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Characteristics of structure and properties of a sintered graded tool materials with cobalt matrix

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ABSTRACT

Purpose: The mechanical alloying (MA) method has been chosen to manufacture tool gradient materials with high disproportion of cobalt matrix portion between core and surface layer.

Design/methodology/approach: The following research studies have been carried out to elaborate a new group of sintered tool gradient materials, tungsten carbide with cobalt matrix, to elaborate their fabrication technology and to determine their structure and properties: a fabrication technology of mixtures and the formation technology of tungsten carbide gradient materials with cobalt matrix WC-Co was applied and elaborated; sintering conditions were selected experimentally, ensuring the best structure and properties; phase and chemical composition of the sintered gradient WC-Co materials was determined using EDX; the structure of sintered gradient WC-Co materials was investigated using scanning microscopy; mechanical and physical properties of sintered gradient WC-Co materials was determined: hardness, resistance to abrasive wear, resistance to brittle cracking.

Findings: The presented research results confirm that the methods of mixing tungsten carbide in cobalt matrix an important effect upon the grain size of mixture. But it is not possible to determine the changes in grain size distribution. The larger particles break down rapidly that the product becomes more uniform.

Practical implications: The material presented in this paper is characterized by very high hardness of the surface and relative ductility of the core.

Originality/value: The obtained results show the possibility to manufacture TGMs on the basis of different portions of cobalt reinforced with hard ceramics particles in order to improve the abrasive resistance and ductility of tool cutting materials.

Keywords: Materials; Cemented carbides; Mechanical alloying; Powder Metallurgy

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MATERIALS

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1. Introduction

Powder metallurgy is a method of producing components by pressing or shaping metal powders which may be simultaneously or subsequently heated to create a coherent object. Powder metallurgy includes activities such as the fabrication of metal powders, characterization, mixing and handling of powder prior to compaction, and conversion of powders into useful engineering shapes, including a sintering step [1, 2, 3, 4, 5, 6].

Mechanical alloying (MA) (Fig. 1) is a high-energy milling process for producing composite metallic powders with a small scale microstructure by milling mixed elemental powders for a prolonged time. Mechanical alloying is carried out with intensive agitated balls that make possible to achieve the alloying by repeated cold welding, work hardening, and fracture events to progressively form composite particles. After milling, the particles are homogeneous [7, 8, 9, 10].

Particulate composites such as oxide-dispersion-strengthened material, have been produced this way since the 1960`s. The process starts with a mixture balls and elemental powders in a stirred mill. Figure 1 shows a schematic diagram of a mill, a balls mill, and the progressive homogenization of ingredients over time. Unlike other milling techniques, this one make possible to keep the particle size fairly the same.

The technique is not particularly energy efficient, however the product and especially final composite powder have important properties. Contamination issues are minimized by making the balls and tank from the same material as the powder. Fluids such as alcohol are important for balancing the milling [8, 9, 13].

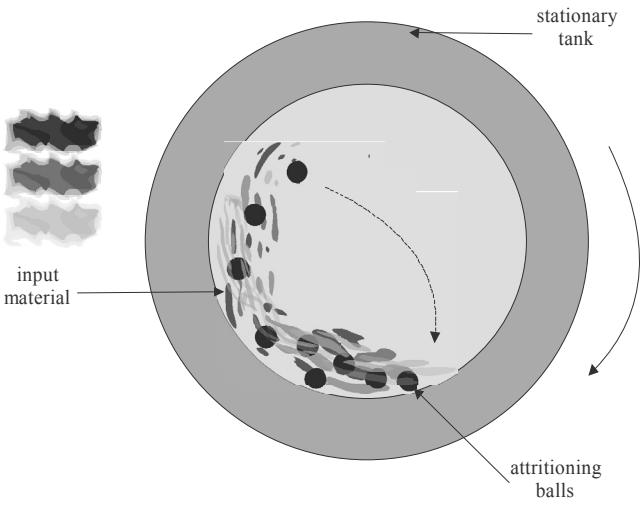

Fig. 1. Mechanical alloying process for creating alloy particles from mixed particles

One of numerous methods facilitating the fabrication of tool gradient materials is the technology of powder metallurgy. Through the application of the powder metallurgy technology for the fabrication of tool gradient materials we can closely control the chemical and phase composition as well as the structure of particular material layers [4, 5, 6, 7, 8, 9, 10].

