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Influence of binder composition on the properties of feedstock for cemented carbides

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ABSTRACT

Purpose: The plastic mixtures shaping of polymer-powder slurries with use of injection moulding and extrusion techniques for development and optimization of metal matrix tool materials reinforced with hard carbide phases.

Design/methodology/approach: Mixtures preparation and preliminary tests, injection moulding and extrusion moulding processes optimization, the grain size measurement with use of laser diffraction method, torque measurement, rheological characterization, differential scanning calorimetry.

Findings: All of investigated polymer-powder mixtures are proper for injection moulding and extrusion processes. Increasing the maximal possible fraction of carbides powder in the mixture is possible due to SA acid addition in the composition of binder. Advantages of SA acid as a component of binder are connected with significant decreasing the viscosity of polymer-powder mixtures as a result of SA acid presence. Binder fraction in injection moulded and extruded materials should be as small as possible, but enough for slurry moulding process. Too large fraction of binder causes the problems during degradation process because of higher shrinkage value and can be a reason of the distortion effect during sintering process. The results of bending strength measurements of injection moulded and extruded samples depends mainly on the moulding conditions, which should be optimized, to obtain the homogeneous structure of material with no discontinuities.

Practical implications: Using investigated PM methods makes it possible to take advantage of injection moulding benefits obtained in area of polymer materials to fabrication of metallic materials, cermets and ceramics. There are wide possibilities of PIM (Powder Injection Moulding) method application for “near-net-shape” production of small size units with complicated shape and extended surface so the range of practical use of this method is wide and covers many aspects of life. The elimination the plastic forming and machining operations causes the significant economic and ecological benefits.

Originality/value: It is expected, that the further research on developing an optimal degradation and sintering conditions may enable achieving the ready to use tool materials based on cemented carbides with the properties exceeding the classical PM processes results.

Keywords: Tool materials; Powder Metallurgy; Sintering; Injection Moulding;Extrusion Moulding

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

The classical powder metallurgy, based on uniaxial pressing and sintering with optional isotactic compacting has significant limitations in respect of shape complexity. Rapid development of powder injection moulding (PIM), powder extrusion moulding (PEM) and pressureless forming makes it possible to obtain units of relatively small size, complicated shape and extended surface simultaneously, so application of these techniques for cemented carbides and cermet fabrication seems to be well-founded and is the object of growing interest. Plastic mixtures shaping of polymer-powder slurries with use of injection moulding or extrusion moulding techniques seems to be interesting in particular. It comes from large-scale applied injection moulding technique for fabrication of thermoplastic polymer materials. Using of this method makes it possible to take advantage of injection moulding benefits obtained in area of polymer materials to fabrication of metallic materials, cermets and ceramics. There are wide possibilities of powder injection moulding method application for "near-net-shape" production of small size units with complicated shape and extended surface so the range of practical use of this method is wide and covers many aspects of life. The additional advantage of this method is the possibility of elimination the plastic forming and machining operations which causes the significant economic and ecological benefits. The modern powder forming methods using polymer binders are the point of interest for tool materials' producers, especially in case of producing high-speed steels, cemented carbides and cermets. The most interesting application for modern powder forming methods seems to be a producing of the cemented carbides. Simple shapes of cutting edges, possible to obtain with locked die, are the limitations for their application and often enforcing engineers to choose resistant to abrasive wear high-speed steels or to choose the combined tools resulting in elongated replacement time. Using the powders of carbides as a charge material for producing the cemented carbides is relatively chip in comparison to the cubic boron nitride or polycrystalline diamond materials. This is the main reason, that in this case constructing of combined tools is not necessary, especially if the size of tool is not large. For that reasons, the development and optimization of metal matrix tool materials reinforced with hard carbide phases with use of polymer binders in process of powder forming seems to be very purposeful [1-29].

Increase of the functional properties of tools as well as reduction of threat to the environment can be achieved by deposition tools with hard, wear-resistant PVD coatings thanks to improvement of the tribological contact conditions in the tool-chip-machined material contact zone as well as thanks to the elimination of cutting fluids. Employing the physical vapour deposition techniques of surface treatment of tool materials to obtain coatings, resistant-to-wear also at elevated temperature, causes the improvement of their functional properties of tools among others during machining and plastic forming operations. This is possible mainly due to friction coefficient decrease, micro-hardness increase, improvement of the tribological contact conditions in the cutting tool-machined workpiece zone and also due to increase of protection against the adhesion and diffusion wear [30-41].

