexity	High	Low	Medium	High
Part weight	Between 0.003 g and 17 kg	Between 0.1 g and 10 kg	From 1 g	From 0.1 g
Wall thickness	0.1–10 mm	2 mm	5 mm	2 mm
Surface manufacturing accuracy	0.4–0.8 μm	2 μm	2 μm	0.4 do 2 μm
Production scale	Mass	Mass	Medium/low	Medium/low

Table 1. Selected characteristics of elements manufactured by various technologies [16].

The injection moulding of a polymer-powder slip allows to produce relatively small parts with complicated shapes and developed area and requires no plastic working or machining, which is in line with the modern direction of producing ready parts, that is, “near-net-shape”. Despite numerous advantages, the injection moulding process is not suitable for fabrication of large parts. The largest dimension should not exceed 100 mm. This is because subsequent debinding is required prior to sintering, as the polymer materials contained in a binder are undergoing gassing during thermal degradation, and the pressure of the gas closed in the pores is rising due to being abruptly heated to sintering temperature. The wall thickness of the parts manufactured by this method is not more than 10 mm, they have complicated shape and high manufacturing precision and low production costs [9, 18]. This method is most often applied for manufacturing parts hard to produce by other techniques, for example, elements with the smallest mass of not more than 0.5 g, in particular orthodontic hooks [16]. The technology, considering a possibility of production automation, high speed and dimensional repeatability and high costs of injection moulders and heating devices, is designed for large-lot or mass production [19, 20]. Owing to the principal advantage of this technique—where ready parts are produced without additional treatment being necessary—the technique is used more and more extensively for producing hard materials, including tool materials, which are exceptionally difficult and costly to machine [6, 9, 13, 15, 21]. The formability of metallic and ceramic powders and their mixtures enables to fabricate metal tools with relatively high ductility, ceramic tools with high hardness or metal matrix composites (MMC) and ceramic matrix composites (CMC) combining high properties distinct for metals and ceramics [22–25]. The forming of metallic or ceramic powders in a matrix of polymer binders, especially injection moulding or extrusion, has been applied for producing tool materials, including high-speed steels, carbide-steels and sintered carbides, characterised by their structure similar to commercial sintered tool materials [26–29]. It is not possible to achieve such high bending strength as for high-speed steels fabricated by hot isostatic pressing or for sintered carbides pressed

isostatically during sintering. The main reason for lower bending strength of the manufactured tool materials is not, however, powder forming technologies, but the process of self-sintering, which does not allow to eliminate completely the locally occurring pores being material discontinuity lowering the material's mechanical properties. It is beyond doubt a benefit of polymer-powder slip forming, mainly powder injection moulding, that plastic working and machining operations are eliminated, hence reducing the related costs, as a result of which application possibilities of the so manufactured tool materials are offered, especially where they are not subject to strong dynamic loads. Moreover, the parts produced this way do not have to act only as tool material but act as an element working in the conditions of tribological wear. An additional benefit of injection moulding of the investigated tool materials is that protective and/or reactive atmospheres can be utilised for sintering, permitting to use furnaces cheaper than vacuum furnaces and hence allowing automation. The use of modern, polymer binder-based powder forming technologies, in particular injection moulding, for preparing tool materials, offers promising perspectives for the manufacture of tool materials and is consistent with the valid development trend of this technology. The sales of products manufactured by PIM and MIM have been growing over the last 25 years and signify the industry's huge interest in such methods [30].

In powder injection moulding, an injected preform is produced, which should then undergo debinding and sintering to achieve high functional properties [16, 18, 27, 30, 31]. Classical injection moulding in moulders is the same as the moulding of thermoplastic polymers (Figure 1).

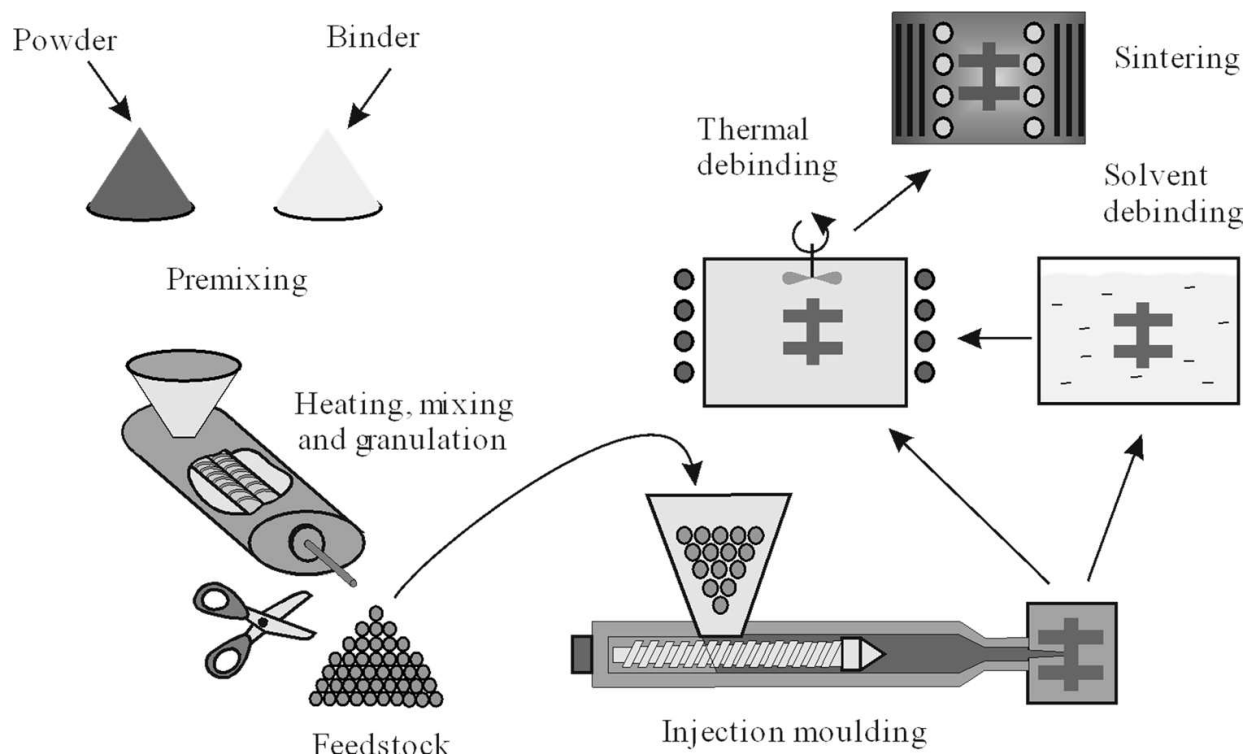


Figure 1. General chart of powder injection moulding.