A considerable share of cobalt matrix results in high ductility of the core, since the propagation of a crack through cobalt is connected with the dissipation of relatively high energy. In contrast, transcrystalline cracks through carbide grains have the character of low energy brittle cracks. The combination of high hardness and resistance to abrasive wear with high resistance to brittle cracking is unobtainable in one homogeneous material. The acquisition of tool materials (Tool Gradient Materials (TGMs)) fabricated with the use of powder metallurgy method, in effect of the gradient change of binding cobalt phase and the reinforcing phase of tungsten carbide, aims to solve the problem involving the combination of high hardness and resistance to abrasive wear with high resistance to brittle cracking, and consequently, to ensure their optimal synergy with operating conditions [2, 5, 6]. The cutting edges of drill bits should combine in themselves these two contradictory properties where the surface layer is resistant to abrasive wear and the base is characterized by raised resistance to brittle cracking [1, 14, 15].

The objective of the presented here is to elaborate a fabrication technology of the newly developed sintered tool gradient materials on the basis of hard phase of tungsten carbide with the cobalt binding phase, and to carry out research studies on the structure and properties of the newly elaborated sintered tool gradient materials[3, 4].

2. Experimental

2.1. Material and preparation of specimens for analysis

The analysis was carried out on specimens produced with the conventional method of powder metallurgy which consists in compacting in a closed moulding the successive, added layers having a gradually changing volumetric share of cobalt and tungsten carbide. In the research studies, we applied the powders of tungsten carbide (Fig. 2) and of cobalt (Fig. 3). When selecting the material, we accepted the requirements involving its application in agreement with the Standard PN-ISO 513:1999.

The studies a set of mixtures of different chemical composition was elaborated, and then the compacts from tungsten carbide with cobalt matrix were formed, coating the moulding with successive layers of variable phase composition (Table 1). The selection of chemical composition of the materials was made experimentally through the change of cobalt concentration as the binding phase within the range from 3 to 9% and the share of tungsten carbide from 97 to 91%. The formation of the tungsten carbide and cobalt powder mixtures consisted in the preparation of appropriate portions of the said powders, adding each time paraffin as a sliding agent of the volumetric share of 2%. The powders prepared in this way were ground within the time interval from 8 hours in a planetary ball mill with the balls from cemented carbides in order to make the powders homogeneous/uniform (Fig. 4).

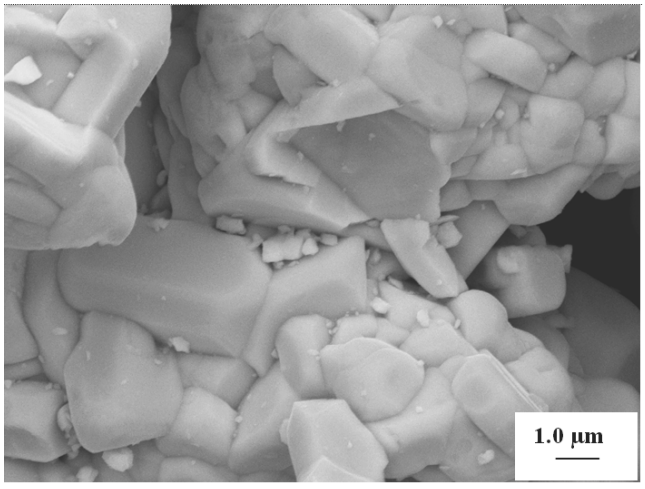

Fig. 2. Tungsten carbide powder

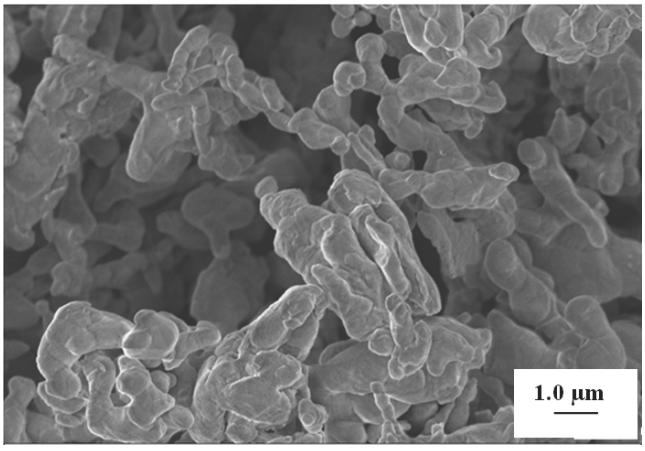

Fig. 3. Cobalt powder

Using the obtained mixtures, WC-Co compacts were prepared for analysis in which, from the surface side of the layer, successive transit layers were formed with progressively lower share of tungsten carbide down to the base. Ultimately, the pressure of 340 MPa was selected for further analyses.