2. Material and research methodology

Commercial mixture of WC carbides and cobalt produced in the form of granules by BAILDONIT company and "Tetra Carbides" mixture of carbides produced by TREIBACHER INDUSTRIE AG was used in the work. Tetra Carbides mixture containing WC, TiC, TaC and NbC carbides has been introduced in Figure 1. Paraffin (PW) and polypropylene (PP) was used as a main slurry components at injection moulding and extrusion processes. The influence of the 4% volume fraction of stearic acid (SA) as a surfactant on the charge material's viscosity was investigated. Investigations were carried on four kinds of powder mixtures, as shown in Table 1.

The mixtures produced in the form of granules by BAILDONIT are characteristic of high flow rate of powder because of their original application for pressing and then sintering processes. Such mixtures, with addition of lubricant, are also characteristic of high compressibility which is required during pressing with use of locked die. The lubricant's friction was taken into account when binder material was selected. Tetra Carbides mixture produced by TREIBACHER INDUSTRIE AG is free of lubricants.

In case of materials produced in the form of granules, the measurement of the particle size is impossible, therefore average particle size data given by the producer has been introduced in Table 1. In case of Tetra Carbides mixture, the grain size measurement was performed with the Malvern Mastersizer 2000 device using laser diffraction method. Particle size distribution of Tetra Carbides powder has been shown in Figure 2.

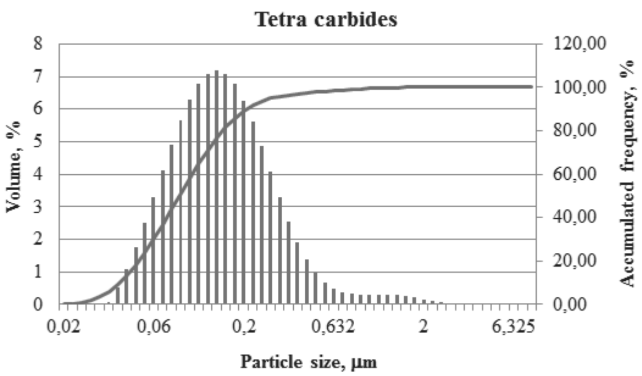

Fig. 1. Particle size distribution and accumulated frequency of „Tetra carbides" powder

Table 1.
Characteristic of powder mixtures

Designation	Producer	Average grain size	Volume fractions of components, %
S10S	Baildonit	2-3 µm	57WC, 20TiC, 14Ta(Nb)C, 9Co
S30		2-3 µm	87WC, 5TiC, 8Co
Tertra Carbides	Treibacher Industrie AG	d_{50}=3.11 µm	33WC, 33TiC, 25TaC, 8NbC, Co

Values of d_{10}, d_{50} and d_{90} parameters of Tetra Carbides powder are respectively: 1.45, 3.11, and 7.36μm. Granules of S10 and S30 mixtures as well as powder particles topography have been shown in Figures 2-5.

