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ZIRCONIUM DIOXIDE/TUNGSTEN CARBIDE COMPOSITE – INFLUENCE OF SINTERING TECHNIQUE ON PHASE COMPOSITION AND MICROSTRUCTURE

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Abstract

The paper presents the results of a comparative experiment on sintering a particulate composite in the ZrO_2/WC system containing significant amounts of carbide additive (20 or 50% by volume) utilizing spark plasma sintering (SPS) or high pressure high temperature (HPHT) techniques. The experiment was conducted using commercial zirconia and tungsten carbide powders. The main aim of the experiment was to verify if it was possible to use the HTHP technique to manufacture composite parts in order to increase the efficiency of the production process. The obtained results showed that the final microstructures of the composites produced by SPS and HPHT differ significantly in their phase composition and microstructure. The materials received by the HPHT process after consolidation contained a large volume of monoclinic zirconia phase, which was a serious disadvantage of the consolidated material due to strong susceptibility to cracking. Furthermore, the short time of sintering prevented the tungsten carbide grains from modifying their shape during the sintering process. The SPS process took more time, but in result the microstructure of the composites contained a non-transformed tetragonal zirconia phase and the carbide grains transformed their shape into convex and isometric ones.

Keywords: particulate composite, zirconia, tungsten carbide, microstructure

Introduction

The implementation of the idea of combining oxide and covalent phases in one polycrystalline material was intensively studied in the last decades of the last century. Practically parallel work was carried out on materials based on alumina [1-3] and zirconium oxide [4-7], containing silicon carbide inclusions (Al_2O_3/SiC or ZrO_2/SiC). The material in the ZrO_2/WC system was intensively studied at the turn of the 20th and 21st centuries [8-14]. Using the activity of ZrO_2 nanocrystallites in the sintering process, relatively dense sinters containing up to 50% by volume of the carbide phase were obtained [9, 11, 13]. Composites

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in the ZrO_2/WC system have interesting mechanical properties, which clearly manifest the synergy effect desired in composite materials. Obviously, the addition of carbide significantly increases the hardness in relation to ZrO_2, but the observed phenomenon of very high strength and resistance to brittle fracture, even higher than that of ZrO_2 [9] is interesting. Some works link this effect with the unique phenomenon of the selective correlation of interphase boundaries between oxide and carbide grains [9, 11]. The best properties are shown by composites sintered using FAST techniques (field assisted sintering technology), of which the most commonly used is the SPS technique [13]. This method of consolidation in ceramic systems is very useful, especially since ceramics are electric current conductors. There is a case of zirconia with a significant amount of WC additive. An immanent feature of this method is the local non-homogeneity in the distribution of electric current flow. It could cause a local concentration of energy and easily put into motion surface diffusion not only on the zirconia grains but also on the carbide ones.

Work on composites of this type is still under development [15-17]. The presented work examines the possibility of sintering ZrO_2/WC composites by means of a method using extremely high pressure, i.e. HPHT. The advantage of this method is its very short consolidation time and the potentially high efficiency of the manufacturing process. The process takes place under ultra-high pressure (7.7 GPa) in a very short time. In fact, using this technique for composites like the Si3N4-SiC system showed that it could be useful for the effective consolidation of two phase materials [18].

Materials

The test samples were made from commercial powders: 3Y-TZP (15 m^2/g, Tosoh, Japan) and WC (2.8 m^2/g, Baildonit, Poland). Using simple mechanical mixing of the component powders, two composite mixtures containing 20 and 50% carbide by volume were produced. Mixing was performed in a prototype mixer mill using a suspension in ethyl alcohol. The mixing time at 400 rpm was 30 min. ZrO_2 grinding media with a diameter of 2 mm were used. The test samples were in the shape of cylinders with a diameter of 20 mm and a height of 4 mm. Consolidation was performed by means of SPS or HPHT techniques.

The SPS processes were carried out utilising an FCT-HP D5 device (FCT System GmbH, Germany) whose heating chamber interior, the components and the die are made of graphite. The weighed portions of the mixtures were poured directly into the graphite matrix. The pressure was 63 MPa and the heating rate 100 °C/minute. The soaking time at maximum temperature (1400 or 1600 °C) was 20 minutes.

