

## Application of powder injection moulding for manufacturing of tool composite materials

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### Manufacturing and processing

#### ABSTRACT

**Purpose:** The goal of this work is development of the tool composites on the basis of T15 HSS contained 10% of carbides. This tool material were manufactured by Powder Injection Moulding method and sintered.

**Design/methodology/approach:** Torque-load test, rheological tests, thermal debinding, sintering, hardness test and microstructure examinations.

**Findings:** Examination of the effect of the binder type and portion on structure and properties of the experimental tool materials revealed that using the stearic acid for covering the carbides surface reduces viscosity, thus improving technological properties of the feedstock. Employment of polypropylene instead of the high density polyethylene reduces viscosity and torque-load of the investigated feedstocks. Therefore, there is a possibility to increase the portion of the metallic and ceramic powder.

**Practical implications:** Stearic acid significantly reduces the viscosity of tested polymer-powder mixtures, so its use is justified. The share of the binder in materials, injection molded or extruded should be minimal and allows only the formation of the slurry. Too high proportion of binder creates difficulties during the degradation and causes greater shrinkage and possibility of a distortion during sintering. Employment of polyethylene instead of the high density polypropylene reduces viscosity and torque-load of the investigated feedstocks. Therefore, there is a possibility to increase the portion of the metallic or ceramic powder. This results in a lower deformation probability and in a lower sinter shrinkage.

**Originality/value:** In the paper the using extruding of the polymer-powder mix gives the possibility to fabricate cermets which, with their structure and mechanical properties, fill the gap in tool materials between the high-speed steels and cemented carbides.

**Keywords:** Powder Metallurgy; Extrusion; Powder Injection Moulding; Feedstock; Tool materials

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## 1. Introduction

Forming and sintering of ceramic or metallic powders is used in manufacturing of many engineering materials, including composites. Furthermore, powder metallurgy is used when the classical melting of metals and alloys cannot be applied [1-9]. This method results in a partial reduction or complete elimination of machining, metal forming and has considerable impact on the development of 'near-net-shape' technology. Since the very beginning, the metallurgy of powders found application in the manufacture of composite materials, which may be sintered with a liquid phase at lower temperature as compared to the sintering temperature in solid state.

The powder injection molding technology (PIM), dynamically developing in recent years, [10-14] is used for the manufacture of components with complex surface. Due to the need to remove of binder, usually a polymer, that are small-sized elements with dimensions not exceeding 100  $\mu\text{m}$ .

High investment costs are connected to the need to use high quality devices, while this technology is dedicated solely to mass production. Despite the high costs, PIM method develops very quickly, especially in North America, Germany, Japan, and recently in China. Data on sales of elements manufactured in the PIM method over 1987-2007 clearly shows how firm is the development of this method. Of particular importance is the formation of metallic powder MIM (Metal Injection Moulding operations). The sum of the sold ceramic, metal and composite elements manufactured in 2007 is estimated at over a billion US dollars. Forecasts for 2014 envisage that this amount will oscillate around 1.9 billion, with ca. 51% of the production contributed by Asian countries [15]. This method is most often used for the manufacture of the products, which are characterized by high complexity and components difficult to manufacture of other techniques. This method is used mainly for the manufacture of small parts, which is related to its limitations. Approx. 98% of the elements manufactured by PIM method does not exceed the mass of 130 g. Elements of mass less than 0,5 g are orthodontic brackets [16]. Dynamic development of injection molding is related to the mastery in a technology of processing of polymers, which originally were molded with the use of injection moulding machines produced in the US and in Germany in 1929. It is believed that the injection molding technology, which enables the die-casting of non-ferrous alloys, was introduced by Sturges in 1849. Undoubtedly, there are certain similarities, however it was the development of the polymers processing, their use as a binder, and the development methods of its degradation that has enabled a wider development of the PIM method. The first publications and patents on injection molding of powder dates back to the 40s. of the last century. History of PIM in Europe is relatively short and is about 30 years old. The first elements manufactured with the use of this method are the orthodontic brackets, produced in Germany in the 80s [16]. In 2007, the number of companies dealing with MIM technology ranged from 50 to 60, and the major players were German companies. Sale of elements manufactured in Europe represents ca. 30% of the worldwide production.