Fig. 2. Morphology of S10S granules

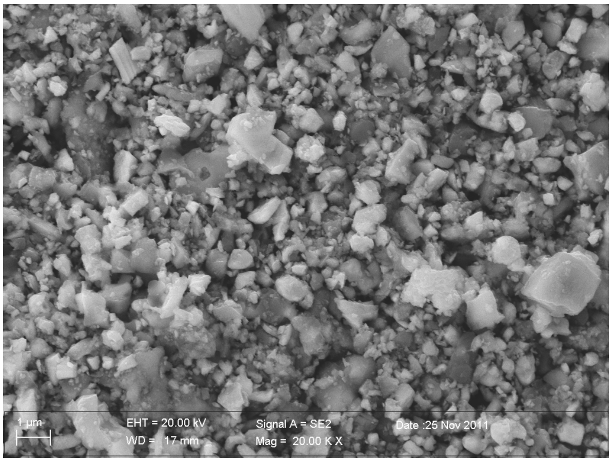

Fig. 3. Morphology of S10S powder

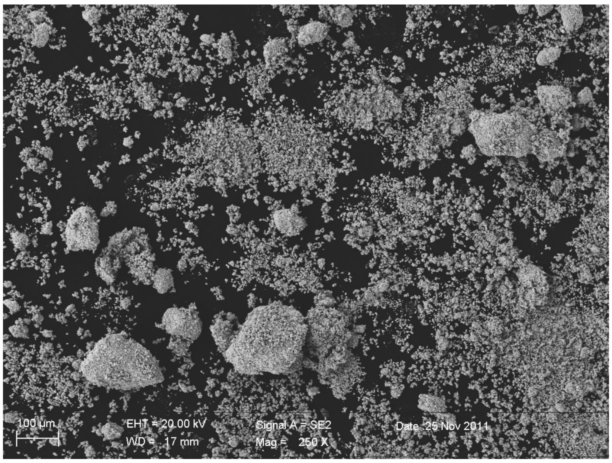

Fig. 4. Morphology of S30 powder

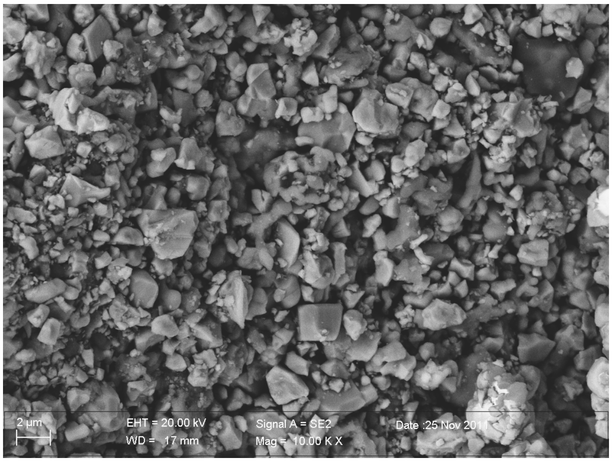

Fig. 5. Morphology of S30 powder

The charge materials was prepared with using of Rheomex CTW100p device by Haake with possibility shoulders torque measurement during homogenization process. The equipment used has been shown in Figure 6.

Fractions of the particular components of binder used, has been shown in Table 2. The SA acid was dissolved with ethanol and after addition of carbide powders, the composition was deeply mixed in 30 min., in order to cover the surface of carbides with surfactant. Then the mixture was heated up to 60°C in order to evaporation of ethanol.

Prepared powders of carbides covered with SA coating was mixed with main PP and PW binders. The rheological characterisation of all type of feedstock were performed in a Rheoflixer capillary rheometer (Thermo Haake) at 170, 180 and 190ºC over a range of shear rates from 10 to 10000 s^{-1}. The dimensions of the die were 30 mm length (L) and 1 mm diameter (D) (L/D ratio of 30). Melting point of binder material measurements was carried out with use of differential scanning calorimetry with Perkin-Elmer's Diamond instrument.

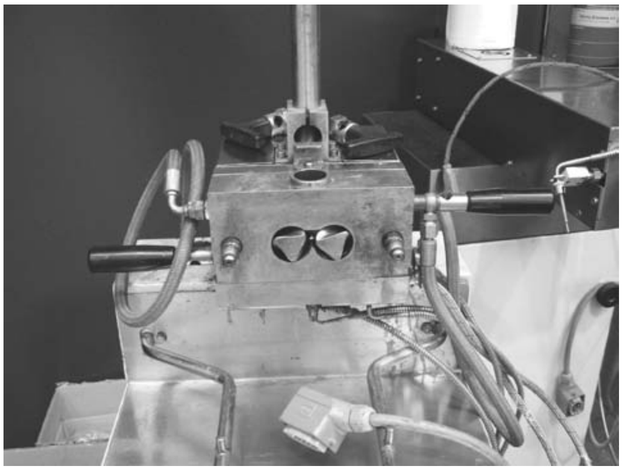

Fig. 6. Apparatus Haake Rheomex CTW100p for torque measurment and homogenization

The injection moulding process was carried out with use of ram injection moulding machine in AB-400 device by AB Machinery, equipped with folded mould, heated up to 150ºC, shown in Figure 7. The extruded sections was manufactured using Rheomex CTW100p device equipped with twin screw extruder.

