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Carbide alloyed composite manufactured with the PIM method

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ABSTRACT

Purpose: Development of a new generation tool materials on the basis of M2 high speed-steel reinforced with the carbides. Application of powder injection moulding as a manufacturing method gives the possibility to produce these materials in a mass scale with relative low cost of production.

Design/methodology/approach: Powder Injection Moulding, solvent debinding, sintering, thermogravimetric analysis, microstructure examination, porosity examination,

Findings: To manufacture the proposed new tool materials was used powder injection moulding processes. It was found out based on the investigations carried out that the powder injection moulding method is suitable for fabrication of M2 high speed-steel reinforced with the carbides. The main advantage of the presented experimental tool materials is the wide sintering window being only about 5°C oftentimes in case of the high-speed steels; whereas, it is about 40°C for the investigated material.

Practical implications: Application of powder metallurgy and especially powder injection moulding to manufacturing of high speed-steel reinforced with the carbides gives the possibility to obtain tool materials with the relative high ductility characteristic of steel and high hardness and wear resistance typical for cemented carbides.

Originality/value: The powder injection moulding gives the possibility to fabricate carbide alloyed composite which, with their structure and mechanical properties, fill the gap in tool materials between the high-speed steels and cemented carbides.

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

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

The history of metal injection moulding (MIM) is very short and have not more than 30 years in Europe. The first MIM parts producer started business in Germany with the mass production of dental brackets in the 1980's. MIM technology has greatly matured since these early days and its acceptance by end users is constantly growing. Now metal injection moulding parts producers can be found throughout Europe. Most of these companies have a background in metallurgy and some of the larger MIM producers were originally traditional powder metallurgy companies. Powder injection moulding gives the possibility to make the best use of the input materials and to fabricate the near-net-shape tools, eliminating in this way the costly plastic working and machining, using the finish grinding and heat treatment only. Forming the plastic polymer-powder feedstock with the injection moulding method seems to be

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especially interesting. This method makes it possible to exploit advantages of the polymers injection moulding for fabrication of metal-, ceramic-, and composite materials [1-4]. Powder injection moulding is also enjoying attention nowadays in tool materials processing, especially the high-speed steels and sintered carbides [5-12]. The high-speed steels do not have considerable quantitative positions in steel production but they still take an important role in machining and plastic working. Searching a new production technology of high-speed steels is very important for improvement of mechanical properties and a reduction of production costs. The production of high-speed steels parts by powder metallurgy (P/M) offer greater improvements in wear resistance, hardness, heat resistance, toughness, and dimensional stability compared with conventional cast or wrought parts. A very difficult aspect during mass production is a control and maintenance of a very narrow sintering window while in many high speed steels the temperature range equals only 5°C. The increases of carbon concentration in steels manufactured with the PIM method, caused by the binder degradation process increases the sintering window and reduces sintering temperature what influences on a reduction of additional costs [13-17]. Therefore, investigation has to be carried out to verify of carbides addition influence on structure and properties after sintering.

The goal of the work is development of a new generation of the composite tool materials with high-speed steel as the matrix material, reinforced with mixture of hard carbides.

2. Materials and research methodology

The investigated specimens were fabricated using the powder injection moulding method. The powder density of M2 HSS measured with the AccuPyc 1330 type pycnometer was 8.16 g/cm^3. The 90% of the particles were less than 16 μm (Fig. 1). The commercial carbides powder mix (tetra carbides) composed of WC, TiC, TaC, and NbC (33.3/33.3/26.6/6.8% in vol.) are shown in Figure 2.The injection moulded test pieces were mixed with the main binder components of 50% polypropylene (PP) and 50% paraffin wax (PW). The density of such binding agent is about 1 g/m^3. Moreover stearic acid as a binder was used. To cover the carbides surface with the stearic acid they 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 mix 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 high-speed steel powder, PP and PW in a Turbula Mixer at room temperature during 1 hour. The maximum metal and carbides powder percentage was determined by torque measurements. Percentages of these powders and binder are shown in Table 1. Next the feedstock formulation was granulated and extruded twice to guarantee a good homogeneity in a twin screw extruder Rheomex CTW100p (Fig. 3). The granulated material was formed by the Arburg injection machine 220-S using the mould for 3-point bending test. The powder injection moulding process was made at 180°C and the temperature of mould was 40°C. The injection forming conditions as a output data from the control panel generated by Arburg injection moulding machine are shown in Figure 4.