The HPHT processes were carried out in a D0044 hydraulic press (Russia) with a maximum pressure of 2500 tons. The press was equipped with a toroidal Bridgman chamber, an electric

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charge heating system and a control system. The process parameters were: 7.7 GPa pressure, 100 °C/s heating rate and 60 seconds of total sintering time.

Experimental part

The apparent density of the sinters and their water absorption were determined by hydrostatic weighing in water. The sample surfaces were subjected to XRD phase composition measurements and the microstructure was documented by means of SEM.
Their phase compositions were analysed using X-ray diffraction XRD (PANalytical, Empyrean). Quantitative XRD phase composition measurements were performed utilising the X'Pert HighScore Plus computer program, developed by PANalytical, with ICDD PDF-2 databases (2004), and the FIZ Karlsruhe ICSD (2012).
The microstructure analysis was performed by means of SEM (Thermo Scientific Apreo 2), combined with EDS.
The electron backscattered diffraction method (EBSD) was utilized to determine the tungsten carbide W_2C phase location. To eliminate fine scratches and relieve surface stresses introduced during polishing, the sample underwent additional polishing with a colloidal silica suspension for 30 minutes. This step was crucial to obtain a high-quality diffraction signal. To mitigate charging effects, the sample was analysed utilising a low vacuum mode set at 50 Pa (without any conductive layer).
Phase identification was performed by overlaying experimentally obtained Kikuchi patterns with computationally generated patterns. For enhanced accuracy in phase determination, the lattice parameters, previously measured using X-ray diffraction (XRD), were incorporated into the software's database.

Results

Both the employed sintering methods lead to a high degree of densification, both at 1400 and 1600 °C. The apparent densities of the sinters are given in Table 1. All the investigated sinters achieved a high degree of densification and did not show water absorption. However, it should be noted that for the samples sintered under high pressure, a relative density of less than 99% signifies insufficient material consolidation. The relative densities in Table 1 were calculated on the basis of the phase composition determined by the XRD measurements performed for each material. These results are collected in Table 2. Examples of XRD diffractograms that were the basis for the relative density calculations are presented in Figures 1 and 2.

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Table 1. Apparent densities, water absorption and relative densities of investigated samples

Material / WC vol. content	Process / temperature, °C	Apparent density, g/cm^3	Wettability, %	Relative density, % of theoretical
TZP/WC-20% vol.	SPS – 1400	7.92	0.0	99.0
TZP/WC-20% vol.	SPS – 1600	7.95	0.0	99.4
TZP/WC-50% vol.	SPS – 1400	10.82	0.0	99.7
TZP/WC-50% vol.	SPS – 1600	10.80	0.0	99.5
TZP/WC-20% vol.	HPHT – 1400	7.84	0.0	98.1
TZP/WC-20% vol.	HPHT – 1600	7.72	0.0	97.0
TZP/WC-50% vol.	HPHT – 1400	10.32	0.0	96.0
TZP/WC-50% vol.	HPHT – 1600	10.37	0.0	96.5

Table 2. Phase composition of starting mixtures and investigated samples after sintering

Material / WC vol. content	Process / temperature, °C	Phase composition, %				
		t-ZrO_2	m-ZrO_2	WC	W_2C	W
TZP/WC-20% vol.	Before sintering	60.8	0.0	39.2	0.0	0.0
TZP/WC-50% vol.	Before sintering	28.0	0.0	72.0	0.0	0.0
TZP/WC-20% vol.	SPS – 1400	61.9	0.0	34.5	3.3	0.3
TZP/WC-20% vol.	SPS – 1600	62.2	0.0	34.0	3.8	0.0
TZP/WC-50% vol.	SPS – 1400	29.9	0.0	66.7	3.4	0.0
TZP/WC-50% vol.	SPS – 1600	31.1	0.2	66.7	4.0	0.0
TZP/WC-20% vol.	HPHT – 1400	57.8	2.5	39.7	0.0	0.0
TZP/WC-20% vol.	HPHT – 1600	39.1	26.6	36.2	0.0	0.0
TZP/WC-50% vol.	HPHT – 1400	2.4	23.4	74.2	0.0	0.0
TZP/WC-50% vol.	HPHT – 1600	3.7	25.8	70.5	0.0	0.0