Table 2.
Components of manufactured polymer-powder slurry

Designation	Powder	PP, % in vol.	PW, % in vol.	SA, % in vol.
TC60SA4	Tertra Carbides	18	18	4
S10S60SA4	S10S	18	18	4
S10S57SA2	S10S	20.5	20,5	2
S10S54	S10S	23	23	0
S3060SA4	S30	18	18	4

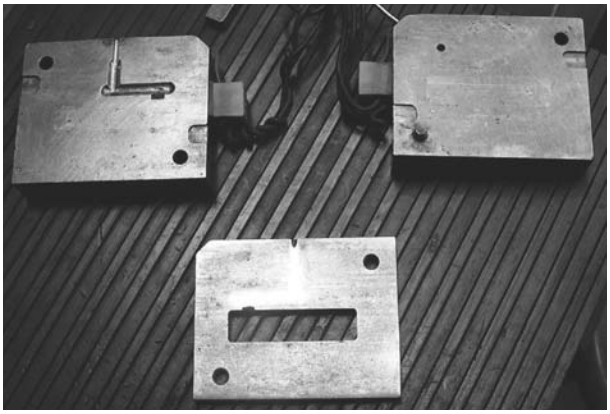

Fig. 7. Folded mould

3. Results and discussion

Results of particle size distribution measurements of the Tetra Carbides powder, especially values of d_{10} and d_{90} parameters, makes possible to evaluate the packing coefficient of injection moulded shape (Sw) according to the equation: $S_W=2.56/(\log(d_{90}/d_{10})$ [3].

Evaluated SW value equals 3.64, what makes the injection moulding process possible. The most recommended for the injection moulding process are powders characteristic of SW coefficient level near 2. Powders characteristics of SW coefficient level near 7 are not recommended for injection moulding process, because of very narrow shape of particle size distribution plot. Particle size distribution’s characteristic curve of the investigated powder is relatively wide, so pores occurring among large particles can be fitted by small particles.

It was found, based on torque measurements during the homogenization process of powders and binders, that maximum fraction of powders should be smaller than 60%. The diagrams of torque distribution for 64% and 50% of S10S mixed with PP and PW at temperature of 170°C have been shown respectively in Figures 8 and 9.

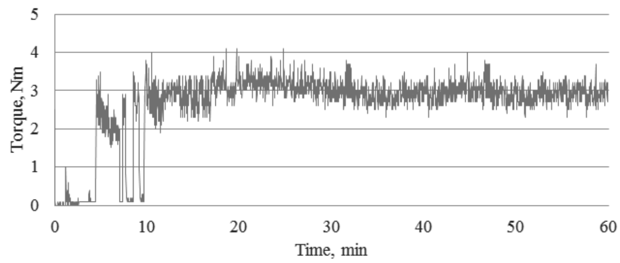

Fig. 8. Torque measurements of feedstock based on PP and PW with 64% amounts of S10S mixture carbides

In case of charge with large fraction of carbides powder, its curve characteristics are unstable. It’s an evidence of inhomogeneous distribution of carbide powder in the binder matrix, in spite of long homogenisation time. Moreover, the curve doesn’t tends to decrease, in spite of long mixing time, therefore such large fraction of carbides powder in mixture is disqualified. In case of the mixture with 50% fraction of carbides, the torque value decreases to under 1 Nm just after 20 min. of mixing time, what is an evidence of low viscosity of polymer-powder mixture.

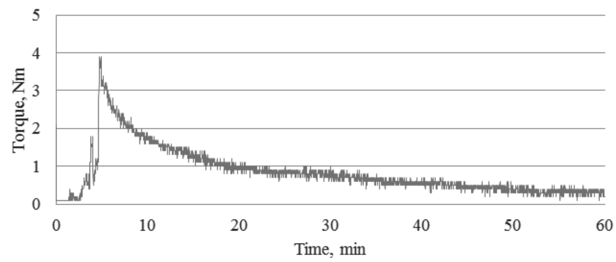

Fig. 9. Torque measurements of feedstock based on PP and PW with 50% amounts of S10S mixture carbides

Using of the 50% fraction of carbides in mixture composition for injection moulding or extrusion machine ensures lower viscosity of the powder, but can be also a reason of many problems during the degradation process and such large binder fraction and can cause a distortion effect during sintering process connected with high shrinkage value of sinter. Well prepared charge material should be characterized by as high as possible fraction of powder and relatively low viscosity, necessary for moulding process quality [3].