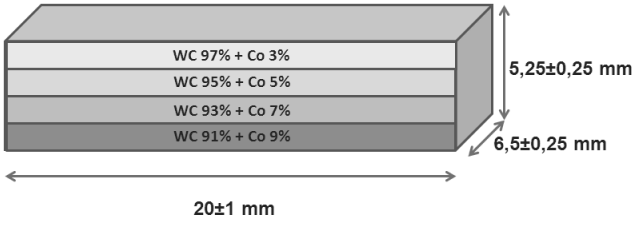

Fig. 5. Schema of compact the 3-7%Co/97-93%WC_4 material

Table 1.
Denotation of WC-Co tool gradient material specimens

Designation	3-9Co/97-91WC_4
Layers	3%Co+97%WC
	5%Co+95%WC
	7%Co+93%WC
	9%Co+91%WC

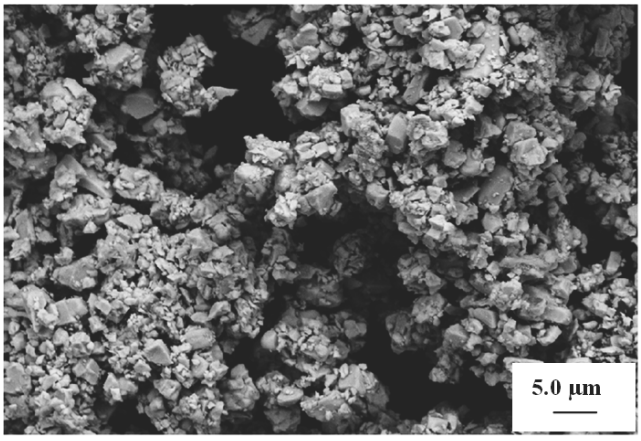

Fig. 4. Mixture of WC powder (97%), Co powder (3%) after 8 hours of milling in the ball mill

The compacts prepared in this way were characterized by smooth surface and had no signs of cracking, delamination or chipping (Fig. 5).

The specimens were sintered in a vacuum furnace (Fig. 6) in the conditions presented in the Table 2. In order to obtain better densification level, after the ultimate sintering, the condensation of sinters through hot isostatic pressing – HIP) was applied at the temperature of 1425°C and under the pressure of 200 MPa, as well as the sintering technology under pressure (Sinter-HIP) at the temperature of 1420°C and under the pressure of 6 MPa (Table 2).

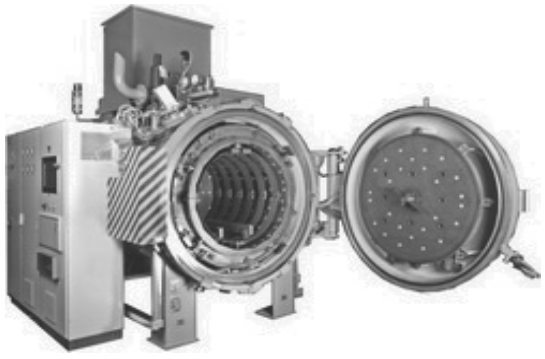

Fig. 6. Sinter-HIP furnace by Seco-warwick [16]

Table 2.
Sintering conditions for the newly manufactured tool gradient material 3-9%Co/97-91%WC

Sintering type	Sintering conditions	
	t_{sp} [min]	T_{sp}
Free sintering	30	1400°C
	90	1400°C + 1425°C
Under pressure	60	1420°C