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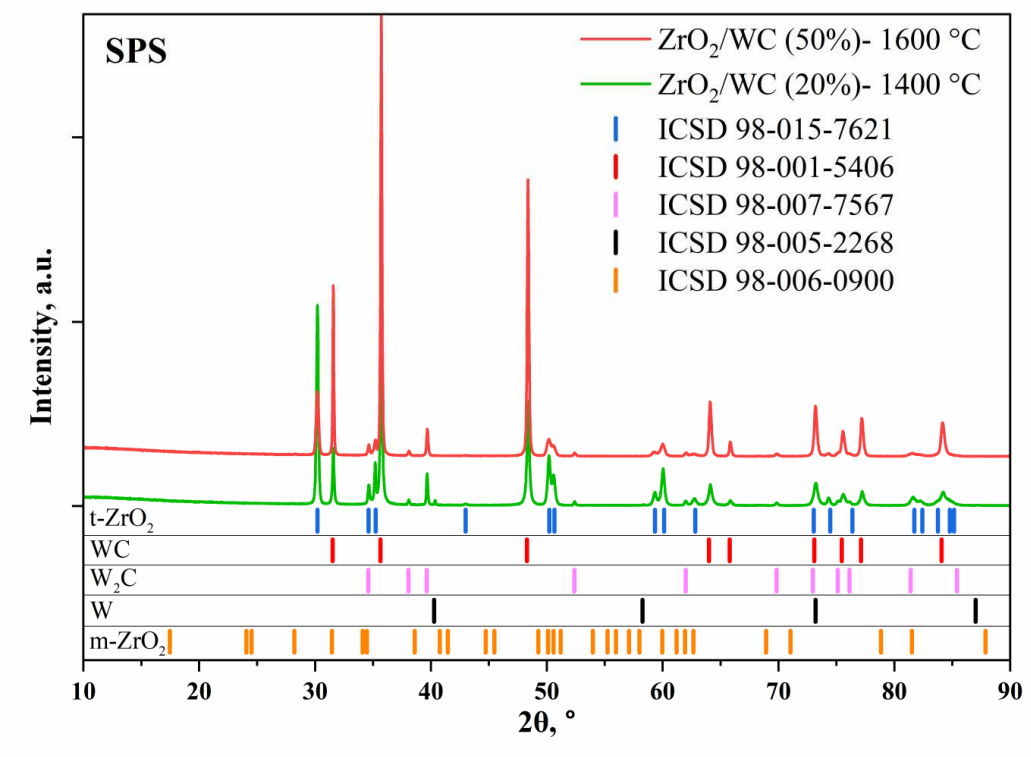

Fig. 1. XRD diffraction patterns of selected samples obtained via SPS technique.