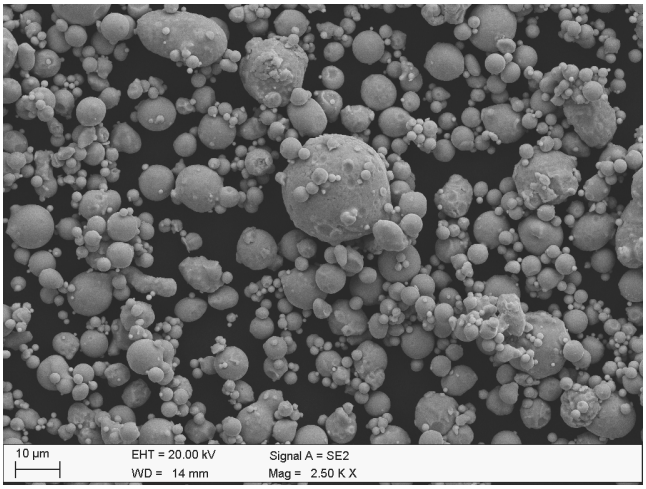


Fig. 1. The powder of high speed-steel M2 type

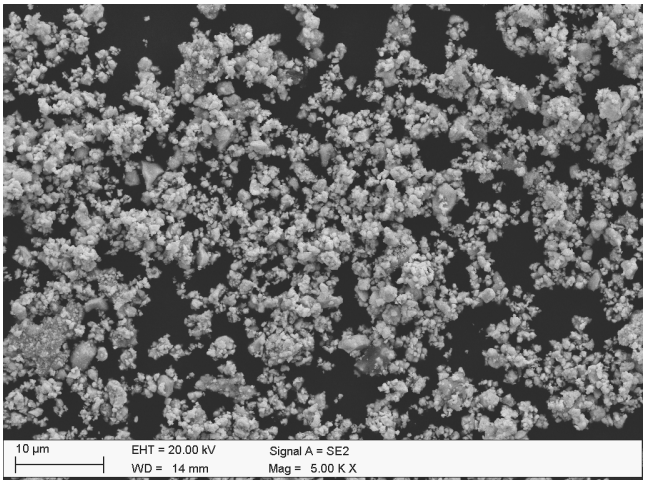


Fig. 2. The powder of tetra carbides (WC, TiC, TaC, and NbC mixtured carbides)

Table 1.
Compositions of injected feedstock

Portion of components in volume, %				
M2	Carbides	PP	PW	SA
58	10	14	14	4

Thermal debinding was carried out in the furnace under argon or N_2-10%H_2 gas mixture at the temperatures of 440°C.

The binder has been partially driven off by solvent and thermal debinding. The moulded samples were debound in heptane at 60°C for 2 h and next in a cylindrical chamber furnace Goceram AB GCDV-50 under N_2-10%H_2 flowing gas

at 440ºC. These atmospheres prevent from the oxidation of metallic powders. Test pieces were sintered in the atmosphere of the flowing N_2-10%H_2 mixture of gases at the temperature between 1200 and 1300ºC in steps of 10ºC for 0.5 h. All specimens in the sintered state were subjected to density tests with the Archimedes method. Carbon concentration, depending on the binding agent degradation and sintering temperatures, was measured with the LECO CS-200 type apparatus. Structure examination and the qualitative X-ray microanalysis were carried out on the SUPRA 25 scanning electron microscope (SEM) equipped with X-ray energy dispersive spectrometer (EDS).