Metallic or ceramic powders, and even their mixtures, are used as feedstock in powder injection moulding. The use of thermoplastic polymers as a binder, which is binding metallic or ceramic powder, enables to transport it and mould it in an injector socket. Two types of binders based on, respectively, paraffin and polymer materials and an aqueous methylcellulose solution (Wiech's or Rivers' solution), are used most often [8]. A powder-to-binder ratio is closely linked to the shape, size of powder particles, material type, powder wettability by a binder, and the properties of the binder itself and is also linked to mixture production conditions [32, 33]. By the rule, it is more difficult to mix ceramic powders with a binder and to inject them than is the case with metallic powders. A binder with larger fraction has to be used for this. **Figure 2a** shows the influence of powder fraction on viscosity curve.

Debinding must be carried out in such a way to prevent cracks, blisters, shape deformation, gas bubbles, or semi-product delamination, so it should be deformed early enough, maintaining the shape of the element produced. The most popular method of debinding used in PIM (**Figure 2b**) is thermal degradation and solvent degradation. A mixed method is linked to combined degradation techniques, for example, solvent and thermal technique.

Currently, for exceptionally small preforms formed, for example, in the μ PIM process, debinding is associated with heating to a sintering temperature [8, 12]. Regardless the semi-product size, debinding is making a preform becoming very brittle. Reducing atmospheres consisting of hydrogen with a high concentration of hydrogen (85%) ensure highest strength, hence, increase carbon concentration in the preform after sintering. Preform density is about 60% of the theoretical density when the binder is completely removed. This density depends on the binder fraction, and this fraction depends on the type of the powder formed. Most often, metal powders are so selected that they are characterised by a circular shape with good wettability, which allows to reduce the binder fraction as much as possible to only 30%. The binder fraction in case of ceramic powders may reach even 55%.

Preform sintering takes place after debinding. Irrespective of the preform density, it is subjected to densification and shrinkage due to sintering. This is natural regardless the preform

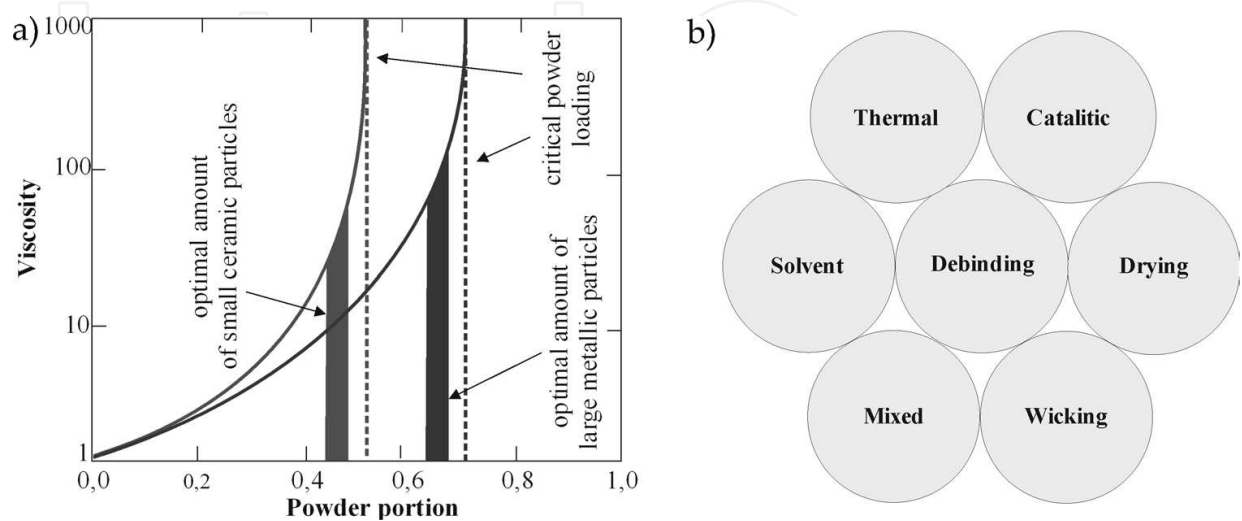


Figure 2. (a) Influence of type and amount of powder on viscosity, (b) debinding methods in PM technologies.

forming method; however, as a result of high porosity, shrinkage is very strong and an uncontrolled change of the sintered elements' shape may occur. Because a change in the volume of the sintered material is inversely proportional to its density after forming, growth in preform density reduces the risk of shape defects of the preform being formed. Injection pressure, powder size, and binder fraction have influence on increase in preform density. Sintering is usually the last operation of the technological process decisive for density and properties of the ready product [18]. If the ready element should have high mechanical properties, final heat treatment and often machining are used to ensure accurate dimensions of the produced sinters. The sintering of injection moulded or pressure-free moulded powders does not differ largely from the sintering of powders formed by other methods. The key properties of sinters, especially tool materials, are improved by the formation of carbonitrides as a result of the interacting atmosphere containing nitrogen during debinding and sintering [23]. Sintering is initiated by growth in the concentration of carbon resulting from debinding, however, in case of some materials such as stainless steels or high-speed steels, carbon concentration must be closely monitored due to their properties or influence on heat treatment. The type of the binder used influences the final carbon concentration [18]. Sintering is also influenced by particle size. Injection-moulded fine-grained powders with a larger specific surface area are filling the volume of the sintered preform more thoroughly and are subject to faster remelting. The powder particle size is also decisive for surface roughness and for the value of the sintered material's edge radius. In case of classical pressing, fine-grained powder is not filling the die socket so well due to low-powder liquidity. An atmosphere inside the furnace chamber is an important factor conditioning sintering [26]. Although the vacuum is not related to direct gas costs, vacuum sintering is a costly alternative considering that furnaces are equipped with vacuum systems and require maintenance. Nonetheless, vacuum is often used for sintering high-speed steels, especially those pressed in a die or pressed isostatically. The sintering of injection-moulded high-speed steels in high vacuum is quite difficult due to the gas products being released, coming from the thermal degradation of base polymer residues. Final heat treatment is required to achieve high mechanical properties for high-speed steels or sintered carbides manufactured by PIM [34–38].

3. Fabrication of high-speed steels and carbide-steels on their matrix by powder injection moulding

Two types of tool materials, that is, high-speed steels and carbide steels with the matrix of the same high-speed steels were fabricated by the powder injection moulding method. The powders of high-speed steels with the chemical composition given in **Table 2** and with the particle size determined by the laser diffraction method in the Malvern Mastersizer 2000 device shown in **Figure 3**, and with density and technological properties presented in **Table 2**, were fabricated by atomising inert gas (**Figures 3 and 4**) by Sandvik Osprey Ltd. A commercially available mixture of carbides, with the trade name of Tetra Carbides (in this chapter TetraC) by Treibacher Industrie AG containing WC, TiC, TaC, and NbC carbide powders with the volume fraction and technological properties presented in **Table 3** and other properties given in **Figure 3** and morphology given in **Figure 4** were used as hard carbide phases.