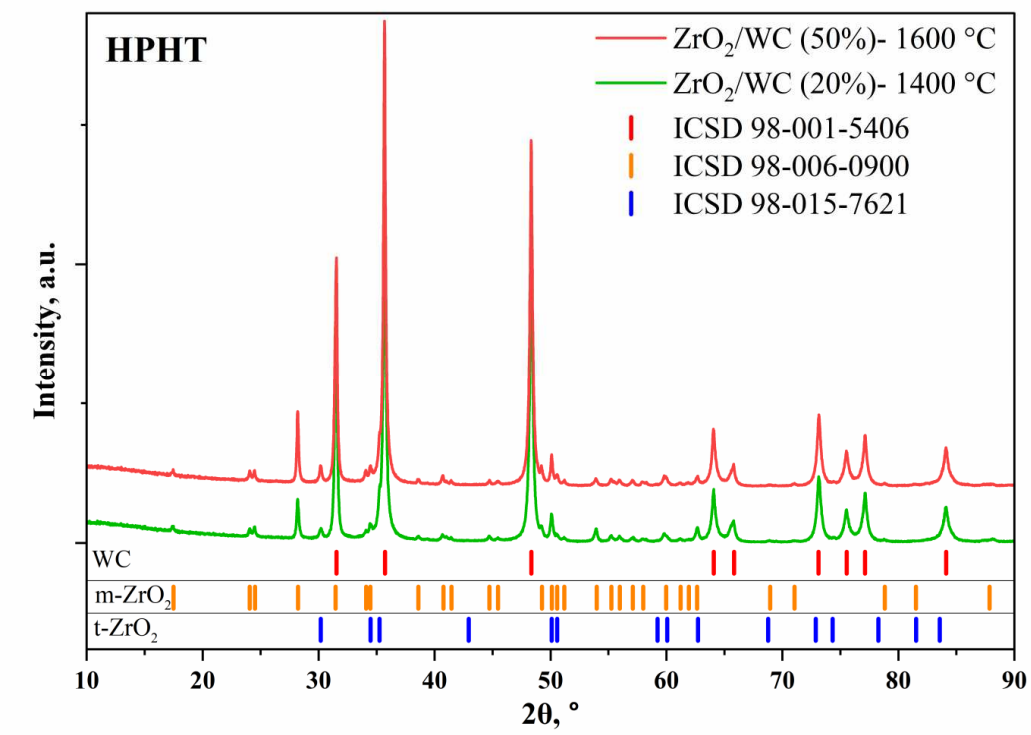

Fig. 2. XRD diffraction patterns of selected samples obtained via HPHT technique.

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The samples sintered by the SPS technique show a phase composition devoid of the monoclinic zirconia phase. A small W_2C carbide content was found in them, and in the SPS 1400 °C 20WC sample, there was a fraction of a percent of metallic tungsten. The HPHT technique produces sinters in which the monoclinic ZrO_2 phase is present, and its amount grows with the increase in the process temperature and the amount of carbide phase.

In the context of phase composition differences, the most important issue seems to be the appearance of a significant amount of zirconia monoclinic phase in the HPHT manufactured composites. This phenomenon is not favourable for the mechanical properties due to microcracks that are caused by the transformation of the tetragonal to monoclinic phase during cooling to room temperature after the consolidation process. These microcracks can clearly be seen in Fig. 3(c, d, g, h). The direct reason for the zirconia phase transformation was most probably the release of very high compressive stresses (>7 GPa) after the HPHT process. This fact, in connection with material shrinkage caused by cooling, gave the possibility of free space for expansion of the tetragonal zirconia grains during the transformation to monoclinic ones.

The small percentage of W_2C carbide which appeared in all the samples consolidated by SPS process (Tab. 2) was the result of local decarbonisation of WC under non-uniform spark plasma sintering conditions. This issue is illustrated in Fig. 4.

The SEM observations clearly show the influence of the sintering technique on the final microstructure of the sinters (Fig. 3). In all the materials consolidated by SPS, the zirconium matrix was completely sintered, and the carbide grains underwent significant modification of their shape. They became rounded and isometric (Fig. 3a, b, e, f) due to the surface diffusion action of the tungsten and carbide atoms. This type of diffusion has the lowest activation energy [19, 20]. This mechanism does not lead to shrinkage but could change the grain shape by changing the sharp edges and corners to more convex shapes. The applied SPS sintering time (20 min.) allowed for the surface diffusion effect to be visible in the microstructure. On the other hand, the carbide grains in the HPHT sinters retained their sharp-edged shape (Fig. 3c, d, g, h). In the case of tungsten carbide, the time of the process was too short to assure a distinct effect of the surface diffusion and the temperatures applied were too low to put in motion other densification mechanisms like grain boundary diffusion or volumetric.

In fact, the densification of the sinters in all the cases was due to the sintering process that took place between the zirconia grains.