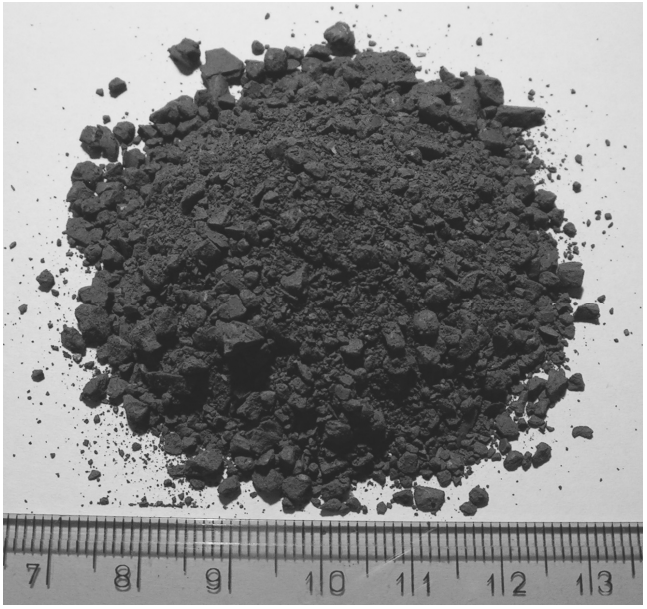


Fig. 3. The granulated feedstock after extrusion and milling

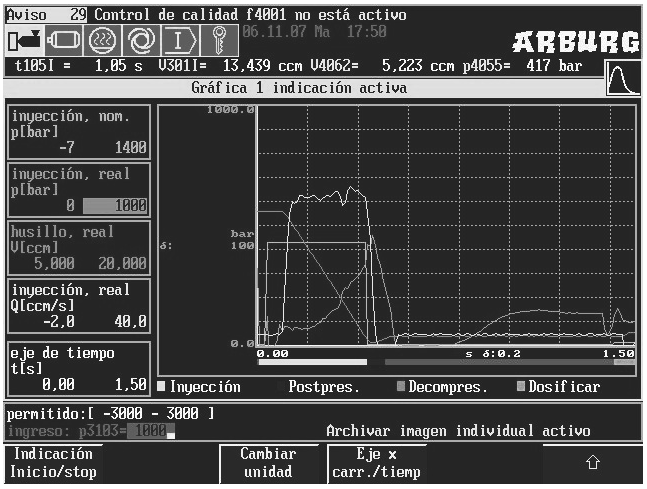


Fig. 4. The injection forming conditions as a output data from the control panel generated by Arburg injection moulding machine

3. Results and discussion

Binder components, and especially paraffin portion in relation to polyethylene being 1:1, were selected intentionally, so that paraffin could be removed at low temperature by solvent- or thermal debinding, forming pores this way in the entire volume of the green samples, making debinding easier of the polyethylene keeping the specimen shape at a higher temperature. Experiments proved that this assumption was satisfied. Based on mass loss examination of specimens dissolved in heptane, at the temperature of 25ºC, it was found out that most of paraffin dissolves within 2 h. The effect of time on solvent degradation is presented in Fig. 5.

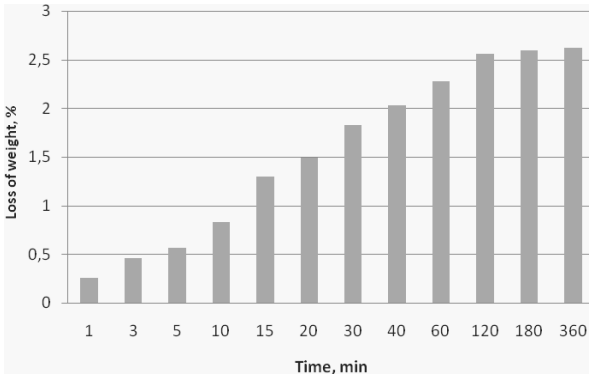


Fig. 5. Influence of solvent degradation time on loss on weigh of debinding samples

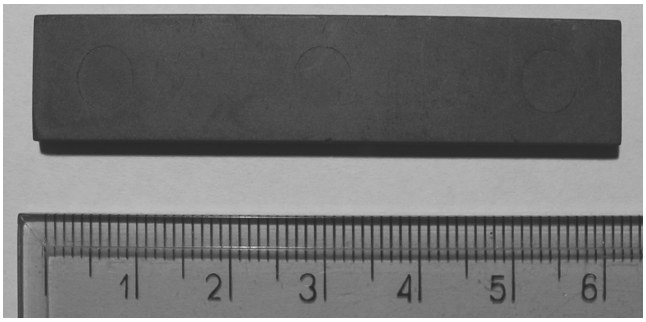


Fig. 6. The view of injected sample

Prolonged dissolving does not affect significantly the mass loss and, therefore, growth of the compact porosity. Dissolving of one of the binder components, i.e., paraffin, results in opening of pores and increasing the specimen surface during its thermal debinding, which hastens the debinding process. Solvent degradation made applying 3.5ºC/min test piece heating rate possible during thermal degradation and applying the short holding time of 30 min.Test pieces inspected with the unaided eye after degradation did not reveal cracks or gas cavities on their surface (Fig. 6). Increase of carbon portion in materials after degradation in respect to the powder used was only 0.3% mass.

Microstructure of the investigated injection moulded materials subjected to solvent- and thermal debinding, and after annealing (presintering) at the temperature of 1000ºC is shown in Figure 7.