Basing on literature data and own research it was stated, that using small amount of SA acid as surfactant causes the significant decrease of powder viscosity value of charge material. Detailed results of the viscosity measurements depending on the shear rate for the material containing S10S powder have been shown in Figure 10.

Because of too high viscosity value of the mixture containing 68% carbides powder, carrying out tests with use of capillary rheometer was impossible. Three kinds of polymer-powder mixtures have been shown in the plot (Figure 11). Two of them containing SA acid addition besides main components of binder. Based on tests results it can be stated, that addition of SA acid as surfactant causes significant decrease of powder viscosity value of polymer-powder mixture.

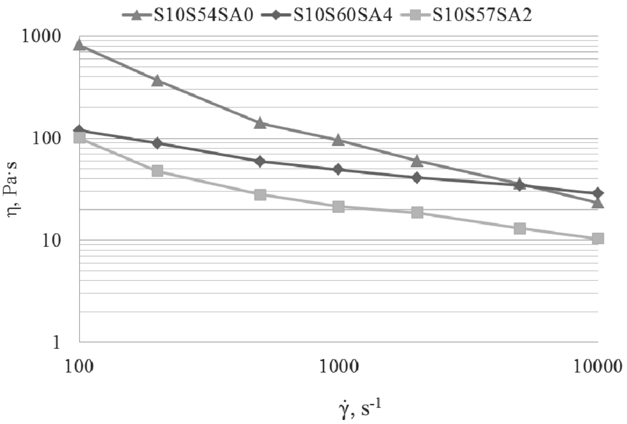

Fig. 10. Influence of SA on rheological behaviour of binder and carbides S10S type mixtures at 170ºC

The smallest fraction of carbide powder mixture with no addition of SA acid is characterized by the highest viscosity value. Viscosity value of S10S54SA0 mixture is properly: equal and lower than in case of S10S60SA4 mixture for shear speed of: 5000 s^{-1} and 10000 s^{-1}. S10S57SA2 mixture is characterized by the lowest value of viscosity regardless of the of the shear speed. Tests results of the viscosity values, depending on the kind of powder used, have been shown in Figure 11. Binder fraction in all presented in Figure 11 mixtures was 40%, containing 4% of SA acid addition.

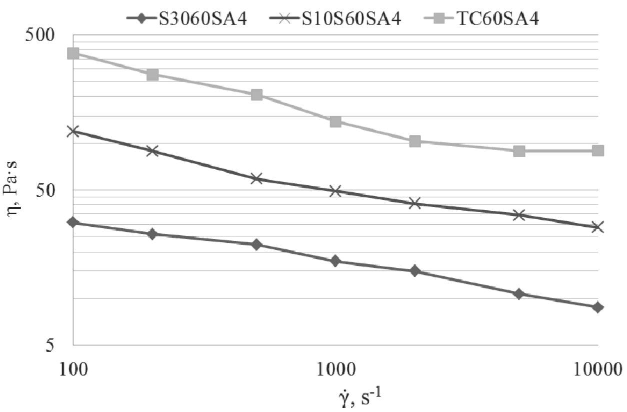

Fig. 11. Influence of type of carbides on rheological behaviour of binder and carbides mixtures at 170ºC

The mixtures containing Tetra Carbides powder is characterized by the higher value of viscosity then mixtures based on BAILDONIT's powders. The original purpose of BAILDONIT's powders is pressing process then it contain about 2% volume fraction of lubricant, mostly the paraffin. The mixture purposed for industrial production of cemented carbides is characterized by good homogeneity and used lubricant cover tightly the surface of carbides then preparing the polymer-powder slurry for injection moulding process is more easy and the slurry is characterized by better properties. The value of viscosity is lower than 1000 Pa*s regardless of the mixture used, and according to the literature data is proper for injection moulding and extrusion processes.

Tests results of the viscosity values for Tetra Carbides based mixture with addition of pure PP have been shown in Figure 12. PP viscosity values is increased in range of shear rate from 100 s^{-1} up to 5000 s^{-1}. This results give also a confirmation, that Tetra Carbides based mixture is proper injection moulding and extrusion processes. The flow curves have been shown in Figure 13. Higher stress values measured in case of S10S60SA4 are connected with higher viscosity of this material.