This technology is being well developed also in Poland, which is evidenced by the production of following items: electronics, elements of drawing die for plastic, spray nozzle for agriculture and oxygen sensors. Nevertheless, the investment

costs connected to the launching of the technology exceed financial capacity of many Polish companies. On the other hand, it is regretful that the Polish companies do not undertake actions to implement PIM technology on a wider scale. The main advantage of this method is the possibility to manufacture of ready-made (prefabricated) elements without the necessity to perform additional processing. Thanks to this feature the method is more often applied in the manufacturing of hard materials including tooling, processing of which is extremely difficult and expensive. This is confirmed by numerous scientific publications. The possibility of the formation of metal, ceramic powders or mixtures thereof enables the production of metal tools characterized by relatively high ductility, ceramic tools of high hardness or metal matrix composites MMC (Metal Matrix Composite) and ceramic CMC (Ceramic Matrix Composite), which combine high characteristic properties of metals and ceramics [17]. The proportion of powder to the binder depends directly on the shape and powder particle size, its wettability by binder, properties of the binder and conditions in which the mixture is manufactured.

The goal of this work is selection of the proper binder and its volume portion, based on the feedstock tests of its technological properties, as well as structure and properties of the metal matrix composite on the basis of T15 HSS reinforced with carbides mixture.

## 2. Material and research methodology

The powders of high speed-steels, atomized by gas, marked as T15 were used for the production of feedstock for powder injection moulding or extrusion process. The 80% of the particles are smaller than 12  $\mu\text{m}$  and spherical in shape (Figure 1).

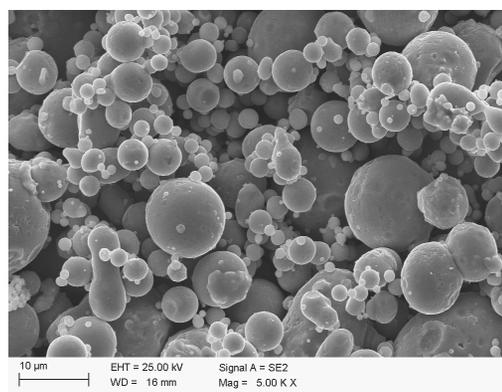


Fig. 1. Morphology of T15 high speed steel powder

The particle size distribution measured by a Laser Particle Sizer Fritch Analysette 22 model is shown in Figure 2. In order to produce high-speed steels matrix composites (HSSMC) the feedstock was reinforced by mixture of carbides (tetra carbides) marked TC containing WC, TiC, TaC and NbC. The torque-load and rheological tests were carried out in order to select the main binder component with a low viscosity. The main component of feedstock was polypropylene (PP) or the high density polyethylene (HDPE). The stearic acid was only used for covering the surface of carbide powders in order to decrease the viscosity and use it for the

powder injection moulding (PIM) or powder extrusion moulding (PEM) method. The feedstock without carbides TC contain 70% of T15 powder and 30% of binder. Independently of the used main binder (high density polyethylene or polyethylene) the half of the binder volume is of paraffin wax (PW). In the case of carbides addition the effect of the stearic acid (SA) on feedstock viscosity was also tested. Knowing the optimum feedstock components percentages with the T15 powder and of the feedstock with maximum content of carbides their portions were selected so that the final mix of HSSMC feedstock contained 58% T15 and 10% carbides. Table 1 presents the marking of the mixtures tested and information concerning the volume fraction of particular components. All types of the feedstock from Table 1 were extruded and injected and finally sintered.

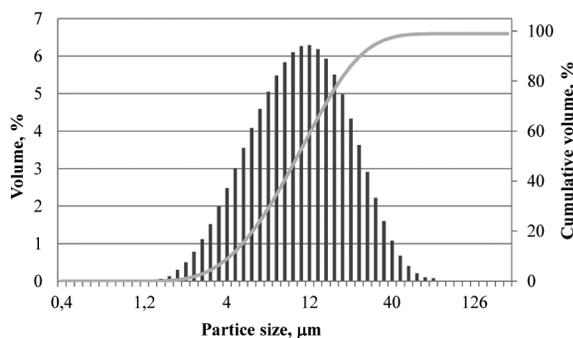


Fig. 2. Particle size distribution of T15 high speed steel powder

Table 1.