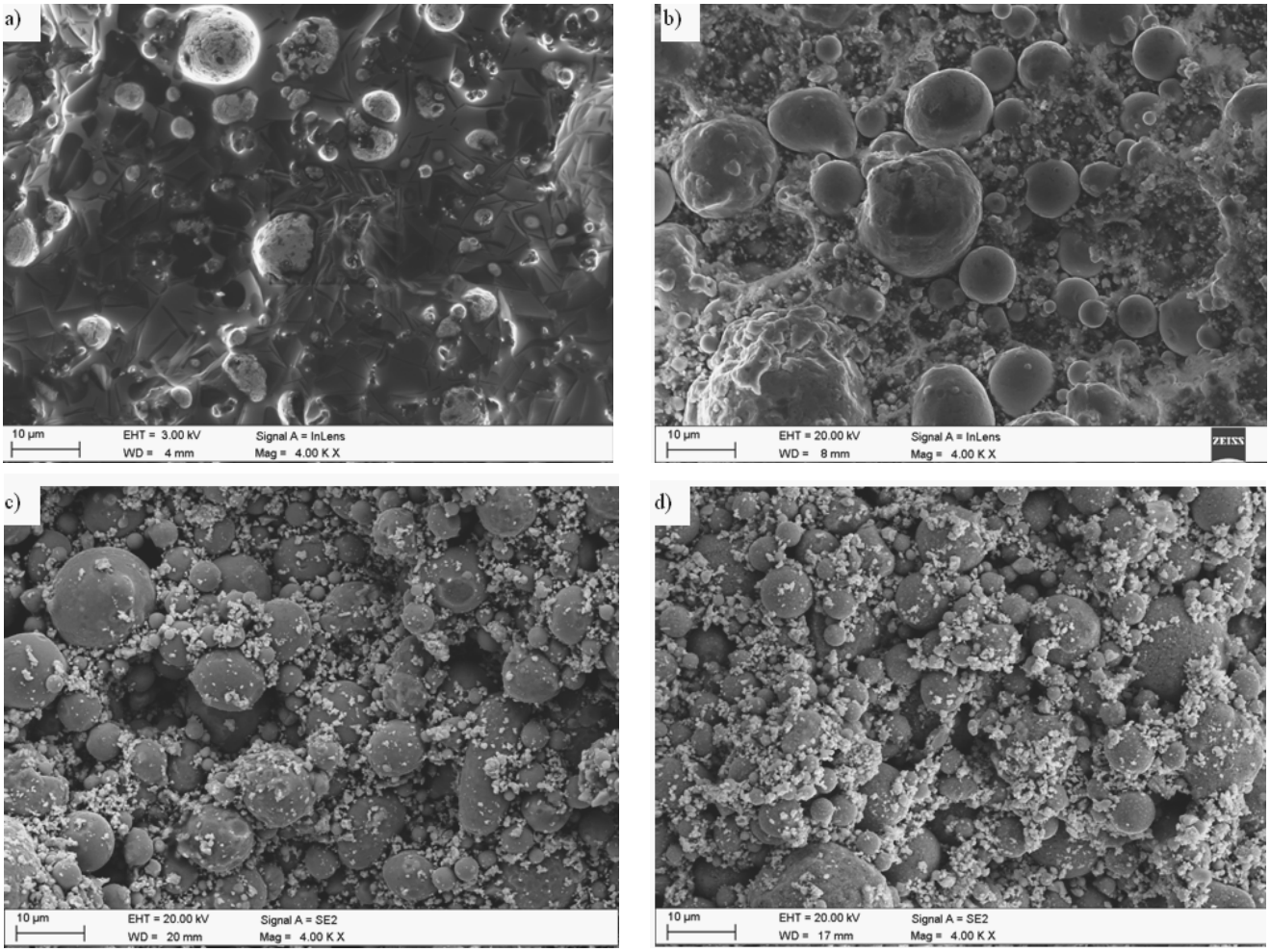


Fig. 7. Microstructure of samples a) injected, b) after solvent debinding, c) after thermal debinding, d) presintered at 1000°C

One may observe the evident green samples porosity growth in the presented microstructures, and therefore, reduction of the binder portion depending on the fabrication stage of the investigated materials.

