ENHANCEMENT OF $C_{DIAMOND}$–(WC–Co)–CrB_2–ZrO_2 COMPOSITE WITH ALUMINA NANOPOWDER

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Abstract. There are many research works performed in order to improve the strength and wear resistance of the drill bits in order to prolong their service time and thus reduce the costs and environmental load. Among others, cemented carbide diamond composites are used, including those with WC-Co matrices and various additives. The superior hardness of diamond provides high wear resistance of the composite, while the cemented carbides ensure its high strength and toughness. In this paper, improvement of the cemented carbide diamond composite was reached due to addition of CrB_2 and ZrO_2 components that inhibited grain growth and promoted the dispersion-driven straightening process. The effect was further enhanced by addition of alumina nanopowder to the sintered powder mixtures. When the Al_2O_3 powder of the grain size between 20 and 100 nm is added in proportion of 0.2-1.0 wt.% to the $C_{diamond}$–(WC–Co)–CrB_2–ZrO_2 composite, several enhancing mechanisms are promoted, such as transformation toughening, dispersion toughening, and the load transfer mechanism. When the tetragonal phase *t*-ZrO_2 undergoes external stress, it transforms to the monoclinic phase *m*-ZrO_2, generating internal stresses that suppress crack propagation. In turn, dispersion toughening is promoted by the Al_2O_3 nanoscale reinforcement due to improved sinterability of the powder mixture, reducing the sintering temperature. Finally, the load transfer mechanism appears due to the presence of reinforcing particles that prevent material of the matrix from crack propagation. As a result, the compressive strength of the $C_{diamond}$–(WC–Co)–CrB_2–ZrO_2–Al_2O_3 composite increased by 34% from 3.965 GPa up to 5.320 GPa compared to the same composition without alumina nanoadditive. At the same time, the wear rate dropped down by almost 80% from 12.45 to 2.67×10^{-13} $m^3 \cdot (N \cdot m)^{-1}$.

Keywords: sintering, mining, drill bits, diamond composite, wear.

Introduction

Nowadays, many modern materials have been developed with nanoscale compositions and structures for various customized tasks. Each year, several new materials appear for specific applications with different nanometric or hybrid structures, including specifically functionalized composite materials [1]. Usage of composites is rapidly growing, including carbon fibre composites mainly consumed by the aerospace industry [2], tribological, self-lubricating and self-healing, high and low temperature resistant polymer matrix composites that are widely applied in various components of automobiles [3], high strength ceramic composites of low density and resistance to elevated temperatures widely used in the aerospace, automotive, and nuclear energy industry [4], and lightweight metal matrix composites reinforced with ceramic particulates that emerged recently and became critical materials in industry due to high stiffness, specific strength, and thermal resistance [5]. Increasing interest of scientists and engineers can be noted in the area of development and improvement of the diamond-reinforced composite materials based on WC refractory matrices with cobalt binders [6]. The WC–Co hard alloys are attractive due to the fact that they exhibit numerous desirable properties, including strength, resistance to the elevated temperatures, significant wear resistance, high hardness, and chemical stability [7]. WC-Co and ZrO_2-WC composites exhibit high wear resistance and find application in tolls designed for harsh work conditions [8]. The cermet coatings WC–12wt%Co, WC–10wt%Co–4wt%Cr, and WC–20wt%Cr_3C_2Ni were demonstrated to be of high hardness and erosion resistance, necessary to protect the magnesium alloy substrate [9].

Diamond is widely recognized as a particulate reinforcement for WC-Co-based composites due to its exceptional hardness, high modulus that promotes crack deflection and thus improves toughness, and low density [10]. In the composite, the high hardness of diamond grit contributes to high wear resistance, while the cemented carbides provide high strength and toughness of the material [11]. Rapid development of deep mining and oil industry pose the urgent requirements on the rotary drilling bit in terms of increased wear resistance, structural and functional integration, higher durability, improved lifecycle and performance [12]. Among commonly applied research strategies, optimisation of sintering methods is often named along with addition of nanomaterials to the matrices [13].