Compositions of final extruded an injected feedstock

Type of Feedstock	Portion of components in volume, %					
	T15	TC	HDPE	PP	PW	SA
T15/HDPE/PW	70	0	15	0	15	0
T15/PP/PW	70	0	0	15	15	0
T15/TC/PP/PW	58	10	0	16	16	0
T15/TC/PP/PW/SA	58	10	0	14	14	4
TC	0	60	0	18	18	4

The specific surface area of carbides mixture is higher than powder of HSS and in order to provide high wettability by binder was covered with the stearic acid. The carbides mixtures with the stearic acid were poured into the acid dissolved in methanol, and were churned for 30 min, so that the SA could cover uniformly carbides coatings. Next the slurry was heated to temperature of 60°C to evaporate the methanol. Mixes of carbide powders with SA coating prepared in this way were initially mixed with the HSS T15 powder, paraffin wax and milled polypropylene (PP) or high density polyethylene (HDPE) in a Turbula Mixer at room temperature during 1 hour. The maximum metal and carbides mixture powder percentage was determined by torque measurements. The results was published in article [18]. As a metal powder was used M2 HSS. For T15 HSS the amount of every component was the same because the grain size of T15 and M2 is

very similar. Next the feedstock formulation was granulated and extruded twice to guarantee a good homogeneity in a twin countercurrent screw extruder Rheomex CTW100p. The rheological characterisation of all type of feedstock were performed in a Rheoflizer capillary rheometer (ThermoHaake) at 170 °C over a range of shear rates from 10 to 10000 s<sup>-1</sup>. The dimensions of the die were 30 mm length (L) and 1 mm diameter (D) (L/D ratio of 30). All feedstock with the optimum binder contents were next extruded as round bars (of 3 mm diameter) and as rectangular ones 5 x 0.7 mm.

### 3. Results and discussion

It was found out based on the torque-load tests during mixing of all feedstock types that regardless of homogenisation duration the mix containing polypropylene has a lower torque value compared with the mix containing polyethylene. The minimum torque value for mix containing polyethylene, homogenised for 30 min is about 3.9 Nm. In case of the feedstock containing polypropylene, the torque is only 2.2 Nm. Figure 3 shows the mixing behaviour of the feedstock with different types of binder. The correctly selected binder should moisten the powder and achieve the homogeneous state within a short time of about 30 min. The feedstock containing PP meets these conditions. One may notice that the curve for the feedstock with HDPE is not stable which may indicate to the non-uniform distribution of the metallic powder in the binder matrix in spite of the 30 minutes homogenisation duration time.

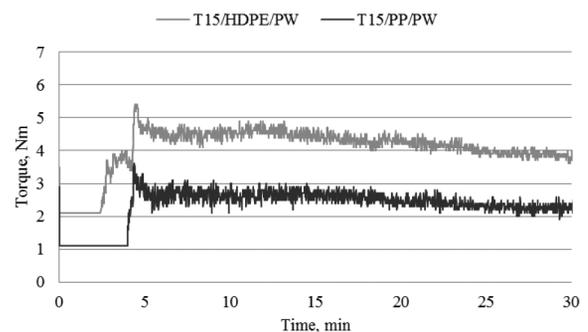


Fig. 3. Torque measurements of feedstock with 70% of T15 and two different binder compositions

In case of the mix in which the polypropylene is used the torque curve is more stable and slightly falls during all homogenisation time. The torque curve should stabilise in this time period. To reduce the feedstock preparation time and ensure its homogeneous structure one may use the twin countercurrent screw extruder or increase the binder amount. The rheological tests results shown in Figure 4 confirm that the viscosity of the curve for selected prepared feedstock with polypropylene is lower than the one with polyethylene.

Only the mixture of TC carbide containing 40% binders in the form of PP, PE and SA, featuring higher viscosity from T15/HDPE/PW at a shearing rate of 5000 and 10000 s<sup>-1</sup>. However, a mixture containing only carbide powders without high speed steel powder is not subject to further testing. On the

basis of rheological tests results excluded the application of further rheological HDPE as a component of the binder and replaced it with a polypropylene. Figure 5 shows the results of rheological studies of the polymer-powder mixture T15/PP/PW without the addition of stearic acid and with the stearic acid (70% T15, 14% PP, 14% PW and 2% SA). Based on the results of research should be noted that the use of stearic acid as surfactant lowers the viscosity of the mixture over the entire range of cutting, as well as the temperature rise of the tested mixture. The use of stearic acid also reduces torque during homogenization of the mixture of polymer-powder as shown Figure 6.

