OPTIMIZATION OF WC-Ni-ZrO_2 STRUCTURE.

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Abstract
Technological routines for fabrication of WC-8wt.%Ni-6wt.%ZrO_2 composites with a uniformly distributed microstructure are described. The structure optimization was held on the different milling and sintering devices. Ball mill, attritor mill and special mixer device in combination with HIP, sinter/HIP and half commercial vacuum sintering technologies were used to find the best parameters for satisfactory microstructure. It was revealed that there is significant influence of milling or sintering technique used on the formation of the microstructure. Compact hard metals composed of fine and homogeneously distributed WC and ZrO_2 grains with little flaws can be achieved after adding 0.2 wt.% of graphite in a combination with 0.4 wt.% of chromium carbide. This grade has also demonstrated the high hardness of 1600 HV in a combination with impressive fracture toughness of 13.2 MPa·$m^{1/2}$.

1 Introduction

Cemented carbides are multiphase materials comprising a hard phase skeleton composed of refractory metal carbides embedded in a metallic binder (Co, Ni, Fe). Cemented carbides are often manufactured by liquid phase sintering of compacted mixtures of carbide and binder metal powders. Due to their high hardness and superior wear resistance, WC-Co hardmetals are widely used as tools for cutting, milling, and machining. Their structures are optimized for different applications by varying the binder content as well as the composition and grain size of the hard phases [1, 2]. It is a well-known fact that the homogeneous distribution of phases in composites is a half the battle for designed mechanical, tribological and other properties of multi-phase materials [1-4]. To obtain the materials of desired microstructure and provide properties required for the different applications a precise technological plan should be considered. There is a great influence of such process variables as mixing/milling parameters on the development of pure, fine and uniform microstructure of the designed product [5-7]. However, the main operation responsible for the final microstructural features of the powder compact is sintering route [7, 8].

WC-Co cermets are widely known materials for their high wear resistance [7, 9-11]. In the present study the technologies of WC-Ni-ZrO_2 cermets development have been discussed in order to find the best way to produce poreless reliable composite for structural applications.

2 Experimental procedure

2.1 Raw materials

The raw materials used for prototyping of WC/Ni/ZrO_2 cermets were commercial high purity WC powder (particle size of ~0,9μm provided by Wolfram GmbH, Germany), as a carbide phase, nickel powder as a binder material, and 3 mol % yttria partially stabilized zirconia (PSZ-ZrO_2, particle size of about 30 nm, provided by TOSOH, Japan) as a toughening agent. Small amount of extra carbon (TIMCAL, Switzerland) with a particle size of 5.5 μm has been added to some mixtures to avoid the formation of η-phase and Cr_3C_2 (Tokyo Tungsten Co., Japan) with a size 2-3 μm has been added as a grain growth inhibitor.

2.2 Milling and mixing variables.

The powders were milled by three different routines. Methods used were: a classical rotary ball mill; a vertical ball mill; and a high energy attritor mill. The devices were used both as the separate operations and as combined operations. Powders milled in high energy attritor were initially milled without PSZ particles to avoid spontaneous transformation of the tetragonal zirconia particles into monoclinic polymorph under high milling energies. Milled mixtures were then mixed in a rotary ball mill and/or vertical ball mill.

To avoid powder contamination ZrO_2 balls were used as a milling media. As the size of grinding media has a great influence on the milling efficiency [5] it was decided to use the grinding balls of two different sizes. As a process control agent (PCA) polyethylenglycol (PEG) was added in different amounts depending on the processing route. Parameters of the milling/mixing process are classified in the Table 1.

Powder name and composition wt.%	**C wt.%**	**Milling technique**	**Powder quantity, g**	**Time, h**	**Plasticizer &PCA**	**BPR, media material and balls diameters, mm**
A 86%WC-8%Ni-6%PSZ	0	Vertical ball milling	35	70	2g caoutchouc &15ml benzene	4:1(ZrO2) 180(Ø3)+ 90g(Ø10)
B 85.2%WC-8%Ni-6%PSZ-0,4Cr_3C_2	0,2	Rotary Ball mill	100	70	3g PEG&100ml ethanol	6:1(ZrO2) 270g(Ø3) +360g(Ø10)
C 88%WC-6%Co-6%PSZ	0,25	Atrittor milling	100	6	3g paraffin&100ml benzene	10:1(WC-Co) Ø13
D 86%WC-8%Ni-6%PSZ	0,4	Atritor&ball milling	100	6+24	3g paraffin&100ml benzene	7:1(WC-Co) & 6:1(ZrO2)
E 85.3%WC8%Ni-6%PSZ	0,7	Vertical ball milling	35	70	2g caoutchouc &15ml benzene	4:1(ZrO2) 100(Ø3)+ 40g(Ø10)
F 85.3%WC-8%Ni-6%PSZ	0,7	Roary Ball mill	100	70	3g PEG &100ml ethanol	6:1(ZrO2) 270g(Ø3) +360g(Ø10)