In the HPHT 1400 °C 20WC sintered sample (Fig. 3c), the presence of numerous nanometric pores enclosed within the zirconium matrix is also visible. They indicate that the densification process was not completed. This material HPHT sintered at 1600 °C has a sintered matrix, but the share of the monoclinic phase is already so large that numerous microcracks appear (Fig. 3d). The HPHT materials with the carbide content of 50% show cracks not only within the zirconium matrix but also numerous cracks of carbide grains are visible (Fig. 3g, h), which

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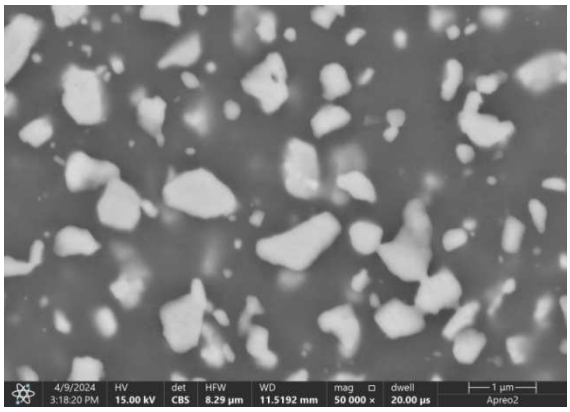
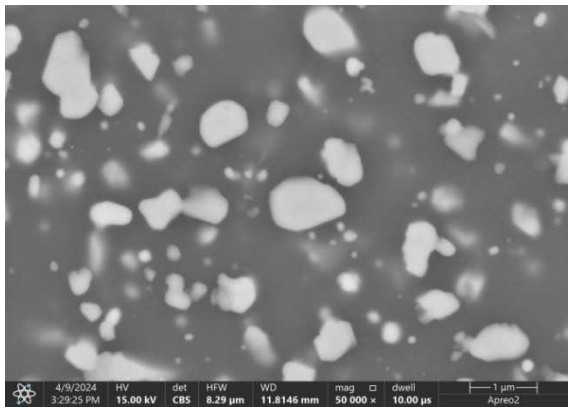
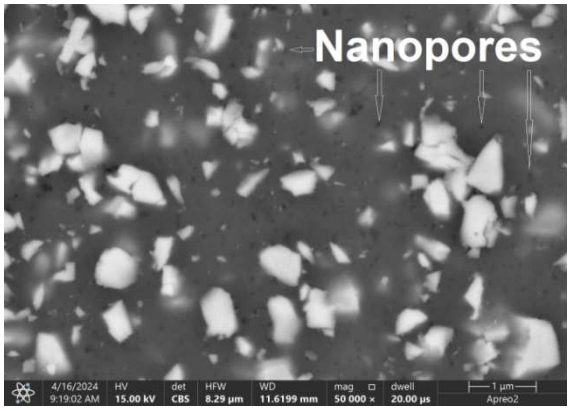
suggests that the applied pressures not only did not intensify surface diffusion, but actually caused degradation of the forming microstructure.