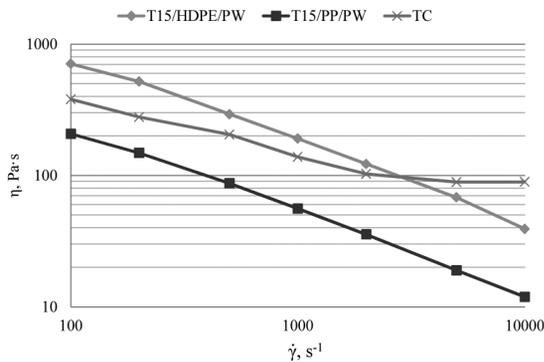


Fig. 4. Viscosity curve for selected feedstock

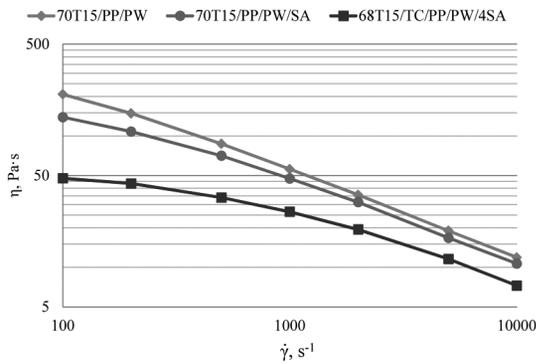


Fig. 5. Viscosity curve for feedstock T15/PP/PW and T15/PP/PW/SA

Additions only 4% of the SA in whole capacity of the polymer-powder reduce the torque in 1 h time after the homogenization ends by about 50%. So, the use of the SA seems to be entirely justified in the process. Figure 7 shows the results of the rheological tests of a polymer-powder slurry type 15/PP/PW tested at the temperature of 170, 180 and 190°C without the addition of stearic acid. The rise of the temperature of the tested composite slightly decreases viscosity of the material, however, at high temperature of 190°C may lead during the homogenization of the mixture in the twin screw extruder to partial degradation of the paraffin wax. Thermogravimetric test results showed that the applied adhesive begins to degrade at a temperature of 196°C. This is the beginning of the thermal degradation of paraffin wax. To protect the polymer-powder mixture from the local heating to the beginning of the heating degradation temperature and due to the slight influence of temperature on viscosity reduction, chosen

injection temperature was 170°C. In order to obtain utility of the composite material with a warp-speed steel after the sintering we must add 10% of the carbides mixture to the polymer-powder mixture containing the steel powder T15 and the binder. This share was selected on the basis of previous studies based on composite M2 steel and TC carbide [18].

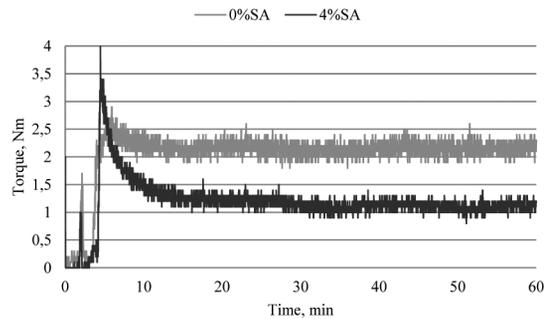


Fig. 6. Torque measurements of feedstock with 70% of T15 and with or without stearic acid

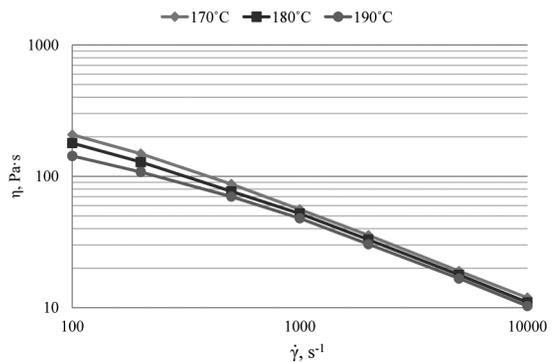


Fig. 7. Viscosity curve for feedstock T15/PP/PW investigated at different temperatures