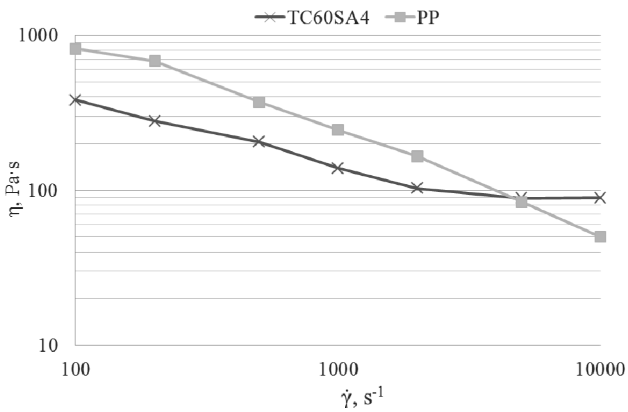

Fig. 12. Comparison of viscosity of mixtere with tetracarbides and polypropylene

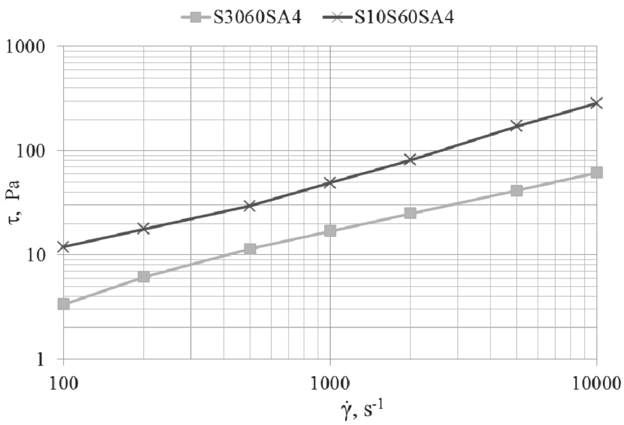

Fig. 13. Flow curves of S10S60SA4 and S3060SA4 at 170ºC

Results of the thermogravimetric analysis of S10S60SA4 mixture have been shown in Figure 14. The injection temperature can't be higher than the beginning of degradation temperature amounting to 217ºC. On other case degradation of the paraffin, used in binder composition, could have occurred. At temperature of 287ºC the change of rate of weight loss was noticed which is evidence of the paraffin degradation process completion. The degradation process of all binder components was completed at temperature of 444ºC. On the basis of the thermogravimetric analysis is possible to determine the thermal degradation point. It was stated, that the direct sintering process is recommended because of insufficient properties of samples after completion of binder degradation process.

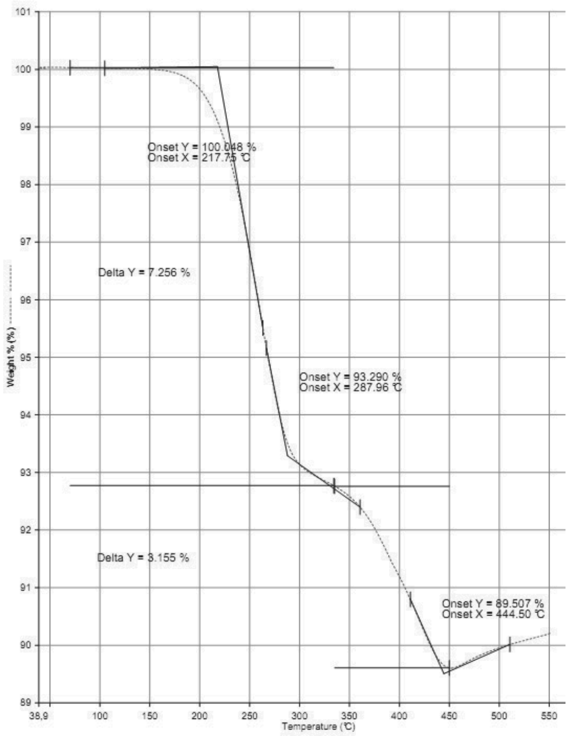

Fig. 14. TGA curve of S10S60SA feedstock

The limitation for use the high-temperature heating unit for the thermal degradation process of binder is settling of degradation products on the surface of heating chamber. Then other unit has to be employed for degradation process. It causes the necessity of the samples movement after degradation process to the chamber of high-temperature so binders degradation process can't be completed because of the necessity of keeping samples shape unchanged by movement. Based on TGA curve analysis it was found that maximum degradation temperature should be 420ºC.