The thermogravimetric examinations results for the formed compact indicate that paraffin begins do debind at the temperature of about 200°C, therefore, the isothermic stop was selected at the temperature of 250°C, to ensure its complete debinding. Because of the polypropylene debinding temperature of about 430°C, the isothermic stop was selected also at the slightly higher temperature, i.e., 440°C, to remove binder completely before sintering. The thermogravimetric curve and the thermal debinding cycle designed based on it are shown in Figure 8. Microstructures of specimens in the sintered state depend on sintering temperature are shown in Figure 9. Specimens from the M2 type high-speed steel were fabricated in the same conditions and with the same binder portions and chemical composition to compare microstructure of the newly developed material in the form of cermet with the high-speed steel microstructure. Both in case of cermets and the high-speed steel sintered at the temperature of 1300°C specimens shape was deformed attesting to the abundance of the liquid phase during sintering.

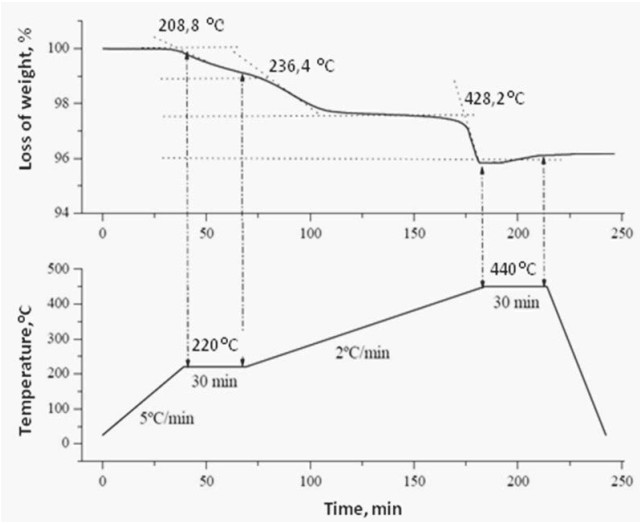


Fig. 8. The thermogravimetric curve and the thermal debinding cycle

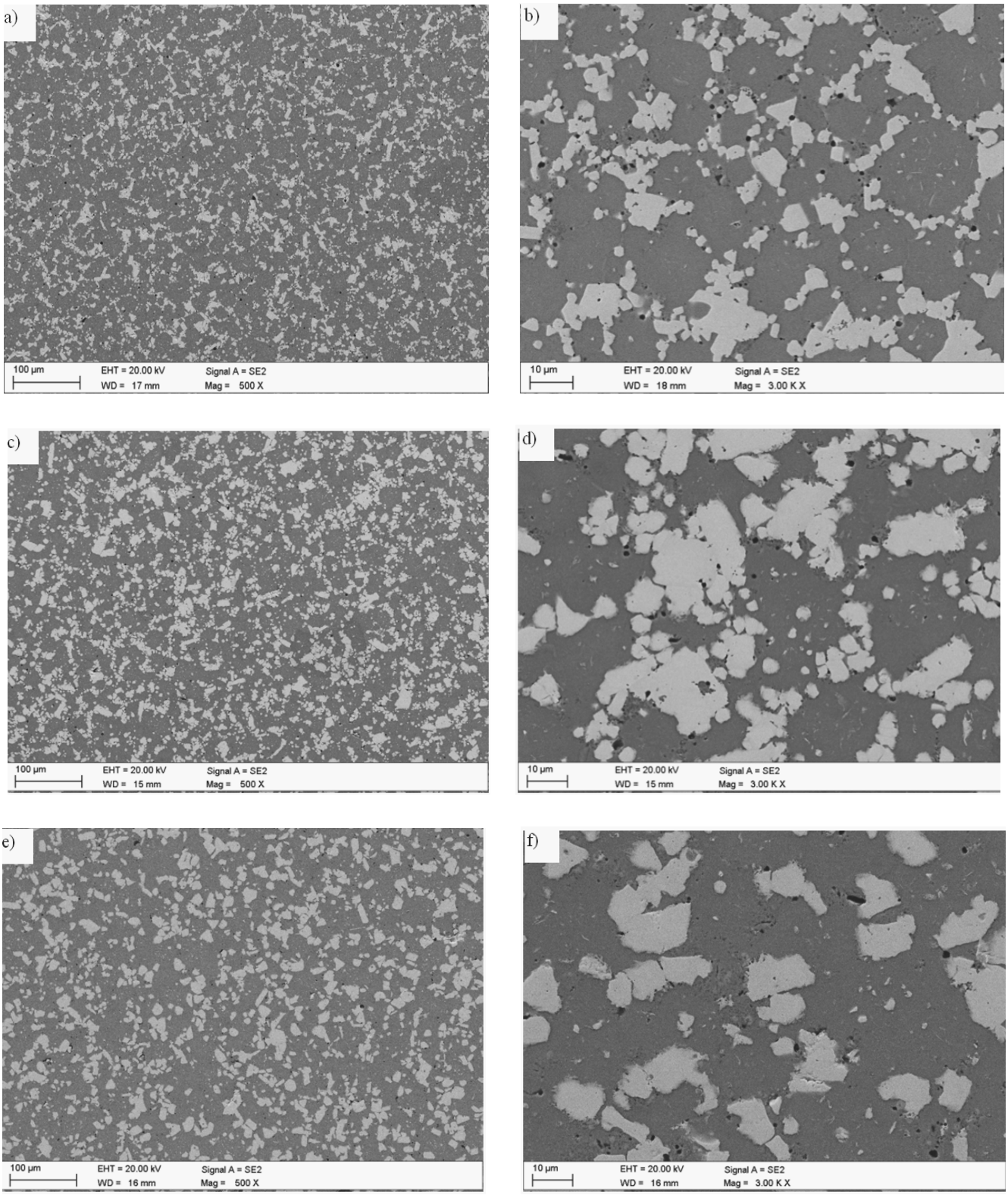


Fig. 9. Influence of sintering temperature on microstructure of carbide alloyed composite manufactured with the PIM method

Table 2.
Influence of sintering temperature on size and portion of primary carbides

	Sintering temperature, °C										
	1200	1210	1220	1230	1240	1250	1260	1270	1280	1290	1300
Portion of primary carbides, %	36.2	36	35.9	34.7	33.8	33.6	33.2	34.1	34.2	33.9	34.2
Average size of primary carbides, μm	1.65	1.87	2.06	2.09	2.2	2.4	2.66	2.76	2,71	2.75	2.82
Maximum size of primary carbides, μm	21.57	22.76	25.68	27.11	28.54	29.36	31.58	34.65	38.17	38.98	40.58

Big precipitations of carbides with the characteristic form of the fish skeleton, appearing as bright phases in the secondary electrons image, and containing mostly tungsten, molybdenum, and a small amount of vanadium, were revealed during examinations on the scanning microscope of the high-speed steel sintered at the temperature of 1300°C. Microstructure of the high-speed steel is shown in Figure 10. In case of cermet sintered at the same temperature no occurrences of the big carbide precipitations were found in spite of the abundant liquid phase portion during sintering.

The maximum size of carbides is about 40 μm, whereas its average value is about 2.8 μm. The size of carbides occurring in cermet sintered at the temperature of 1300°C is comparable to size of carbides occurring in cermets sintered at a lower temperature.