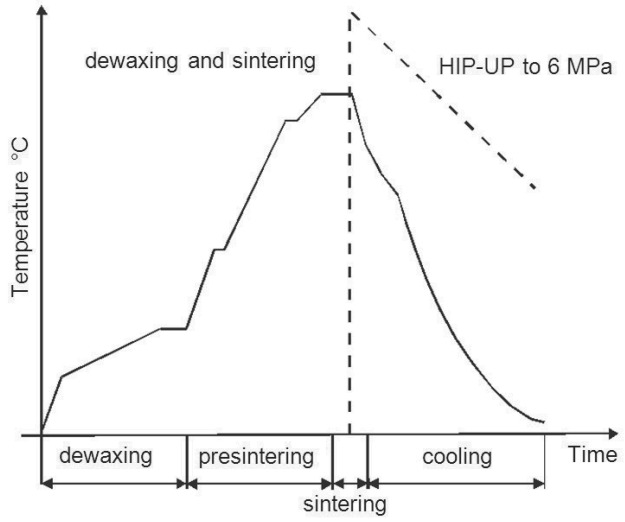

Fig. 7. The example of Sinter – HIP technology cycle [16]

In one apparatus and in one cycle the processes (Fig. 7) of dewaxing, cementing and hot isostatic condensation in argon atmosphere under the pressure of 6 MPa were carried out. Then, for the obtained tool gradient materials, metallographic tests were carried out, physical and mechanical properties of the sinters were determined and the distributions of internal-stresses in the material after sintering and during the operation were analysed.

2.2. Methodology

The structure of the fabricated WC-Co tool gradient materials was observed in the scanning electron microscope Supra 35 (Zeiss Company). To obtain the images of the investigated specimens, we applied the detection of secondary electrons (SE) and of backscattered electrons (BSE) with the accelerating voltage from 5 to 20 kV and with the maximum magnification of 20000 x. The quantitative and qualitative X-ray analysis and the analysis of surface distribution of elements was carried out in the scanning electron microscope (SEM) Supra 35 of Zeiss Company furnished with the X-ray energy-dispersive detector EDS.

The hardness of the materials was determined using the Vickers method with the indenter load of 10 and 30 N respectively. The operating time of the total loading force applied on the indenter was 15 seconds. The measurement was carried out along the whole cross-section width of the sintered specimens, starting the measurement 0.22 mm away from the external surface of the surface layer and finishing the measurement around the base area.

The testing on abrasive wear was carried out with the application of apparatus designed in the Institute of Engineering Materials and Biomaterials of the Silesian University of Technology (Fig. 8). The tests were carried out with a diversified number of cycles 5000, which translates itself respectively into 4 m and with different loading 2.5 and 10 N. Due to the combination of the assumed in this way testing conditions, four results were obtained for the surface layers of each investigated specimen, whereby the abrasive wear could be determined. The same set of tests was carried out for the particular materials of the base, and then the respective measurement results were compared to verify the influence of the structure gradient on the functionality properties. The extent of wear was determined basing on geometric measurement of the wear and calculating its volume. The decrease of volume as the indication of absolute wear is applied when the decay of mass is too small and difficult to estimate. The observation of wear was also carried out on the confocal microscope LMS 5 Exciter and in the scanning electron microscope (SEM).

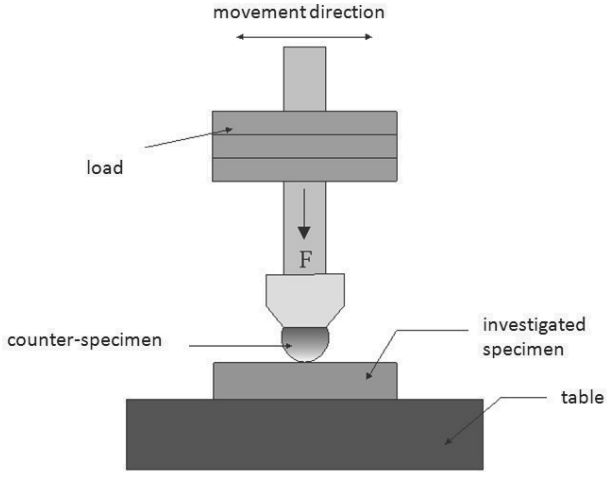

Fig. 8. Diagram of the apparatus for testing the resistance to abrasive wear

The tests involving the resistance to brittle cracking (K_{IC}) were performed in congruence with the Standard ISO 28079:2009, making use of the Palmqvist method. The tests were carried out on the appropriately prepared specimens, polished to eliminate surface stresses which had been introduced to the hard surface layer through the gradation of chemical composition of the material, and then etched in the Murakami reagent of the composition ($[K_3Fe(CN)_6 + KOH + H_2O]$) to ensure a precise read-out of the cracking length.