Steel grade	Mass concentration of elements (%)							
	C	W	Mo	V	Co	Cr	Mn	Si
EN HS 6-5-2	0.84	6.54	4.81	1.95	–	3.97	0.36	0.35
EN HS 12-0-5-5	1.47	11.8	0.06	4.75	4.64	4.76	0.5	0.43

Table 2. Concentration of alloy elements in high-speed steels powders used.

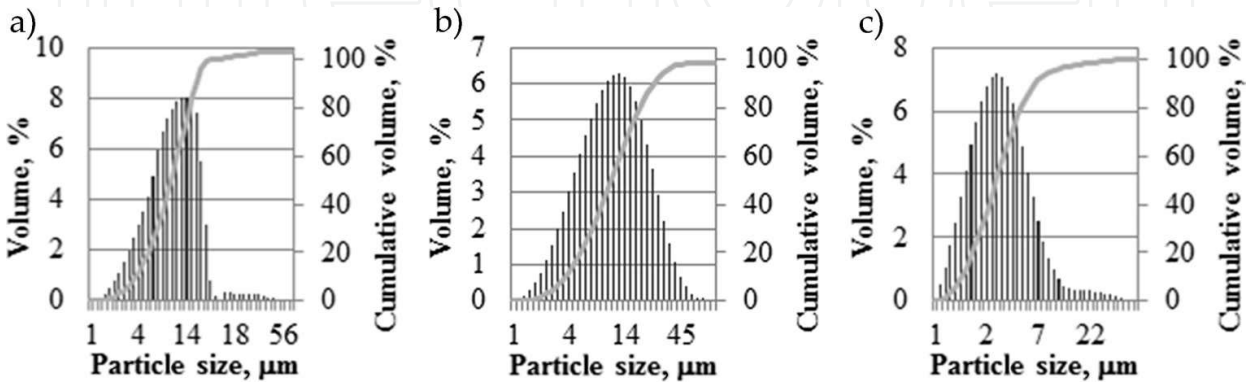


Figure 3. Particle size distribution of (a) EN HS 6-5-2, (b) EN HS 12-0-5-5 high-speed steels powder, and (c) carbides WC, TiC, TaC, NbC mixture (TetraC).

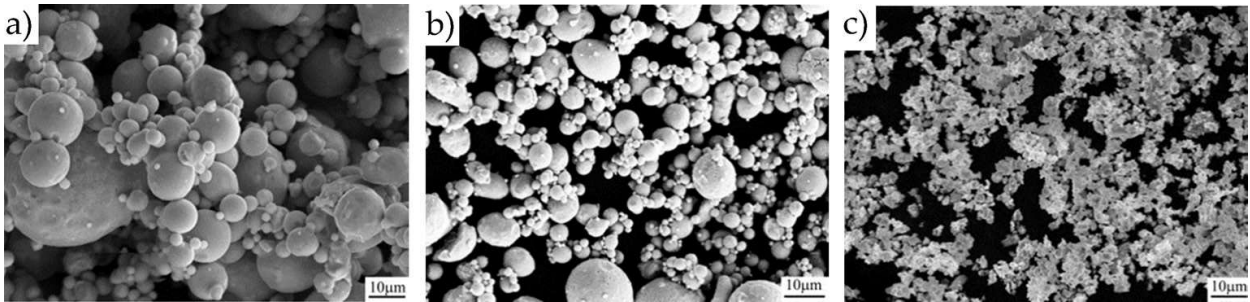


Figure 4. Morphology of (a) EN HS 6-5-2, (b) EN HS 12-0-5-5 high-speed steels, and (c) mixture of EN HS 12-0-5-5 high-speed steel and carbides WC, TiC, TaC, NbC mixture (TetraC).

Powder	Powder properties		
	Density (g/cm ³)	Bulk density (g/cm ³)	Tap density, (g/cm ³)
EN HS 6-5-2	8.16	2.89	4.02
EN HS 12-0-5-5	8.19	3.05	4.25
Mixture 47% WC, 14% TiC, 33% TaC, 6% NbC (TetraC)	10.23	4.38	5.64

Table 3. Technological properties of used powders.

The applied high-speed steel powders meet the condition indicating that ball-shaped powder with the average particle size of below 20 μm is most suitable for injection moulding of powders. The ball shape is most desired due to high wettability, low slipping agent viscosity, and high-packing density of particles. The size distribution of particles is also an important factor. If particle size distribution is relatively broad, then the pores forming between large grains may be filled by small particles, as signified by the Sw curve inclination coefficient Eq. (1) [18].

$$Sw = \frac{2.56}{\log \frac{D_{90}}{D_{10}}} \quad (1)$$

The powder with the Sw coefficient of about two is most recommended for injection moulding. It is not recommended to mould powder with the Sw coefficient of seven with its powder grain size distribution characteristic being very narrow. The powder particle size analysis is shown in **Table 4**. Pure steel powder, EN HS 6-5-2, has the highest Sw coefficient value. If a mixture of WC, TiC, TaC, and NbC carbides is introduced into the powder of high-speed steels, this is broadening the powder grain size distribution characteristic, thus advantageously reducing the Sw coefficient whose lowest value for the mixture of high-speed steels EN HS 12-0-5-5 with carbides is 2.69. The calculated Sw coefficients of the applied powders do not exceed the value 4, which signifies that they can be used for injection moulding [18]. **Table 5** presents information about the components of the formed powder and polymer-powder mixtures.

The purpose of the stearic acid used was to cover the surface of carbide powders before mixing them with high-speed steel powders. Stearic acid covering the carbides with a thin layer is increasing their wettability when mixing with other binder components and decreasing a ready feedstock's viscosity [8, 13, 31, 39]. Next, the covered carbides together with a binder and high-speed steel powder were initially agitated in a chamber of a universal Rheomex CTW100p stirrer by Haake enabling to measure torque and rotation speed of stirrers and charge temperature. The results of rheological tests for the mixtures of high-speed steel powders, carbides and binder, carried out with a capillary rheometer, Rheoflizer by ThermoHaake, at 170, 180 and 190°C, with the homogenisation speed of 10–10000 s^{-1} and with the torque depending on the phase composition of the examined polymer-powder mixtures and their homogenisation time, allowed to select a mixture with relatively low viscosity, high volume fraction of powders, good powder wettability by applying a binder and thus with the ability of fast homogenisation.