The surface portion of carbides occurring in cermet sintered at the temperature of 1200°C is largest and is about 36%. The portion of carbides drops to the value of about 33% along with the temperature rise, after sintering at the temperature of 1260°C, and grows next to the value of 34.2% after sintering at the temperature of 1300°C. One may also note that the average carbide size grows from the value of 1.7 to about 2.8 μm along with the temperature growth from 1200 to 1300°C. Growth of the bright carbides appearing in the secondary electrons image, rich in W, Mo, and Fe, is limited by the surrounding grey phases rich in Ti and V. Magnification in Figure 9 was selected so that it would correspond to magnification in Figure 10 to present the difference between the high-speed steel and cermet microstructures. The average and maximum carbide sizes and their volume portions in cermets, depending on their sintering temperatures are presented in Table 2.

It was found out based on examinations of cermet structure in the sintered stat that regardless from the sintering temperature one can observe the primary grains of the high-speed steel powder surrounded by numerous light carbide precipitations. These carbides grow along with the rising sintering temperature but do not create the eutectic structure typical for the high-speed steel sintered at the excessively high temperature. No occurrences of eutectics were revealed also based on examinations of cermet sintered at the highest temperature, i.e., 1300°C. Basing on that one can assume that the introduced carbides with the regular structure stable at high temperatures do not cause origination of eutectics but only grow and coagulate at high sintering temperatures. This offers the possibility to use the heating units with the higher temperature tolerance during holding. Employment of the (N_2−10%H_2) nitrogen rich atmosphere during sintering causes development of the fine spherical carbonitrides of the MX type stable at high sintering temperatures. However, this effect is more explicit in the high-speed steels without the additionally introduced carbides. Microstructure of carbide alloyed composite sintered at 1200°C with carbides mix cluster and with cabonitrides shown Figure 11. The density values were not related intentionally to the theoretical density of the fabricated material which, according to calculations, should be 8.69 g/cm^3.