3. Results

3.1. Structure and chemical composition of the tool gradient materials

The research demonstrated that the grinding in a high-energy mill yields exceptionally good results as early as after 8 hours. The mixture of powders is forming numerous conglomerates but it is homogeneous, and the cobalt grains enclose the WC carbides. The mixture of WC-Co powders after grinding in a ball mill over the same time period is also homogeneous with locally occurring large carbides of the size of about 6 μm which were not fully powdered during the grinding process (Fig. 9).

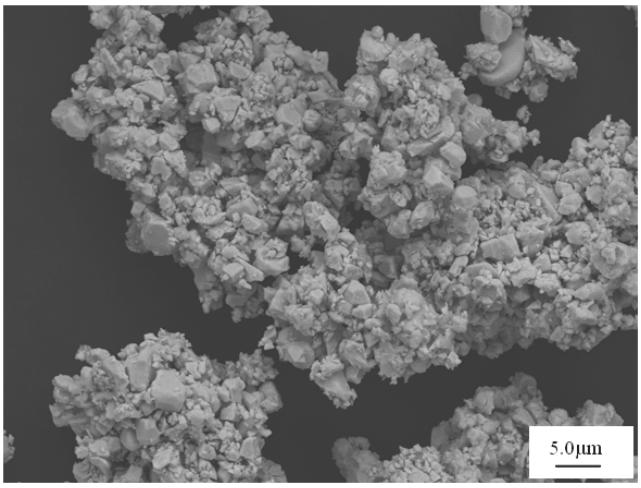

Fig. 9. Powder mixture WC (95%), Co (5%) after 8 hours of grinding in a ball mill

The tests on the flow rate of the produced mixture were not successful since the powders did not pass through the designed for such tests Hall funnel. In spite of poor flow rate and low bulk density of the powders mixture, the compacts were characterized by sharp edges and did not exhibit cracks or chipping, which presents the compact, illustrates the borders between successive layers. In order to consolidate the powders we applied free sintering, sintering with isostatic compacting or hot pressing. For the free sintering and for the sintering with isostatic condensation we applied the temperature of 1400°C and 1400°C + HIP. The hot isostatic sintering was carried out at the temperature of 1420°C.

The sintering methods were selected basing on the results described in works [12] in which, very frequently, for economical reasons or to simplify or accelerate the technological process of the fabricated tool materials, pressing and sintering is combined into one operation. It involves pressing in raised temperature or sintering under pressure. Irrespective of the phase composition of the specimens it can be observed that all materials were deformed after sintering.

The presence of cobalt in the material results in the formation of liquid phase which during the sintering brings about the formation of low-melting eutectic phase. In this process it is most difficult to maintain the gradient which has a tendency to fade due to the oriented mass transport. In order to avoid such a phenomenon, a high-temperature synthesis with short sintering time is applied. Since most of the infusible grains in the material have the size from 2.5 to 3 micrometers and the dissolution process involves only a small portion of their volume, therefore the final product consists of great oval grains of the basic phase bound by the unified liquid phase (Fig. 10).

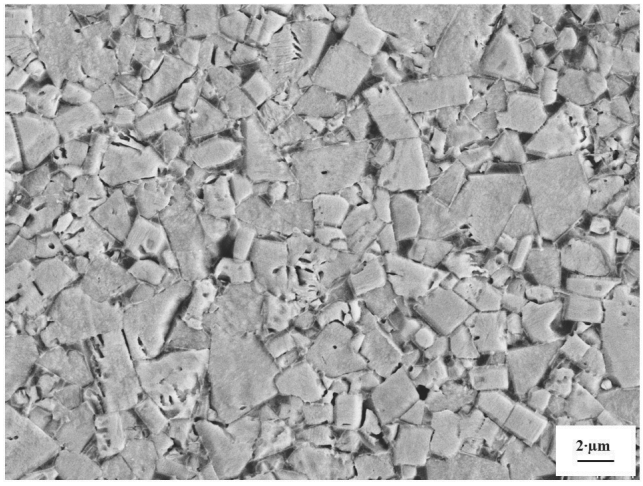

Fig. 10. Structure of surface layer sintered in a vacuum furnace at temperature T_{sp}=1400°C and subjected to hot isostatic condensation at the temperature T_{sp}=1425°C

In spite of low volumetric share of cobalt, at high sintering temperature this phase is melting and is partially dissolving the surface of WC carbides. Hence the rise of the volumetric share of liquid phase i.e. low-melting eutectics during the sintering process, which moistens the WC solid phase (Fig. 10). In effect of the above, the capillary forces occurring around grain borders decrease the volume of the pore, increasing in this way the density of the material. The liquid phase during cooling and crystallization assumes the form of small layers separating solid grains.