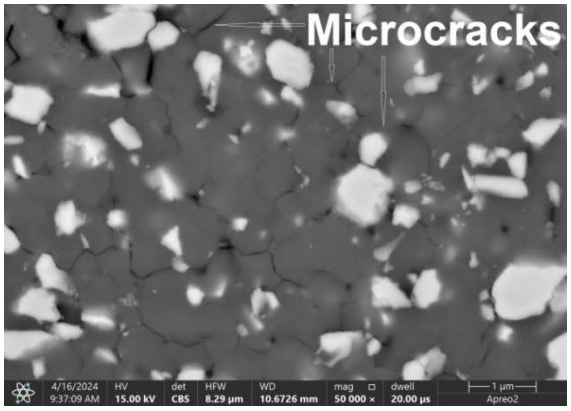
a) SPS 1400 °C 20WC



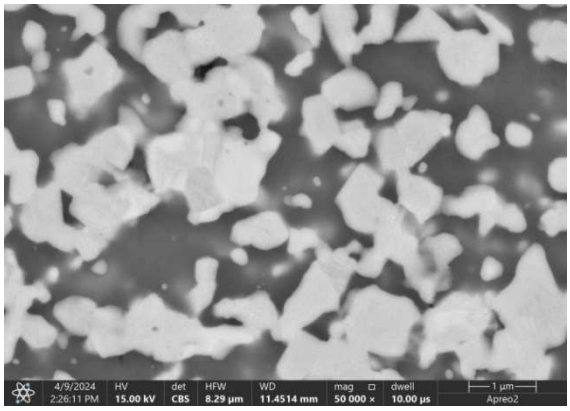
b) SPS 1600 °C 20WC



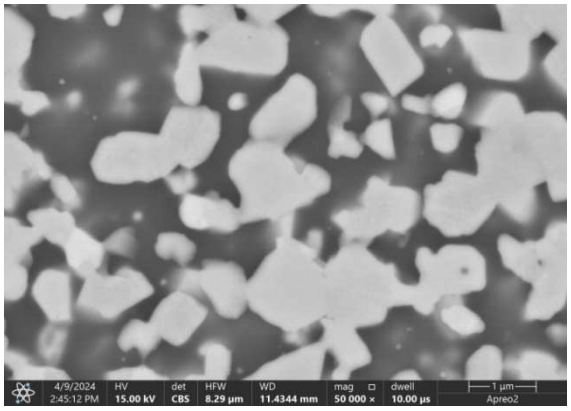
c) HPHT 1400 °C 20WC



d) HPHT 1600 °C 20WC



e) SPS 1400 °C 50WC



f) SPS 1600 °C 50WC

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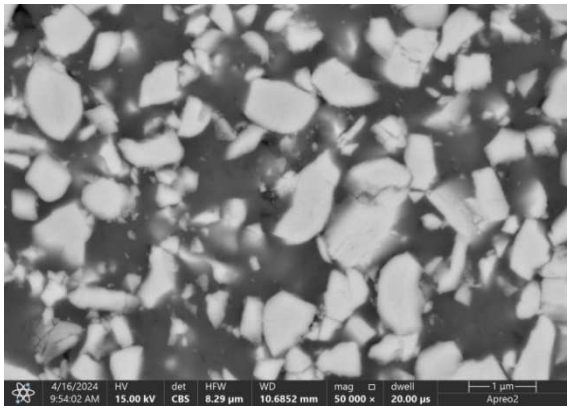
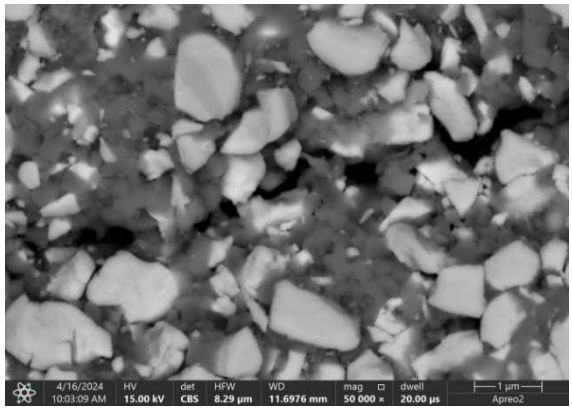


g) HPHT 1400 °C 50WC



h) HPHT 1600 °C 50WC

Fig. 3. SEM microstructures of investigated samples.

The EBSD technique is particularly advantageous for composites with significantly differing atomic masses. Unlike standard BSE imaging, EBSD operates at shallower depths, enabling accurate grain size analysis without interference from underlying phases in the material. This allows precise identification of grain boundaries with phase identification, offering more reliable microstructural insights.

The measurements performed on the SPS 1600 °C 50WC sample were intended to show the distribution of the W_2C carbide phase in relation to the original WC phase. The obtained results (Fig. 4) reveal that the carbon-poor W_2C carbide phase appears in the microstructure in a random manner, in the form of whole grains evenly dispersed throughout the sample volume. No conclusions can be drawn from these observations that would suggest the formation of W_2C carbide in an orderly manner.