At the beginning of degradation temperature, amounting to 217ºC, speed of the heating process should be decreased, because otherwise increase of the degradation product pressure accumulated in pores can cause the cracking of samples.

The results of differential scanning calorimetry analysis have been shown in Figure 15. Peaks of the paraffin melting point and the PP melting point amounting properly: 55ºC and 147ºC are visible on thermogram. Based on DSC and TGA curves analysis the injection temperature of 170ºC was determined.

The injection moulded sample, made in folded matrix with inlet channel filled. The injection temperature was 170ºC while the matrix temperature was 50ºC. The sample is characterized by relatively small shrinkage value because of large fraction of solid particles contained. The samples presented in Figure 16 were extruded at temperature of 140ºC. It's characterized by smooth, compact structure what is the evidence of proper extrusion parameters chosen.

S10S60SA material extruded at the temperature of 170ºC (equal to injection moulding temperature chosen) has been presented in Figure 17. The surface of sample is characterized by large number of pores came from extrusion process.

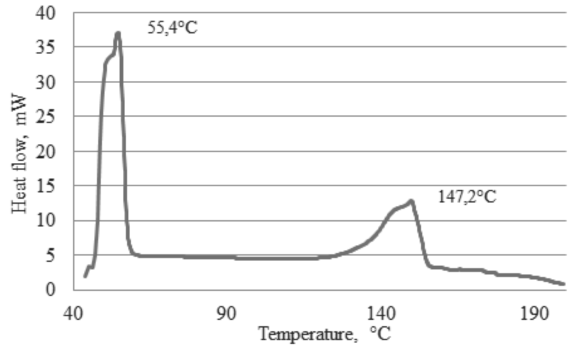

Fig. 15. DSC curve of S10S60SA feedstock

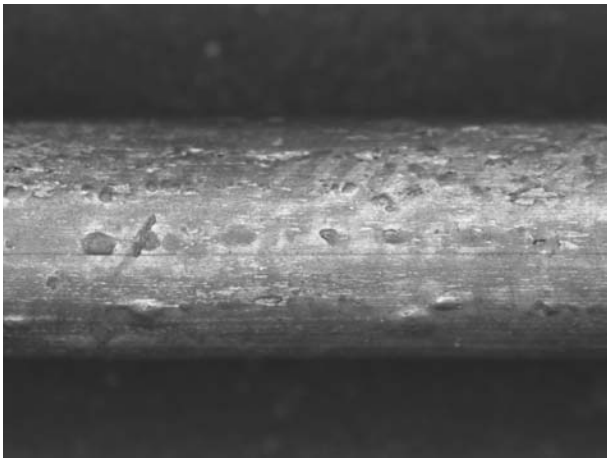

Fig. 16. View of the S10S60SA surface extruded at 140ºC

Fig. 17. View of the S10S60SA surface extruded at 170ºC

The results of bending strength measurements of injection moulded and extruded samples have been shown in Figure 18.