Table 1. Powder compositions mixing and milling parameters

2.3 Sintering

After milling the powders were dried in the air environment and sieved. Thereafter, dried powders were subjected to cold isostatic pressing at a compaction pressure of 10 MPa with a die dimension 15x10x5 mm. Green bodies were held at 600 °C in hydrogen for 30 min to burn out plasticizers.

Sintering of the powder compacts was carried out via three sintering route: Sinter/HIP, AIP-HIP (AIP stands for American Isostatic Pressing, USA) and the half commercial vacuum furnaces (HCVF) with temperature varying in the range of 1400°C-1500°C for varying dwell time periods. It has been shown [14-15] that sintering at this temperature range should be enough for the formation of the dense composite.

Choice of the sintering routines has the most significant influence on the formation of the product microstructure and its mechanical properties. To find the best suited technological parameters sintering was conducted under various conditions, such as: heating/cooling rate, sintering atmosphere, pressure, temperature and holding time. Sintering parameters are listed in Table 2.

Specimen	Sintering technique	Temperature °C	Pressure MPa	Heating rate °C/min	Cooling rate °C/min	Dwell time min
C1,D1,E1,F1,	Sinter/HIP	1390	3	18(45min)+6.5(90min)	5.8	35
C2,D2,E2,F2,		1415	3	11	8	50
A1, D3,E3,F3,	AIP-HIP	1410	150	10	7.5	60
A2,D4,E4,F4,		1450	200	12	8	60
B1		1460	150	12	8	60
D5,F5,C3, E5	HCVF	1500	$5X10^{-6}$	10(115min)+7(50min)	10	30
F6, C4, E6		1430	$5X10^{-6}$	10(115min)+7(50min)	10	60

Table 2. Sintering techniques and parameters

2.4 Characterization

Prior investigations, all samples were smoothly polished with diamond paste to obtain optically reflective surfaces. The microstructural examination of the composites was conducted scanning electron microscopy (TM-1000, Hitachi, Japan). X-ray diffraction analysis was conducted on a θ–θ diffractometer (Bruker AXS D5005) using Cu K_α radiation (40 kV, 30 mA). The bulk Vickers hardness was measured using Indentec 5030 SKV at the load of HV20 or 200N according to ISO 6507. The fracture toughness was obtained by the Vickers indentation technique, based on crack length measurements of the median crack pattern produced by HV20 indentations [16]. The density was measured using Archimedes technique.

3 Results and discussion

3.1 XRD analysis

XRD analysis has revealed η-phase in specimens with no additive carbon in the initial mixture, Figure 1. Peaks of Ni_2W_4C phase can be observed on the 0 wt.% C HIPed pattern. There are no peaks present on the pattern produced from the powder mixture doped by 0.2 wt.% C confirming the η-phase formation in grades with carbon deficiency.

The same pattern shows tetragonal polymorph of the zirconia particles in the cermet matrix. This is a preferable phase of the particles for the formation of the designed composite. Being in tetragonal modification, it has a potential to be transformed into a monoclinic polymorph under loading. This may result in enhancement of materials resistance to fracture.