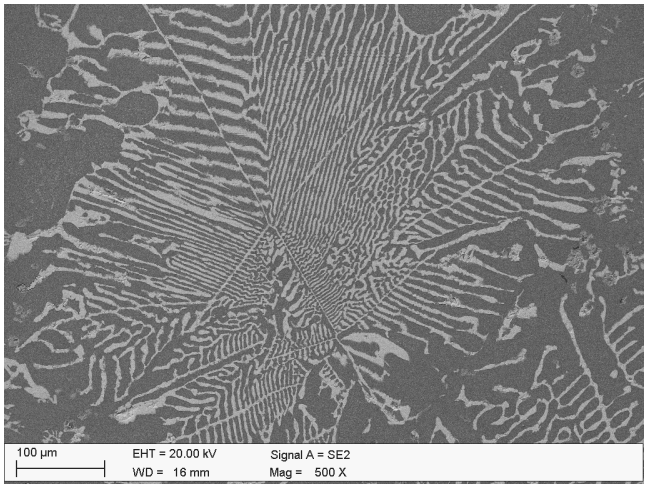
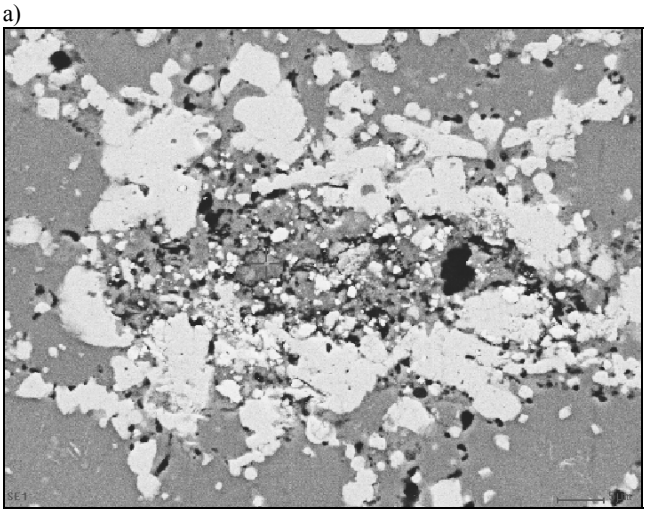


Fig. 10. Microstructure of M2 produced by PIM and sintered at 1300°C

However, it is difficult to state what should be the density of this material sintered in the N_2-10%H_2, atmosphere reacting, moreover, with the sintered material.

As the chemical composition keeps changing during the binder degradation and sintering, the portion grows of carbon, which is left after the binder degradation, likewise the portion of nitrogen, which keeps diffusing during sintering and originates carbonitrides. However, the introduced WC, TiC, TaC, and NbC carbides dissolve during sintering at a high temperature and create the M_6C and MC type carbides characteristic of the high-speed steel, identified with the diffraction methods. Density of the newly created phases of the MC or M_6C types differs from the introduced carbides. Therefore, the more interesting information is the porosity presented in Figure 12.

a)



b)

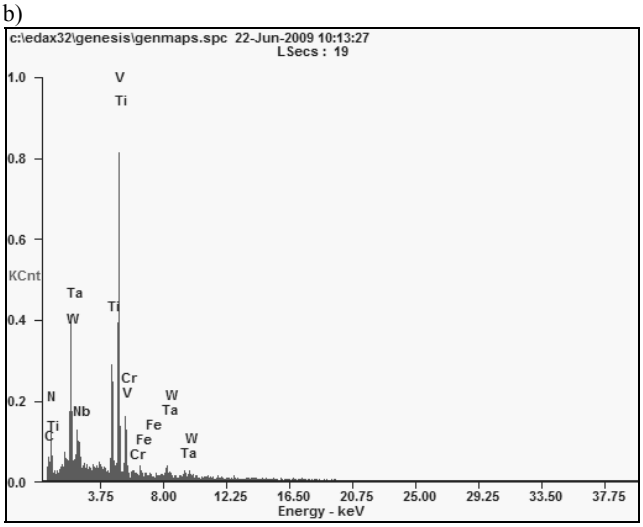


Fig. 11. a) microstructure of carbide alloyed composite sintered at 1200°C with carbides mix cluster and with cabonitrides, b) plot of EDS of marked area