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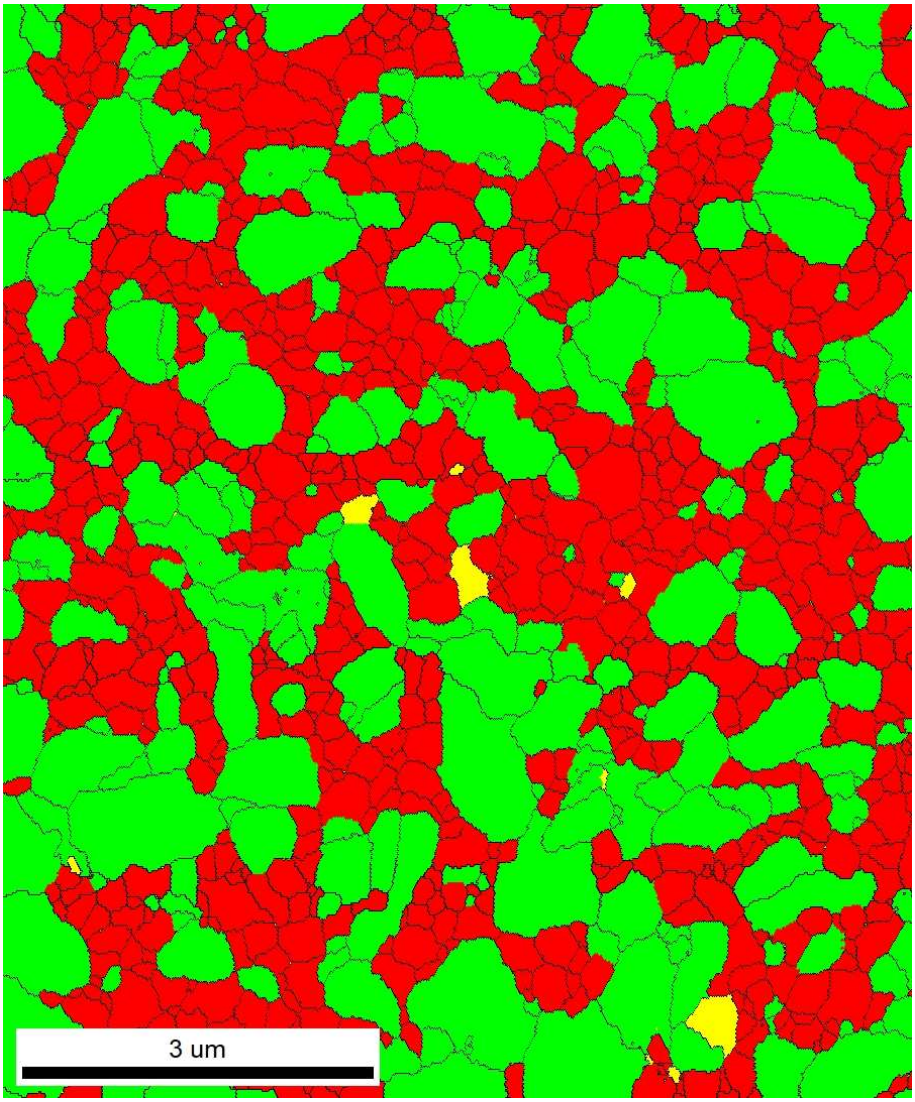

Fig. 4. EBSD microstructure reconstruction of SPS 1600 °C 50WC sample. Red grains – tetragonal zirconia phase, green grains – WC phase, yellow grains – W_2C phase.

Conclusions

The use of the SPS technique in the densification of ZrO_2/WC composites results in materials with a high degree of sintering, in which the shape of the carbide grains is modified during sintering, which should have a beneficial effect on the distribution of residual stresses. The phase composition observed in these materials shows a lack of the monoclinic phase of zirconium dioxide, which improves the mechanical properties. Small amounts of W_2C carbide grains appearing in the composites sintered using the SPS technique are distributed in a stochastic manner throughout the volume of the material.

Sintering by means of the HPHT technique does not allow modification of the shape of the carbide grains by surface diffusion, and the phase composition of the materials exhibits high shares of the monoclinic phase, which disqualifies these materials for structural applications.

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