3.2. Mechanical properties and resistance of the tool gradient materials

The measurement results involving HV hardness (Fig. 11) of the manufactured tool materials of the growing share of WC carbide with respect to cobalt matrix in the direction towards tool surface are indicative of a gradual rise of hardness. The hardness of the 3-9%Co/97-91WC_4 material sintered in vacuum, depending on the sintering temperature, can be placed within the range of 1370-1440 HV in the surface layer and is decreasing, with the rise of the distance between the measurement point and the external surface of the surface layer, to 1300-1330 HV in the base.

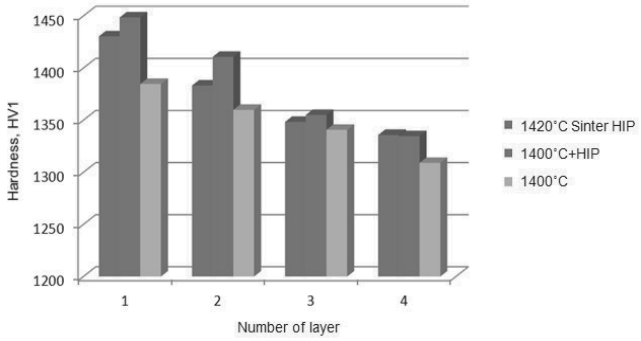

Fig. 11. Diagram of HV1 hardness, volumetric share and sintering temperature for the material 3-9%Co/97-91%WC_4

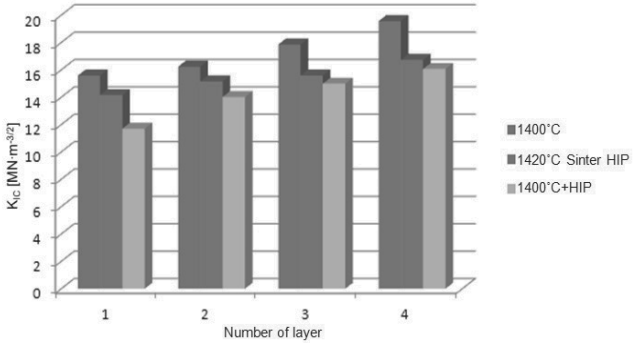

Fig. 12. Diagram of the dependence of brittle cracking on temperature and Co volumetric share for the 3-9%Co/97-91%WC_4 material sintered in a vacuum furnace

The hardness of the 3-9%Co/97-91WC_4 material sintered and subjected to isostatic condensation at the temperature of 1425°C is within the 1400 HV in the surface layer and is decreasing to 1330 HV in the base. The hardness of the 3-9%Co/97-91WC_4 material sintered with isostatic condensation at the temperature of 1420°C is within the 1425 HV in the surface layer and is decreasing, with the rise of the distance between the measurement point and the external surface of the surface layer, to 1330 HV in the base. In effect of the carried out hardness tests we did not find any considerable difference in hardness of the investigated materials subjected to free sintering and those with isostatic condensation.

The relation involving the changes of HV hardness of materials with the changing share of Co phase, volumetric share and sintering conditions was described with the use of a regression function. The value of the multidimensional correlation factor and that of its significance level confirm the correct dependence of hardness on sintering conditions and on cobalt present in particular layers of the material.

The research results involving the resistance to brittle cracking K_{IC} of the sintered tool gradient materials of different volumetric share of WC and Co phases in each material layer are presented in Fig. 12. The results involving the K_{IC} factor are indicative of a considerable dependence between sintering parameters and the resistance to cracking of particular tool materials. The average value of K_{IC} factor of the surface layer of the material is 13 [MNm$^{-3/2}$] and of the base 17 [MNm$^{-3/2}$].