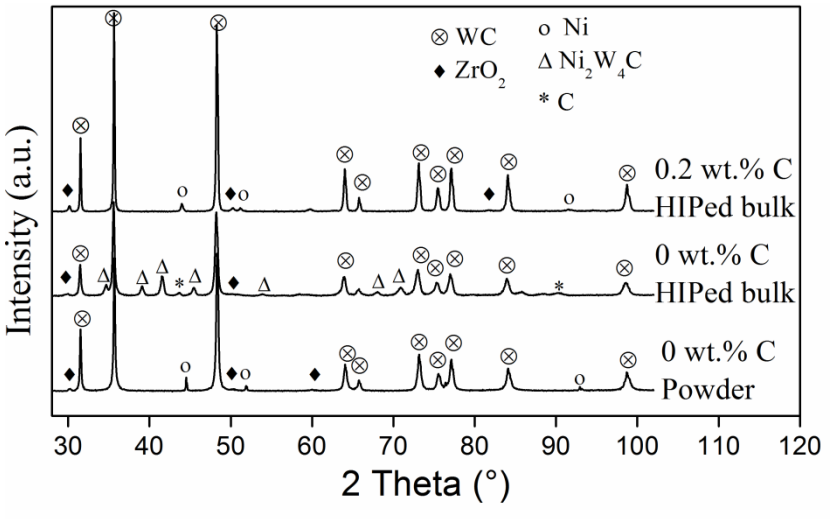

Figure 1. XRD pattern of the powder containing 0wt.%C; HIPed specimen with no carbon; and HIPed specimen with 0.2wt.%C.

3.2 Processing and mechanical properties

The first step in this study was to determine the correct sintering temperature and free carbon content. Influence of sintering routine and carbon content on the density and hardness of the sintered grades is illustrated in Figure 2. Both hardness and density decrease drastically with more than 0.2 wt.% of carbon addition to the initial composition.

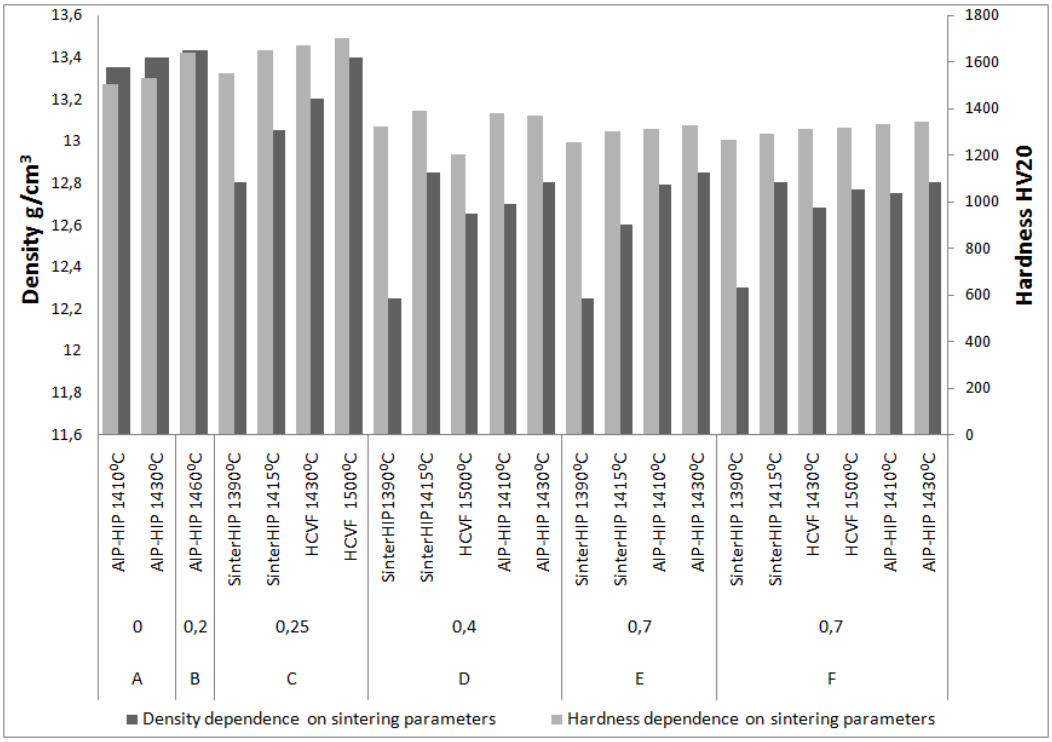

Figure 2. Hardness and density in dependence on sintering technology and carbon content.

The technological cycle sufficient for the production of the consolidated conventional tungsten carbide cermet cannot be entirely applied for sintering of the materials toughened by zirconia (Figure 2). In all cases Sinter/HIP sintering at 1390°C shows the lowest density and hardness. Hence, it can be concluded that sintering of the materials of the chosen composition at this temperature is not suitable for obtaining fully consolidated composite of high mechanical reliability.