Powder	High-speed steels		Carbide mixture in TetraC	Mixture of appropriate high-speed steels with mixture of TetraC	
	EN HS 6-5-2	EN HS 12-0-5-5		EN HS 6-5-2	EN HS 12-0-5-5
Undersize D_{10} (μm)	3.5	4.68	1.45	2.8	2.8
Undersize D_{90} (μm)	16	28.5	7.3	17	25
Coefficient Sw	3.87	3.25	3.64	3.26	2.69

Table 4. The curve slope coefficients of the particle size distribution Sw calculated on the basis of undersize D_{10} and D_{90} .

Metal matrix	Carbides	Binder
EN HS 6-5-2	–	PW, PP, HDPE, SA
EN HS 12-0-5-5	–	
EN HS 6-5-2	Mixture 47% WC, 14% TiC, 33% TaC, 6% NbC (TetraC)	
EN HS 12-0-5-5		

Table 5. Components of the formed powder and polymer-powder mixtures.

The possibility of injection moulding of the applied polymer-powder mixture was initially evaluated based on the results from measuring the torque of stirrers during skip homogenisation. The maximum fraction of solid particles was thus established while maintaining relatively low viscosity of the polymer-powder mixture enabling injection moulding or extrusion. A high fraction of powder ensures minimum shrinkage in sintering, while an increase in binder fraction ensures easy forming but extends degradation time and increases sinter shrinkage which often causes the occurrence of distortions [9]. Irrespective of the polymer-powder mixture type, paraffin fraction was always equal to the fraction of the main binder component, that is, polyethylene or polypropylene.

Figure 5a shows the influence of high-density polyethylene (HDPE) and polypropylene on the torque curve during homogenisation of polymer-powder slip containing 70% of EN HS 12-0-5-5 steel powder. Regardless the homogenisation time and type of high-speed steel powder, a mixture containing a polypropylene-paraffin (PP/PW) binder is characterised by the lowest torque of stirrers in relation to a mixture containing an HDPE/PW slip. The minimum torque value for stirrers during the homogenisation of a mixture containing polyethylene for 3 h is about 2.2 Nm. In case of a feedstock containing polypropylene, torque after such long homogenisation time is 1 Nm. A curve for a mixture with polyethylene applied is not stable, which may signify inhomogeneous distribution of metallic powder in the binder matrix,

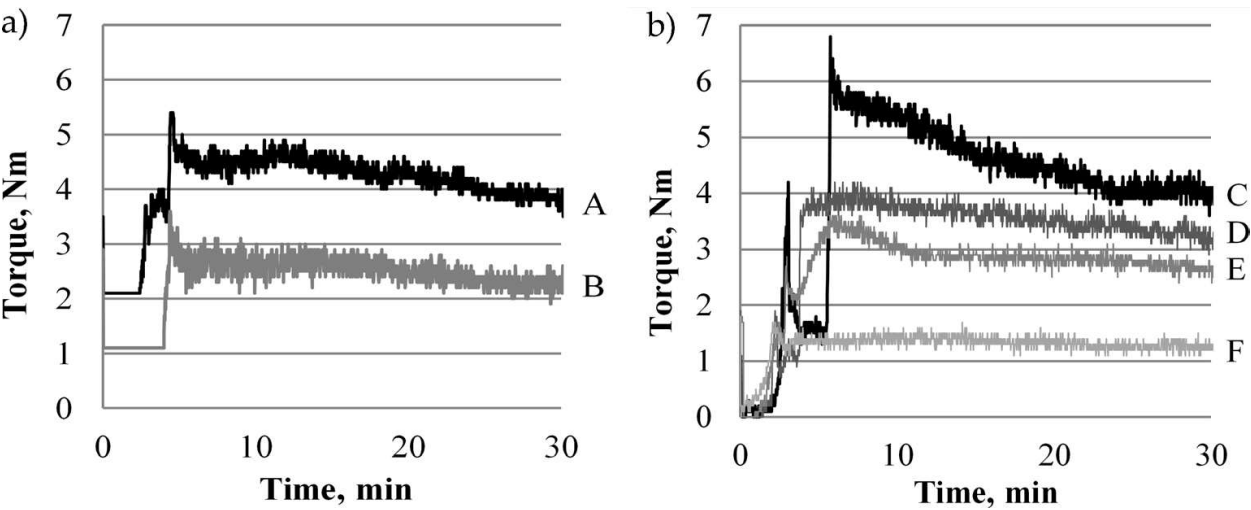


Figure 5. Torque measurements of feedstock with (a) 70% of EN HS 12-0-5-5 and two different binder compositions: A – HDPE/PW, B – PP/PW, (b) different amount of EN HS 6-5-2 powder: C – 75%, D – 70%, E – 65%, F – 60%.

despite long homogenisation time. Torque for a mixture with PP applied is going down over the entire homogenisation range, that is, over 3 h.

A correctly selected binder should wet the powder and reach the homogenous state within short time of about 30 min, and the torque characteristic should then stabilise. The longer time of homogenisation may lead to partial degradation of the low melting binder component, paraffin (PW) in this case, or to breaking PP and HDPE chains and to re-netting. The consequence of this would be higher torque, which is precluded by a falling tendency of the analysed curves.

Figure 5b shows torque variations depending on the fraction of high-speed steel EN HS 6-5-2 powder. If powder fraction is decreased by 5%, the torque characteristic is more uniform and the torque value after 30-min homogenisation falls from 4.0 to about 3.1 Nm. If powder fraction is again decreased by 5 and 10%, this causes the characteristic to be further equalised and torque to be reduced to the minimum value of about 1.2 Nm. The torque of the stirrers homogenising (for 1 h) a polymer and powder slip containing 60% of TetraC and a PP/PW binder is about four times higher in relation to the torque of the similar mixture containing EN HS 6-5-2 steel powder. The torque value is substantially decreased by using stearic acid (SA) covering the surface of carbides. Stearic acid was not used for covering high-speed steel powders due to its adverse impact on the high-speed steel structure after sintering, characterised by large precipitates of carbides on grain limits [31].

A low value of torque of mixtures containing polypropylene (PP) and paraffin (PW) corresponds to low viscosity. Powders of the EN HS 12-0-5-5 steel mixture with PP and PW exhibit smaller viscosity in relation to a mixture containing HDPE instead of PP, and this is independent of the homogenisation rate (**Figure 6a**). A mixture of high-speed steel with TetraC, which is accounting for 10% of the volume fraction, also has low viscosity similar to the mixture of EN HS 12-0-5-5 steel with PP and PW. Paraffin, apart from lessening the density, allows to use solvent degradation expediting the rate of thermal degradation and shortens the duration of the whole cycle.