Rheological testing of the mixture of the polymer-powder containing 58% of the T15 powder, 10% tc, and binder shown in Figure 6 show that the viscosity as compared to other compound is the lowest and is suitable for injection molding. Binder components, and particularly the proportion of paraffin to polyethylene amounting to 1:1, has been chosen deliberately so as to remove paraffin wax at a low temperature by solvent borne or thermal degradation, thereby forming pores in the whole volume of the molding and making it easier degradation of the polyethylene, which maintains the shape of the sample at higher temperature. Studies have shown that this assumption is met. On the basis of an examination of weight loss samples dissolved in heptane at 25°C, it was found that most of the paraffin dissolves within 2 h (Fig. 8). Longer dissolution does not significantly affect weight loss and thereby increase porosity of injected parts. Dissolving the one component of a binder it is paraffin wax causes the opening of the pores and increased size of the sample during thermal debinding, which can accelerate the degradation process. In the material in which was used 4% SA and lowers the share paraffin of 2% at the same time, the ability to remove the binders by solvent degradation are reduced as shown

in the chart. Stearic acid does not dissolve in heptane, so the part of pores will decrease after the thermal degradation. This forces the use of a slower warm-up and longer heating time during thermal debinding. Figure 9 shows the results of thermogravimetric research of T15/PP/PW/SA mixture.

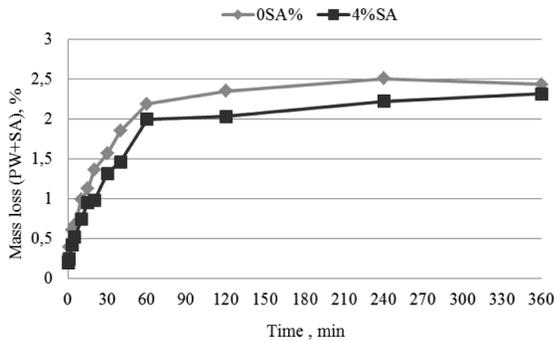


Fig. 8. Influence of solvent debinding time on mass loss of feedstock with or without stearic acid

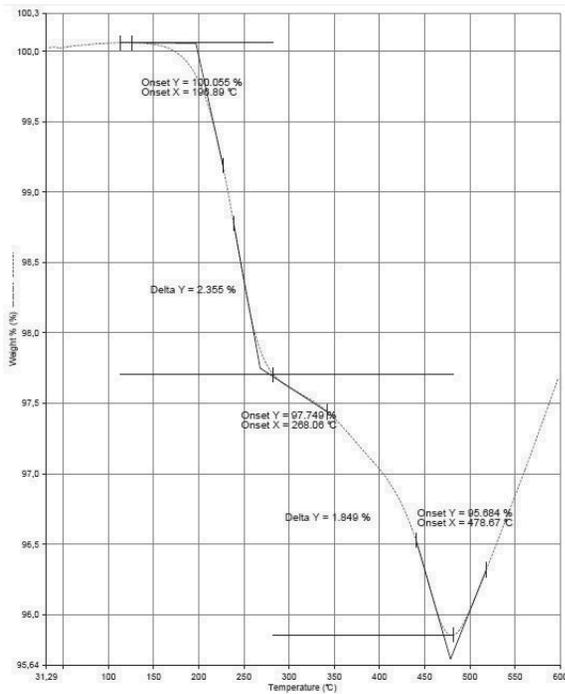


Fig. 9. TGA curve of T15/PP/PW/SA feedstock

Due to the initiation temperature of thermal degradation which is 196°C, injection temperature cannot be higher than this value. Otherwise, may experience thermal degradation of paraffin used as an binder ingredient. At a temperature of 268°C, there is a change in the speed of weight loss, which indicates the end of the degradation of paraffin. At a temperature of 478°C, the adhesive is completely thermal degradation. Based on the results of thermogravimetric we can select temperature of thermal degradation. Due to the low properties of molded after the total thermal degradation is necessary directly sintering.

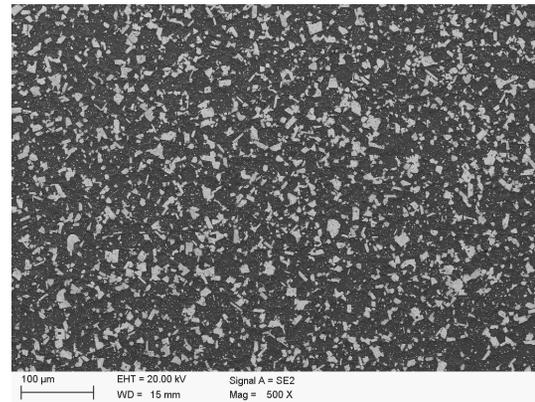


Fig. 10. Microstructure of metal matrix composite on the basis of T15 HSS sintered at 1250°C under the N<sub>2</sub>-10%H<sub>2</sub> atmosphere