Slight influence of the sintering technique on degree of consolidation has been noticed. All specimens having higher than 0.4 wt.%C content have almost the same density values (excluding Sinter/HIP 1390°C). Dependence of hardness on the sintering technique is similar for all materials having about 15-50HV units higher values for the AIP-HIP produced specimens. There is an increase in hardness and density for the grade sintered at 1460°C under 150 MPa pressure (AIP-HIP) and this grade also demonstrates the highest densification degree of all produced materials. However, these results are believed to be the consequence of adding 0.2 wt.% of graphite together with 0.4 wt.% of Cr_3C_2 (grain growth inhibitor) to the initial mixture that has resulted in a fine grained structure. The "E" and "F" grades having the same chemical composition and containing 0.7 wt.%C while prepared using different mixing parameters demonstrate no dependence on the ball mill mixing technology and PCA or plasticizer used for preparation of the mixture. Both "E" and "F" grades depend on the sintering parameters though behave similarly.

The next step in this study was to determine fracture toughness of the material. The influence of the sintering methods and carbon content on the mechanical properties of the produced specimens is represented in Figure 3. Here the "C" specimen with lower binder content shows the lowest fracture toughness and reflects typical behavior for the cemented carbides. The grade "B", which has demonstrated the best densification, reveals both high hardness and sufficient fracture toughness value of 13.4 $MPa \cdot m^{1/2}$. Low carbon content has resulted in a higher hardness of about 1640 HV20 units and the density of 13.4g/cm^3. The grade "B" provides the best combination of density, hardness and toughness, but is only marginally better than "A" grade.

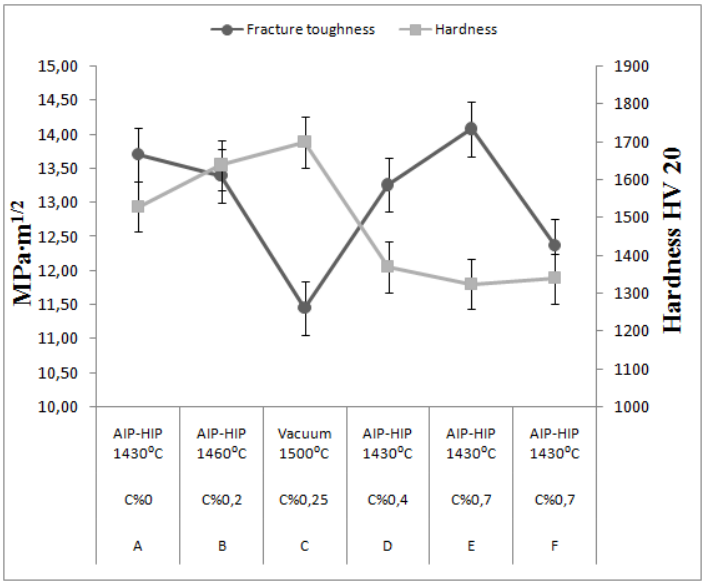

Figure 3. Fracture toughness and hardness dependence on the sintering parameters and carbon content. Error bars are given for fracture toughness values.

Increasing carbon content over 0.25 wt%C in the grades results in lower hardness, while the fracture toughness shows inverse tendency with increase in carbon content.

3.3 Microstructural analysis

The SEM images of microstructures of WC-ZrO_2-Ni composites are presented in Figure 4. The bright phase is WC, whereas the dark phase is ZrO_2 and grey one is nickel. The zirconia grains are homogeneously distributed throughout the composites indicating sufficient powder mixing. The individual ZrO_2 grains of sizes between some nm up to some microns are mainly present the agglomerates of nano-sized particles.