The average values of the K_{IC} factor of the material sintered at the temperature of 1400°C are respectively 15 [MNm$^{-3/2}$] for the surface layer and 19 [MNm$^{-3/2}$] for the base. The dependence of K_{IC} factor for the investigated materials of different Co concentration on the volumetric share and sintering conditions is presented by means of a regressive function. The value of multidimensional correlation factor and that of its significance level confirm the dependence of K_{IC} factor on sintering conditions and volumetric concentration of cobalt in the particular layers of the material.

The lack of distinguished difference of the K_{IC} factor in the surface layer and in the base of materials sintered with isostatic condensation can be explained by too long sintering time, resulting in partial or total decay of gradient structure.

In order to compare the tribological properties of the fabricated gradient materials, the test on the resistance to abrasive wear was carried out in the system 'investigated specimen and Al_2O_3 ball' as a counter-specimen. The results of the carried out abrasive trial (Table 3) show that the materials sintered with isostatic concentration are characterized by much lower abrasive wear than the materials obtained as a result of free sintering. The wear of gradient materials subjected to free sintering, depending on the share of binding phase, temperature, load and number of cycles is presented in Table 3.

The measurement results involving the abrasive wear of the sintered tool gradient materials of tungsten carbide with cobalt matrix are indicative of a gradient change of the properties of the investigated materials, depending on the share of binding phase. Therefore, the wear of gradient materials is conditioned by many factors: the share of binding phase, loading value of counter-specimen and also the friction path (number of cycles).

4. Conclusions

The goal of this work was to produce mixture of powders witch one will be taken to gradient material using traditional powder method. Prepared powder mixes were investigated by XRD and scanning electron microscopy. The final material: WC97%+Co3% after 8 hours milling, WC95%+Co5%, WC93%+Co7% and WC91%+Co9% might be useful to the tool gradient material.

However the method of mixing tungsten carbide and cobalt have an important effect upon the grain size of mixture, it is not possible to determine the changes in grain size distribution.

In effect of diffusion processes running during the sintering process, local unification of phase composition in the joint areas is taking place despite the laminar output structure of the compacts fabricated by coating the moulding with successive powder mixtures of a step-wise changing share of WC and Co concentration and then pressing, the gradient of changes of the final structure of the sinter is continuous and not step-wise as in the compact.

Table 3.
Tribological wear of gradient material 3-9%Co/97-91%WC_4

Layer denotation	T_{sp} [˚C]	Load [N]	Number of cycles	Statistical quantities	
				Arithmetic average [mm^3]	Standard deviation
97%WC - 3%Co	1400	2.5	5000	9.73×10^{-4}	0.98×10^{-4}
		10	5000	21.25×10^{-4}	1.72×10^{-4}
91%WC - 9%Co		2.5	5000	14.64×10^{-4}	1.13×10^{-4}
		10	5000	31.59×10^{-4}	1.64×10^{-4}
97%WC - 3%Co	1400 + 1425	2.5	5000	9.71×10^{-4}	0.56×10^{-4}
		10	5000	27.70×10^{-4}	1.69×10^{-4}
91%WC - 9%Co		2.5	5000	10.97×10^{-4}	0.55×10^{-4}
		10	5000	31.52×10^{-4}	2.06×10^{-4}
97%WC - 3%Co	1420	2.5	5000	2.45×10^{-4}	0.18×10^{-4}
		10	5000	27.70×10^{-4}	2.84×10^{-4}
91%WC - 9%Co		2.5	5000	12.65×10^{-4}	1.28×10^{-4}
		10	5000	38.56×10^{-4}	2.59×10^{-4}

Hardness, resistance to abrasive wear and brittle cracking of the sintered tool gradient materials are dependent respectively on the WC share and Co concentration as a binding phase and on the conditions of technological process applied for the fabrication of these materials, i.e. milling of powder mixtures, formation of the compact and sintering, yet the surface of the material is characterized by high hardness of 1450 HV, due to high WC share of 97%, and the core is characterized by higher resistance to brittle cracking 19 $MNm^{-3/2}$ as compared to the surface because of higher Co concentration of 9%, with the difference of 4 $MNm^{-3/2}$ between the K_{IC} values on the surface 15 $MNm^{-3/2}$ and in the core 19 $MNm^{-3/2}$.

Acknowledgments

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