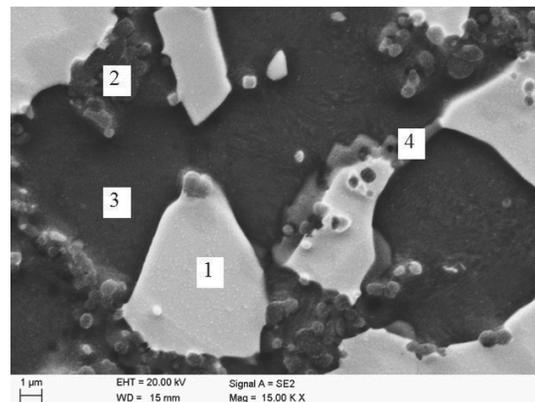


Fig. 11. Microstructure of metal matrix composite on the basis of T15 HSS sintered at 1250°C under the N<sub>2</sub>-10%H<sub>2</sub> atmosphere (selected area from Figure 10)

Often, in view of the degradation products deposited on the surface of the heating chamber, high-temperature heating device can not be used to degrade the adhesive. In case of that we should use an another device to degradation. The necessity of transport of the samples after the degradation into the high-temperature device, requires the use of incomplete degradation of the binder, which ensures minimum mechanical properties allow to transport of samples. Analysing the TGA curve, the maximum of thermal degradation temperature should be less than 478°C. At a temperature of 196°C when the degradation of paraffin is started, the heating rate should be reduced because the pressure of the gas contained in the pores released during the degradation process increases may lead to cracking of moulders.

Results of the scanning electron microscope show that the degradation of the binder and sintering of test materials at 1250°C to give a homogeneous distribution of carbide composite matrix ferrite alloy (Fig. 10). Analyzing the backscattered electrons image shown in Figure 11, were found three different carbide precipitates and Fe-rich matrix. The chemical composition of individual precipitates are shown in Table 2. The bright carbides are characterized by the largest size is probably rich in W and Fe M<sub>6</sub>C carbides. It was also found that in case of sintering in nitrogen i.e. N<sub>2</sub>-10%H<sub>2</sub> rich atmosphere, comes to fine

carbonitride precipitates rich in V, N and C. High concentrations of Fe may come from the surrounding matrix because the volume of the precipitates is less than 1  $\mu\text{m}$ . They have a spherical shape and create aggregations between large and bright carbides rich in W. In addition, there are local carbides were rich in Cr and Fe, which surround the a large clear separations.

Table 2.  
The chemical composition of precipitations of investigated materials observed in SEM

Number of precipitation	Element	Wt%	At%
1	Mo	02.19	02.54
	V	01.97	04.31
	Cr	02.64	05.65
	Fe	22.38	44.62
	W	70.81	42.88
2	C	08.27	23.99
	N	10.41	25.87
	Ti	04.04	02.94
	V	50.12	34.26
	Fe	17.98	11.21
3	W	09.18	01.74
	Cr	04.43	05.01
	Fe	87.89	92.53
	W	07.68	02.46
4	V	05.52	06.31
	Cr	18.88	21.16
	Fe	66.88	69.77
	W	08.72	02.76

## 4. Conclusions

Based on studies it was found that the use of a binder as a paraffin and polyethylene enables forming a mixture of carbides and HSS powders by extrusion or injection molding. All of the described mixtures of polymer-powder can be used for powder injection molding or extrusion. Presented results of the rheology research proves this. The use of stearic acid as a surfactant enables increase the participation of the powder in relation to the participation of the powder in the slurry without SA.

Stearic acid significantly reduces the viscosity of tested polymer-powder mixtures, so its use is justified. The share of the binder in materials, injection molded or extruded should be minimal and allows only the formation of the slurry. Too high proportion of binder creates difficulties during the degradation and causes greater shrinkage and possibility of a distortion during sintering. Employment of polyethylene instead of the high density polypropylene reduces viscosity and torque-load of the investigated feedstocks. Therefore, there is a possibility to increase the portion of the metallic or ceramic powder. This results in a lower deformation probability and in a lower sinter shrinkage.

One can state, based on the presented results, that the chemical composition of the newly developed composite materials was selected properly and the finally obtained material is characteristic in the sintered state of the homogeneous structure with the fine precipitations of carbides in the alloy ferrite matrix. The essential advantage of the investigated injection moulded

material is its mass production possibility, which is just offered by the injection moulding of the powder.

It is expected that further investigations of these materials will make possible their injection moulding, as well as their sintering and heat treatment increasing hardness and strength of matrix and thereby of the whole tool material.

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