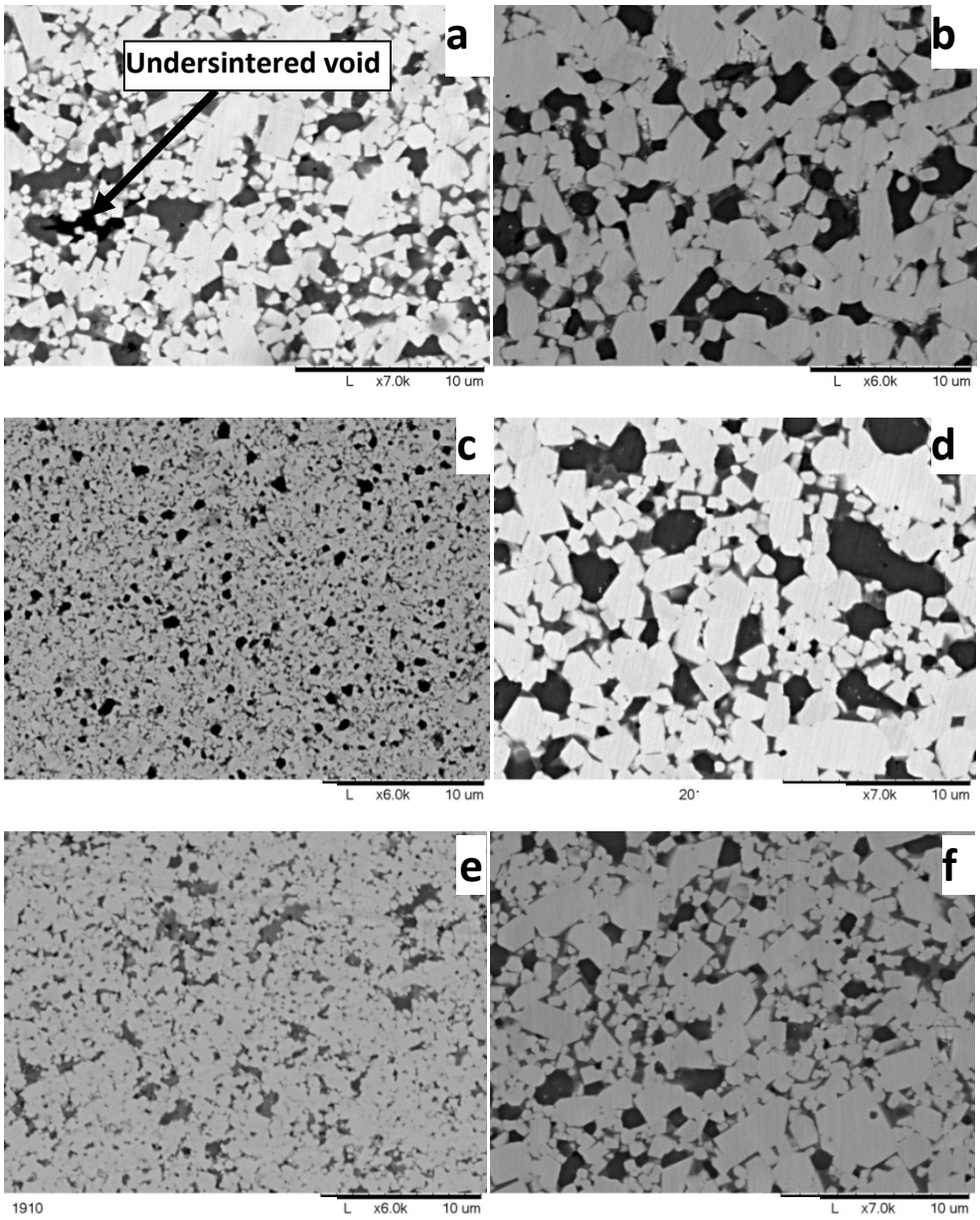

Figure 4. SEM micrographs of the a)E-2 (30min dwell time) b)E-4 (60 min dwell time) c)B added by Cr_3C_2 (60min dwell time) d)F4(60 min dwell time) e)C4 (60min dwell time) f)D4(60min dwell time)

The grown tungsten carbide grains and agglomerated zirconia particles are presented in cermets sintered from the powders milled by either classical ball mill or vertical ball mill and

showed no dependence on the PCA being used for mixing (Figure 4a -mixed in benzene, d – mixed in ethanol). In both cases the microstructure developed and properties obtained after sintering were almost the same.

Milling with high energy attritor mill resulted in the formation of finer grains as compared to others mixing methods, Figure 4e. Figure 4f represents the microstructure of the specimen which was milled with attritor mill and then added with zirconia and followed by rotary ball mill. Despite the fact that it was attritor milled there are still some large grains indicating discontinuous grain growth. Discontinuous grain growth can be attributed to the long dwell time at maximum temperature during sintering. However, the specimens sintered for only 30 min dwell time resulted in fine grained material suffered from a lot of under-sintered zones, Figure 4a. Thereby it should be concluded that the optimal time for sintering of this material should be somewhere in between 30 and 60 minutes; however, during this period of time grain growth will occur. Cr_3C_2 powder added to the "B" grade as a grain growth inhibitor resulted in a very fine grained microstructure, Figure 3c. The amount of added graphite into this grade is 0.2 wt%C.