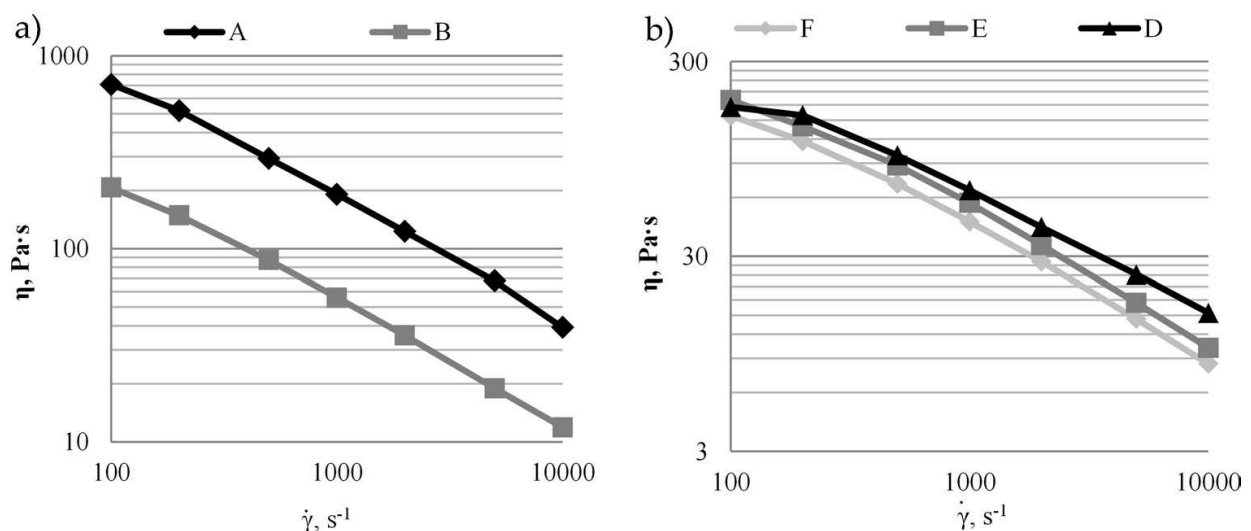


Figure 6. Viscosity curve for selected feedstock with (a) EN HS 12-0-5-5 and two different compositions: A – HDPE/PW, B – PP/PW, (b) different amount of EN HS 6-5-2 powder: D – 70%, E – 65%, F – 60%.

Metallic powder with a 60, 65 and 70% fraction containing a polypropylene-paraffin binder generally shows low viscosity regardless the fraction of powder. A mixture with the lowest content of powder exhibits the lowest viscosity (**Figure 6b**). Polypropylene and paraffin are the main binder component regardless the content of stearic acid.

Stearic acid improves wettability of metallic and ceramic powders by covering their oxidised (polar) surface that adsorbs the hydrophilic part of the chain as a result of the existing electrostatic forces between the powder and the wetting agent. The nonpolar part of the chain should be mixed without limitations with other polymers present in the binder. Apart from reducing viscosity, stearic acid is acting as a slipping agent in contact between the powder and the die surface or the surface of another particle. It also prevents powders from migrating during high-speed homogenisation. A process of migrating the powder inside the capillary or the destruction of the binder structure occur most probably during the high-speed homogenisation of a mixture not containing stearic acid. This is manifested by strongly falling viscosity together with an increased homogenisation rate. The viscosity of the mixtures containing stearic acid is not so much dependent on a homogenisation rate; hence, the growing rate of homogenisation does not have such a strong effect on the structure of a homogenous mixture. The torque is only negligibly decreased by increasing the content of stearic acid by another 4%; hence, its content did not exceed 4%.

Considering the feedstock viscosity, the maximum applicable fraction of carbides not coated with stearic acid is 50%. If stearic acid is used for a mixture containing 50% of carbides, viscosity is greatly reduced and a higher volume fraction of carbides can be obtained. The maximum volume fraction of powders which can be applied in a mixture for injection moulding was established by analysing the technological properties of polymer and powder mixtures containing binder-carbides, and hence, a mixture with only a 10% volume fraction of carbides was applied. Four different polymer-powder mixtures for injection moulding were selected and prepared. The fraction of such mixtures was presented in **Table 6**. The letter F was used in denomination to differentiate the injector’s feedstock from pure powder.

The injection moulded materials were then subjected to solvent degradation, thermal degradation, sintering, and heat treatment. The specimens were sintered in a pipe furnace in the atmosphere of a flowing mixture of N₂/10%H₂ gases with the maximum sintering temperature of 1450°C. The sintering time of the moulded parts, regardless the furnace type and sintering

Injector feedstock	Fraction volume of component (%)						
	EN HS 6-5-2 (O)	EN HS 12-0-5-5	TetraC	PP	HDPE	PW	SA
F EN HS 6-5-2	68	–	–	–	16	16	–
F EN HS 12-0-5-5	–	68	–	–	16	16	–
F EN HS 6-5-2/TetraC	58	–	10	14	–	14	4
F EN HS 12-0-5-5/ TetraC	–	58	10	14	–	14	4

Table 6. Types of injection-moulded polymer and powder mixtures.

temperature, was 30 min each time. A sintering temperature was selected experimentally. The sintering temperature range was determined based on preliminary tests of 1180–1300°C with 20°C steps. Heating speed to sintering and cooling temperature was 5°C per min. Further heat treatment was performed with classical hardening from an austenitisation temperature of 1220, 1240 and 1260°C, and triple tempering in the same temperature of 540, 570, 600 or 630°C for 1 h was carried out directly after hardening in oil.

The conditions of solvent degradation were selected experimentally taking account of the element mass depending on the paraffin solving time and bath temperature. Correctly performed debinding should ensure a uniform concentration of carbon within the entire volume of the specimen. EN HS 6-5-2 steel subjected to thermal degradation at 450°C, in the atmosphere of N₂-10%H₂ and sintered at 1240–1260°C, reaches density close to theoretical density, that is, it does not exhibit any pores (**Figure 7a**). The density of EN HS 6-5-2/TetraC carbide-steel sintered within the same temperature range was shown in the **Figure 7** to compare the influence of carbon additives on the optimum sintering temperature ensuring highest density. EN HS 6-5-2/TetraC carbide-steel reaches the maximum density of 8.77 g/cm³ after sintering at 1260°C. The density values were deliberately not referenced to the theoretical density of the material fabricated, which, based on the calculations, should be 8.69 g/cm³. A varying chemical composition of the sinter as a result of an increased concentration of carbon, dependent upon debinding and upon the nitrogen coming from the atmosphere during sintering and forming the carbonitrides, does not allow to determine accurately what should be its maximum density. In addition, the WC, TiC, TaC and NbC carbides introduced are dissolving in a high-speed matrix during sintering at a high temperature and create M₆C and MC-type carbonitrides or MX carbonitrides in it, in case of sintering in an atmosphere containing nitrogen, identified with the diffraction methods. The density of the newly created phases differs from the carbides introduced, which is impacting the sinter's overall density. For this reason, the sinter porosity presented in **Figure 7b** is a very interesting piece of information. Regardless the sintering temperature, EN HS 6-5-2/TetraC carbide-steel is characterised by low porosity not exceeding 1%, appropriate for tool materials. The share of pores in the most