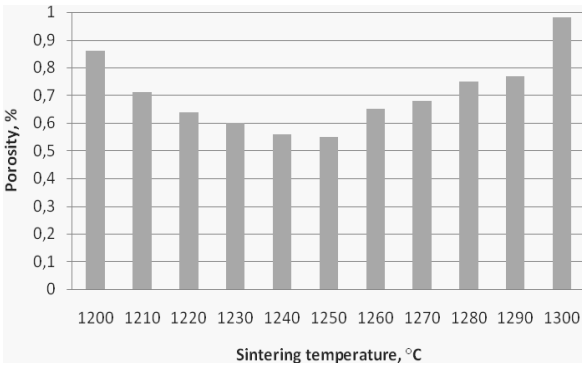


Fig. 12. Influence of sintering temperature on porosity evaluation of carbide alloyed composite

It was found out based on porosity examinations that the specimen sintered at the temperature of 1250°C is characteristic of the lowest percentage portion of pores equal to 0.55. Moreover, all materials are characteristic of the low porosity which does not exceed 1%, typical for the tool materials, regardless of the sintering temperature. The portion of pores is about 0.6% in the most interesting temperature range, i.e., from 1240 to 1260°C. Pores, in their majority, have the spherical shape, however, the big irregular pores may occur locally, presented in Figure 13, which - most probably - result from the big amount of binder occurring in this zone, or from air during injection moulding.

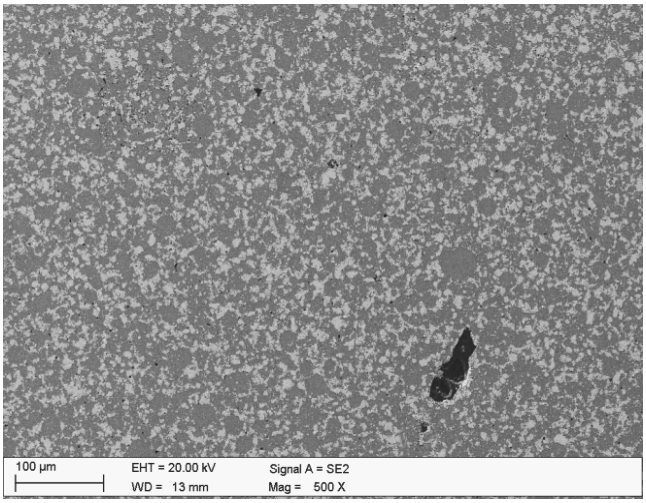


Fig. 13. Microstructure of carbide alloyed composite sintered at 1260°C with big irregular pore

The hardness after sintering is not very high. The maximum value is about 57.5 HRC and growing to 69 HRC after heat treatment. The hardness corresponding with the porosity and density. Influence of sintering temperature on hardness shown in a Figure 14.

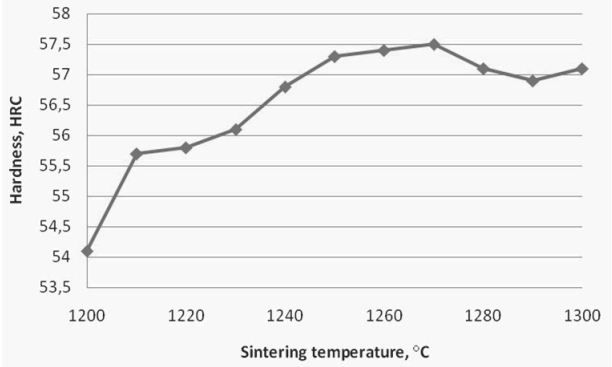


Fig. 14. Influence of sintering temperature on hardness of carbide alloyed composite

4. Conclusions

One can state, based on the presented results, that the chemical composition of the newly developed materials - cermet - 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. Moreover, the broad range of the optimum sintering temperatures and the relatively small effect of the sintering temperature growth on the carbides growth makes using the industrial heating equipment possible, especially the flow ones, for which temperature regulation accuracy and keeping the stable temperature during sintering is difficult.

Introducing the tetra carbides into the high speed-steel makes using higher sintering temperatures possible, therefore, a lower sinter porosity can be attained. Moreover, carbides with the regular lattice do not get dissolved in the matrix and do not create the eutectic structure at the high sintering temperature. In addition, sintering in the atmosphere of the protective gases N_2-10%H_2 causes diffusion of nitrogen into the sintered material and development of phases rich in this element.

Porosity examination revealed that the average portion of pores does not exceed 1% in the investigated materials; however, one may observe locally occurring big pores which may decidedly impair the mechanical properties of the investigated materials.

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