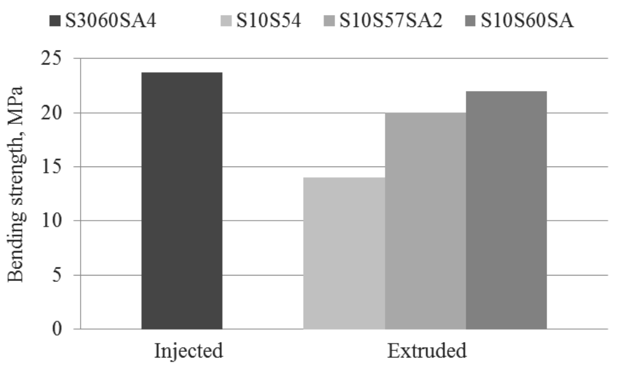

Fig. 18. Bending strength of injected and extruded materials

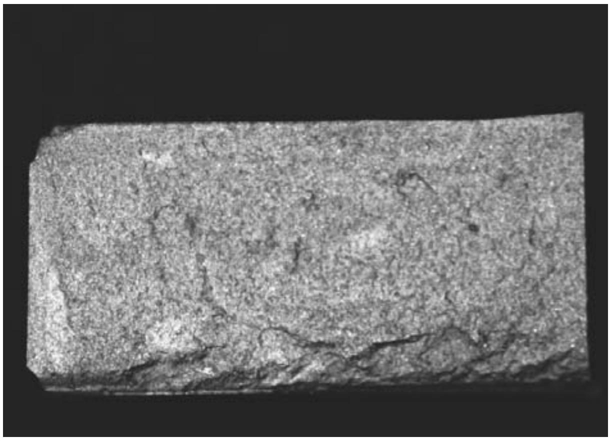

Fig. 19. View of the fracture surface of injected S30S60SA4 materials

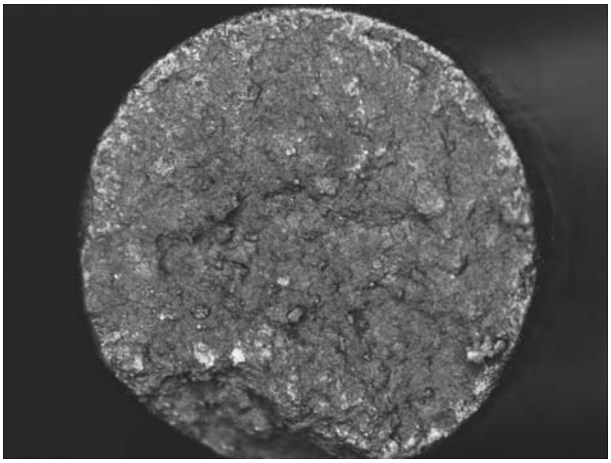

Fig. 20. View of the fracture surface of extruded at 140ºC S10S60SA materials

The injection moulded samples are characterized by the higher bending strength values because of the higher forming pressure as well as lower number of pores formed. The fracture surface of S30S60SA4 material has been shown in Figure 19. No gaseous pores, which may occur during the injection moulding process and decrease the bending strength, was found in the structure of the material.

The increased values of bending strength noticed in case of extruded samples are related to content of the SA acid covering the surface of powder and increasing the binder-powder connection strength. The bending strength results depends strongly on the extrusion process conditions. Fracture surfaces of the samples extruded at the temperature of 140 ºC and 170ºC have been shown in Figures 20 and 21.

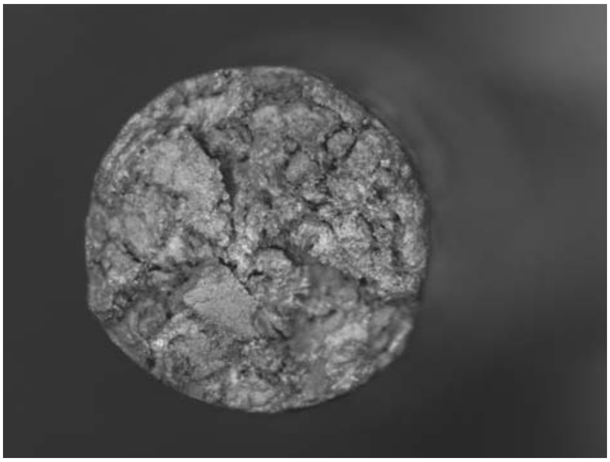

Fig. 21. View of the fracture surface of extruded at 170ºC S10S60SA materials

4. Conclusions

Based on the examinations made it can be stated, that using the binder, composed of PP and SA acid, allows to mould the carbides powder mixture by injection moulding and extrusion.

All of investigated polymer-powder mixtures are proper for injection moulding and extrusion processes. It was demonstrated with use of rheological tests.

Increasing the maximal possible fraction of carbides powder in the mixture is possible due to SA acid addition in the composition of binder. Advantages of SA acid as a component of binder are connected with significant decreasing the viscosity of polymer-powder mixtures as a result of SA acid presence.

Binder fraction in injection moulded and extruded materials should be as small as possible, but enough for slurry moulding process. Too large fraction of binder causes the problems during degradation process because of higher shrinkage value and can be a reason of the distortion effect during sintering process.

The results of bending strength measurements of injection moulded and extruded samples depends mainly on the moulding conditions, which should be optimized, to obtain the homogeneous structure of material with no discontinuities.

It is expected, that the further research on developing an optimal degradation and sintering conditions may enable achieving the ready to use tool materials based on cemented carbides with the properties exceeding the classical PM processes results.

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