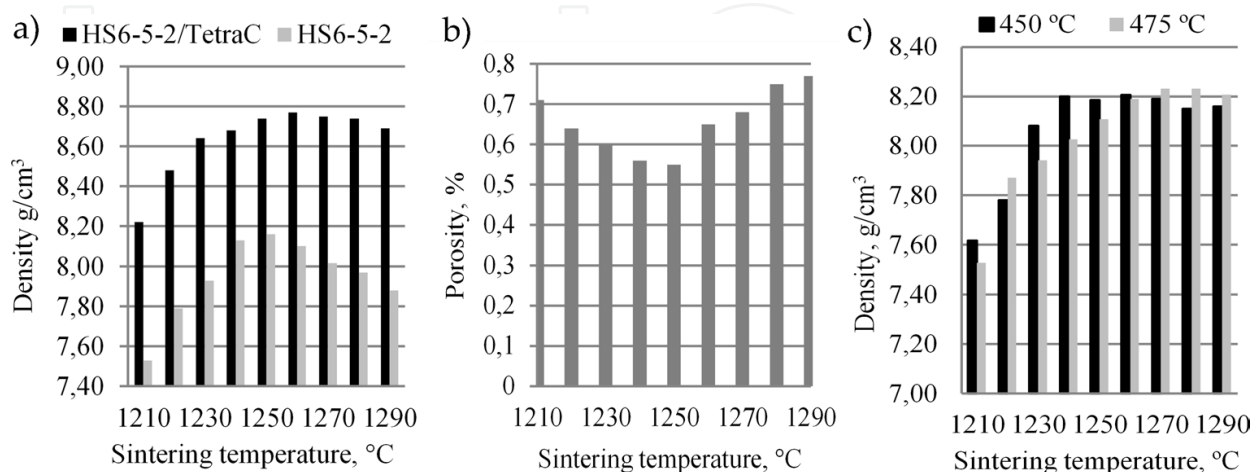


Figure 7. Influence of sintering temperature on (a) density of EN HS 6-5-2 and EN HS 6-5-2 /TetraC, (b) porosity of EN HS 6-5-2/TetraC, (c) density of EN HS 12-0-5-5 depend on debinding at 450 or 475°C and sintering temperature.

interesting range of the sintering temperature of 1240–1260°C is about 0.6%. The pores are ball shaped in the majority of cases and do not exceed the size of 2 μm ; however, large pores may exist locally, which are forming most probably as a result of gas bubbles being formed during injection moulding or thermal degradation. Changes in the EN HS 12-0-5-5 steel density presented in **Figure 7c** points out that a lower degradation temperature is reducing a sintering temperature. The maximum density in the sintering temperature of 1240°C occurs after degradation at 450°C. If the degradation temperature is increased by 25°C, it becomes necessary to increase the sintering temperature by 30°C to achieve the maximum sinter density. Generally, EN HS 12-0-5-5 steel can be sintered within a broader temperature range versus EN HS 6-5-2. It was found by observing the structure of the sintered carbide-steels in which TetraC was applied covered with stearic acid that both, in EN HS 6-5-2/TetraC material and in EN HS 12-0-5-5/TetraC, the carbides surrounding the high steel grains are inhibiting their growth. The grain size of the sinter matrix is comparable to the particles of the high-speed steel powder employed. It is feasible to manufacture tool materials with high functional properties by selecting an appropriate binder, binder fraction and by controlling the technological process conditions, which enables to increase a concentration of carbon coming from thermal degradation products of the binder surrounding the nitride particles and activating a sintering process. Unfortunately, the locally occurring bubbles of the gas created during injection moulding or thermal degradation are not eliminated during free sintering, despite the presence of the liquid phase, which effectively compromises the bending strength of the sinter. Due to large gas bubbles existing in the material, further heat treatment does not influence bending strength, and the maximum value of about 1400 MPa is lower than the strength of conventional EN HS 6-5-2 cast and heat treated steel. The binder used, apart from its key task, that is, to enable injection moulding, plays an additional role as a source of carbon activating sintering. A rising concentration of carbon is dependent here upon the type of the binder and its debinding conditions.

4. Results of own investigations of the structure with nanostructural elements of high-speed steels and carbide steels on their matrix fabricated by powder injection moulding

In case of high-speed steels, dispersion carbides are released during tempering, and more rarely as pre-eutectoid precipitates when cooling from austenitisation temperature. In carbide-steels, small dispersion precipitates of the nanometric size occur extensively after quenching and tempering and after sintering. Such precipitates are surrounding large M_6C carbides and primary austenite grains blocking their growth. Moreover, they dissolve more quickly in austenitisation because of their small size, and alloy additives responsible for the secondary hardness effect are passing more easily to the matrix. The structure of EN HS 6-5-2/TetraC carbide-steel sintered at 1230°C shows small growth and coagulation of carbides in relation to the high-speed steel structure, sintered at the same temperature. Despite this, the structure of carbide-steels is still homogenous and fine-grained with carbides surrounding circular grains of high-speed steel. When comparing EN HS 6-5-2 and EN HS 6-5-2/TetraC

materials sintered in the same conditions at the temperature of 1300°C, one may conclude that a strong distortion occurred in the both cases, signifying an extensive liquid phase existing during sintering. A structure of carbide-steel sintered at 1300°C (**Figure 8c**) does not exhibit, however, an eutectic typical for a high-speed steel presented in **Figure 8b**. Carbides in high-speed steel with a characteristic “fishbone” shape are revealed as light phases in the image of secondary electrons and contain mainly Fe, W, Mo and a small concentration of V. The precipitates are sized up to 1 μm . If a mixture of carbides is employed, in particular interstitial phases with a regular network, stable at a high sintering and austenitisation temperature, the growth of primary austenite grains is inhibited and the hardness of carbide-steels after heat treatment is improved in relation to high-speed steel. Irrespective of the type of the binder used, which is influencing the way a polymer-powder slip is formed, and also irrespective of the sintering temperature and atmosphere, the precipitation of large, eutectic carbides typical for high-speed steels sintered freely at temperature exceeding the solidus line was completely eliminated in carbide-steels and also sometimes austenitised in such conditions, causing local remelting. Owing to such property, it is not necessary in sintering to use heating devices equipped with very accurate measuring and control systems ensuring temperature stability within a very narrow range, that is, approx. 5°C for the EN HS 6-5-2 steel applied.