4 Conclusion

In the present work the effect of different technological parameters of sintering and additives on development of WC-Ni-ZrO_2 cermets has been studied. Formation of η-phase was avoided by adding some amount of carbon. Tetragonal zirconia polymorph was observed in the sintered compacts. Density and mechanical properties such as hardness and fracture toughness have been measured to reveal the influence of the technological routine. The most promising material is grade "B" possessing high hardness (1640 HV20) and fracture toughness (13.4 $MPa \cdot m^{1/2}$), as well as high degree of densification and microstructural integrity. The specimen "B" has been added by the Cr_3C_2 particles; milled using classical ball mill in ethanol PCA; and sintered in AIP-HIP for 60 min at 1460 ^{0}C. Influence of graphite addition on the mechanical and microstructural parameters has also been observed and the critical amount of free carbon to be added to the precursor powders is estimated to be 0.2 wt%.

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References

[1] Russias J., Aguni S. Y. , Fantozzi G., Bienvenu K., Fontaine J. Influence of titanium nitride addition on the microstructure and mechanical properties of TiC-based cermets. *International Journal of Refractory Metals & Hard Materials,* **23**, pp. 358–362, (2005).

[2] Lin A. , Jingtao H., Jun C. Microstructure and mechanical properties of WC-20wt% Co/ZrO_2(3Y) cermet composites *Journal of University of Science and Technology Beijing, Mineral, Metallurgy, Material,* **13**, pp. 174-177, (2006).

[3] Hussainova I., Antonov M., Voltsihhin N. Assessment of zirconia doped hardmetals as tribomaterials. *Wear*, **271**, pp. 1909-1915, (2011).

[4] Hussainova I., Antonov M., Jasiuk I., Du X. Characterization of microstructure and mechanical properties of cermets at micro- and nanoscales. *Int. J. Materials and Product Technology*, **40,** pp.58 - 74 (2011).

[5] Suryanarayana C. Mechanical Alloying and milling. *Progress in Materials Science,* **46**, 1-184, (2001).
[6] Sony P.R. *Mechanical alloying Fundamentals and Applications*, Cambridge International, Cambridge (2001).
[7] Andren H-O. Microstructure development during sintering and heat-treatment of cemented carbides and cermets. *Materials Chemistry and Physics,* **67**, pp. 209-213, (2001).
[8] Kimmari E., Hussainova I., Smirnov A., Traksmaa R., Preis I. Processing and microstructural characterizationof WC-based cermets doped by ZrO_2. *Estonian Journal of Engineering*, **4**, pp. 275-282, (2009).
[9]Upadhyaya G. S. *Cemented Tungsten Carbides: Production, Properties, and Testing.* Noyes Publications, New York, (1998).
[10] Pirso J., Viljus M., Letunovitš S. Friction and Dry Sliding Wear Behaviour of Cermets. *Wear,* **260**, pp. 815 – 824, (2006).
[11] Hussainova I. Microstructure and erosive wear in ceramic-based composites. *Wear*, **258,** pp. 357 – 365, (2005).
[12] Basu, B., Ventkateswaran, T. and Sarkar, D., Pressureless sintering and tribological properties of WC–ZrO2 composites. *Journal of the European Ceramic Society,* **25,** pp. 1603–1610, (2005).
[13] Jiang, D., Vleugels, J. and Van der Biest, O., ZrO2–WC nanocomposites with superior properties. *Journal of the European Ceramic Society,* **27,** pp.1247–1251 (2007).
[14] Ünal N., Kern F., Övecoglu M.L., Gadow R. Influence of WC particles on the microstructural and mechanical properties of 3 mol% Y_2O_3 stabilized ZrO_2 matrix composites produced by hot pressing. *Journal of the European Ceramic Society*, **31**, pp. 2267–2275, (2011).
[15] Voltsihhin N., Cura, M.E., Hussainova, I., Hannula, S-P. *Sintering routes for zirconia doped hardmetals* in *8th International DAAAM Baltic Conference.* Tallinn, Estonia, (2012).
[16] Sergejev F., Antonov M. Comparative study on indentation fracture toughness measurements of cemented carbides. *Proceedings of the Estonian Academy of Sciences,* **12,** pp.388–398, (2006).