The average size of carbides in carbide-steel sintered at 1300°C is rising by approx. 0.1 μm in relation to carbides existing after sintering at 1280°C. The average and maximum size of carbides and their fraction volume in EN HS 6-5-2/TetraC sintered within the entire temperature range are given in **Table 7**. The so-selected chemical composition of carbide steel sintered in the atmosphere of a flowing mixture of N_2 -10% H_2 gases enables sintering within a wide temperature range ensuring a homogenous structure. If the protective atmosphere of N_2 -10% H_2 is applied, surface oxidation is prevented during thermal degradation and especially during sintering, while introducing at the same time, the desired nitrogen into the sinter forming fine nanometric carbonitride precipitates limiting the grain growth of other carbon precipitates and matrix grains, in particular carbide steels. When sintering temperature is raised from 1200 to 1300°C, the average size of carbides is increased by about 70%.

WC carbides with light colour based on secondary electrons are presented in **Figure 9**. A phase with grey colour rich in W, Fe, V, and Mo was formed from the alloy additives situated in high-speed steel or from elements coming from the solved carbides introduced into the steel. No existence of WC carbides was found at an elevated sintering temperature, which is con-

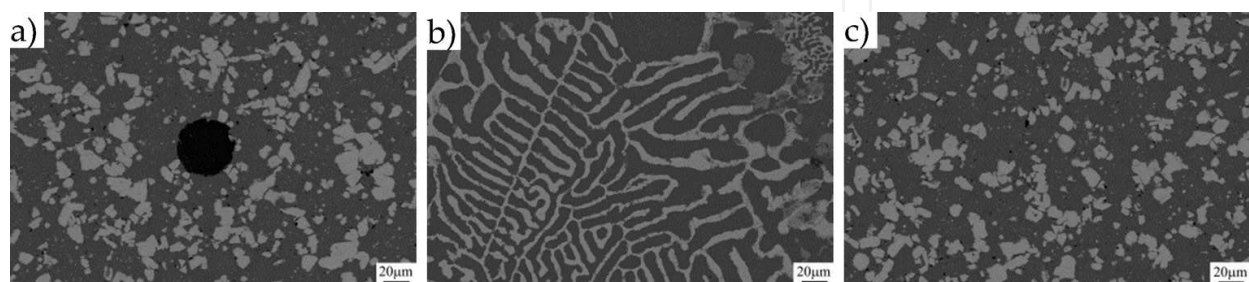


Figure 8. (a) Microstructure of metal matrix composite on the basis of EN HS 6-5-2/TetraC with large spherical pore, (b) and (c) structure of sintered at temperature 1300°C, (b) EN HS 6-5-2, (c) EN HS 6-5-2/TetraC.

Sintering temperature (°C)	1200	1220	1240	1260	1280	1300
Carbides amount (%)	36.2	35.9	33.8	33.2	34.2	34.2
Average size of carbides (µm)	1.65	2.06	2.2	2.66	2.71	2.82
Maximum size of carbides (µm)	21.57	25.68	28.54	31.58	38.17	40.58

Table 7. Average and maximum size of carbides precipitation and their amount versus sintering temperature.

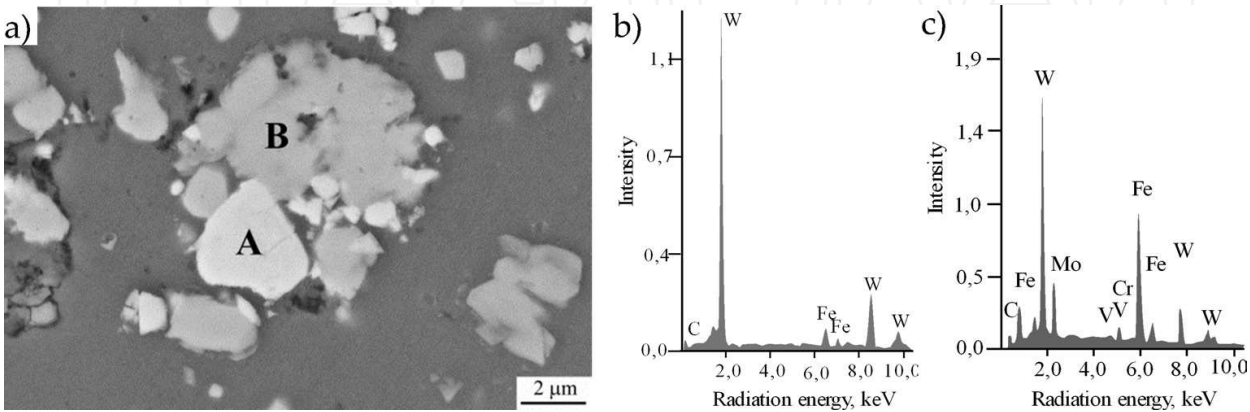


Figure 9. (a) Structure of EN HS 6-5-2/TetraC carbide-steels sintered at 1200°C and a charts of scattered X-ray radiation for the areas marked in (a) (b) A and (c) B, respectively.

firmed by the results of an X-ray phase analysis. M_6C and MC carbides typical for high-speed steel were identified, though. The growth of light carbides, shown in the image of secondary electrons, rich in W, Mo, and Fe, is limited by the surrounding grey, spherical precipitate rich in Ti and V, presented in **Figure 9a**, the size of which does not exceed mostly several dozens of nanometres, and the largest ones do not exceed 1 µm. In order to better present such nanometric precipitates, **Figure 10** shows the morphology of carbides in the form of sediment of electrolytically isolated precipitates.

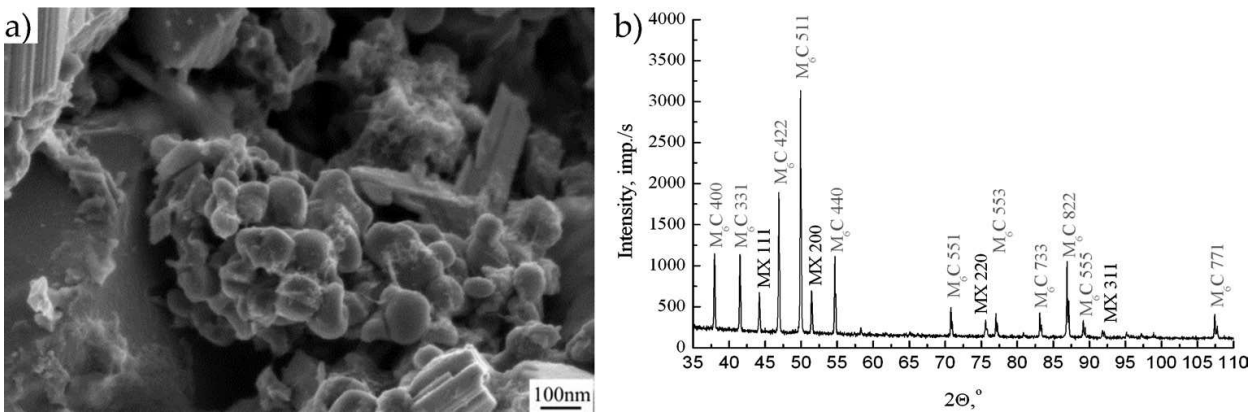


Figure 10. Structure of EN HS 6-5-2/TetraC carbide-steel sintered at 1280°C, (a) sediment of electrolytically isolated precipitates, SEM, (b) X-ray diffraction pattern of electrolytically isolated precipitates from EN HS 6-5-2/TetraC carbide-steel tempered and quenched at 540°C.

The existence of M_2C carbides typical for EN HS 6-5-2 high-speed steels, rich in molybdenum, in the form of long needles, precipitated at a high sintering temperature and considerably reducing mechanical properties, was not found [40]. M_6C and MX precipitates exist only in the sediment of electrolytically isolated carbides (**Figure 10**).

Nanometric precipitates in EN HS 6-5-2/TetraC carbide-steel are presented in **Figures 11a** and **12a** present results of examinations of precipitates coming from EN HS 6-5-2/TetraC carbide-steel after heat treatment in a transmission electron microscope. The diagram of the function of scattered X-ray radiation for such precipitates presented in **Figures 11b** and **12b** proves that carbides are rich in tungsten and molybdenum, which rather indicate the M_6C phase, not MC or M_2C phase released in high-speed steels during tempering. Undoubtedly, their size does not exceed 200 nm. It should be added that typical dispersive MC or M_2C carbides, precipitating during tempering, have their size ten times smaller. A higher fraction of retained austenite in carbide-steel in relation to classical high-speed steels is caused by a higher concentration of carbon remaining after debinding. In addition, carbon is released as a result of carbonitrides being formed and the introduced carbides being dissolved. If carbon concentration is increased, the start temperature of martensite transformation is decreased; hence, a fraction volume of retained austenite after quenching in such materials is up to 62%. A higher tempering temperature of approx. 600°C has to be applied due to variations in retained austenite fraction in the matrix of the analysed carbide-steels, in relation to high-speed steel with the analogous chemical composition of the matrix. EN HS 6-5-2 high-speed steel should be quenched at below 600°C. In case of carbide-steels and a large fraction of retained austenite in such steels after hardening, it is necessary to temper at a higher temperature ensuring the transformation of retained austenite into martensite and high hardness after heat treatment. Unfortunately, M_6C carbides may precipitate at such high temperature; hence, most probably, the precipitates seen in **Figures 11** and **12** are the result of it. Precipitates with a nanometric size, formed during sintering, are rich in other elements such as V, Ti, and N.

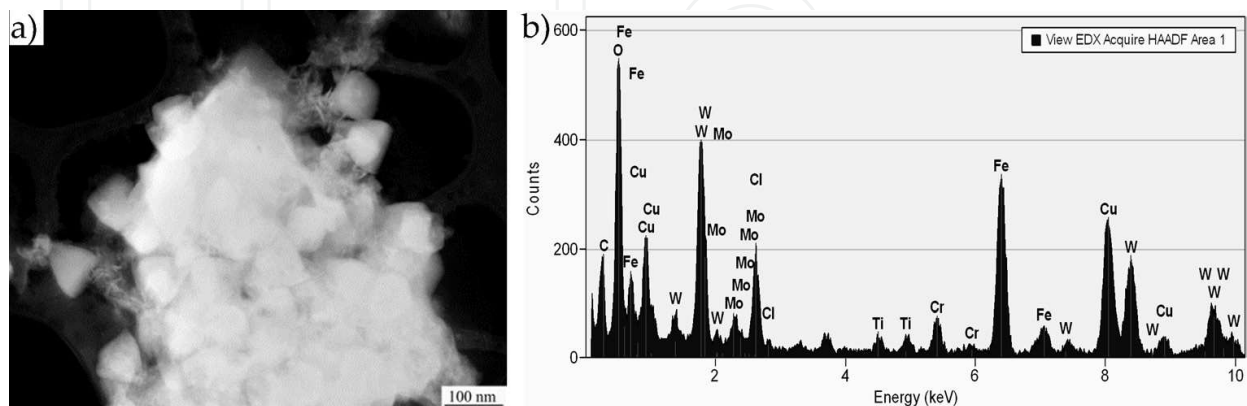


Figure 11. (a) HAADF image of precipitate in EN HS 6-5-2/TetraC carbide-steel after quenching and tempering twice at 630°C, SEM, (b) diagram of the function of scattered X-ray radiation for the carbide shown in (a).

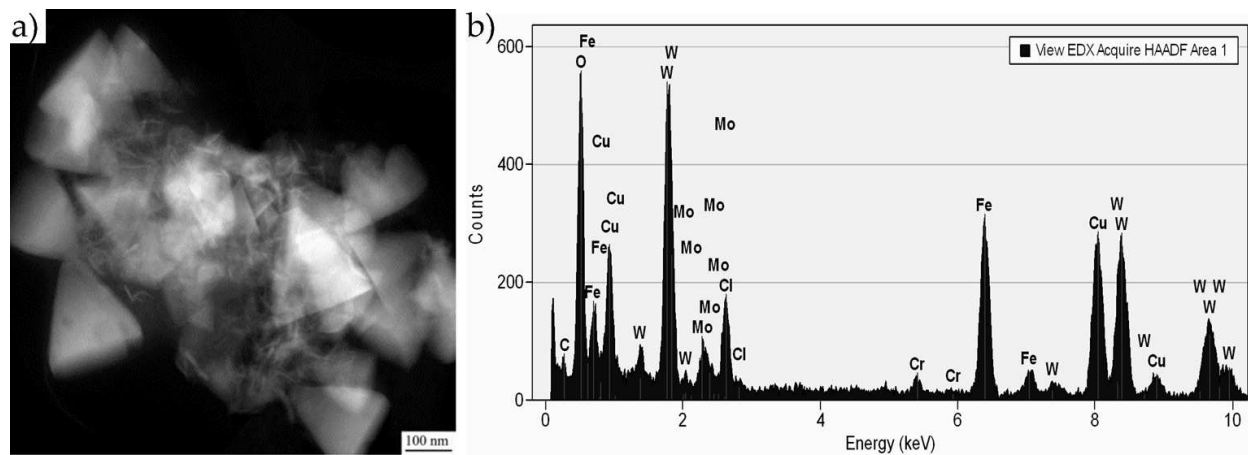


Figure 12. (a) HAADF image of precipitate in EN HS 6-5-2/TetraC carbide-steel after quenching and tempering twice at 630°C, SEM, (b) diagram of the function of scattered X-ray radiation for the carbide shown in (a).

Additional information

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