The aim of this study was to develop an enhanced cemented carbide composite with diamond reinforcement. The composition $C_{diamond}$–(WC–Co)–CrB_2–ZrO_2–Al_2O_3 was chosen, which implemented

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an integrated approach to controlling the microstructure and mechanical properties through the introduction of nanodispersed aluminum oxide. Particular attention is paid to the mechanisms of transformation hardening typical for zirconia, dispersion hardening and load transfer typical for CrB_2 additive, as well as their impact on the strength and wear resistance of the material with addition of alumina nanopowder.

Materials and methods

To modify the structure and suppress grain growth of WC, the following additives were introduced into the composition:

- chromium diboride (CrB_2), which acts mainly as a grain growth inhibitor and microstructure stabilizer.
- zirconium dioxide (ZrO_2), predominantly in the tetragonal phase, providing a transformation strengthening effect.
- nanodispersed aluminium oxide (Al_2O_3) with a particle size in the range of 20-100 nm, introduced in an amount of 0.2 to 1.0 wt%.

Sintering of the samples was performed using graphite moulds via the electroconsolidation method [14] in vacuum of 6 Pa at temperature $T_{sint} = 1400$ °C under a uniaxial pressure $P = 30$ MPa for 4 minutes. The heating rate was 500 $°C \cdot min^{-1}$. The high heating rate, relatively low sintering temperature and the short holding time prevented grain recrystallization and ensured an equilibrium state, improving the properties of the composite. After sintering, the sample surfaces were polished to achieve a mirror-like smoothness. The experimentally checked compositions of the tested materials in percentage by mass are shown in Table 1, ordered according to the alumina content. The measured modulus of each composition is provided in the last column.

Table 1

Examples of the tested material compositions

No.	$C_{diamond}$, wt%	WC, wt%	Co, wt%	CrB_2, wt%	ZrO_2, wt%	Al_2O_3, wt%	Modulus E, GPa
1	23.0	67.0	4.0	2.0	4.0	-	655
2	29.9	63.4	4.8	0.8	1.0	0.1	640
3	30.0	63.0	3.8	1.0	2.0	0.2	615
4	23.0	64.0	4.5	1.2	6.5	0.8	605
5	29.6	63.4	3.9	1.1	1.0	1.0	620

A Micro Combi Tester (MCT, Anton Paar GmbH, Ostfildern, Germany) was used to measure the Young's modulus, as specified in Table 1. The maximum indenter load was 1 N, and the loading/ unloading rate was 1 $N \cdot min^{-1}$. The hold time at maximum load was 30 s. The compressive strength of the specimens was determined using the MTS870 Landmark (MTS) dual-column servohydraulic test system. The elements with a cross-sectional area of 2×2 mm were fabricated for this purpose.

Among the most important indicators of the efficiency of the engineering systems is the wear resistance of components, dependent on the applied wear-resistant material and working environment [15]. The wear resistance of the composites was tested with a typical machine tool, turning the granite cylinder with the cutter fabricated according to the abovementioned methodology, fixed in a holder, as shown in Fig. 1. The turning area of the lathe is shown in Fig. 2. The granite cylinders were delivered by Korostyshev Granite Plant, Ukraine. The rotational speed was 400 rpm, cutting depth 0.5 mm, and feed of 0.5 mm per rotation. The diameter of the cylinder before the turning test was 70 mm, and the single path was performed on the length of 200 mm. The system was cooled with technical water.

The specific wear rate W_s was assessed using the following formulas [16]:

$$W_S = \frac{\Delta V}{L \cdot P}, \tag{1}$$

$$L = \pi D n t, \tag{2}$$

where ΔV – volumetric loss of the material during the test time, m^3;
L – friction path, m;
P – normal loading force, N;
D – diameter, m;
n – rotational speed, rpm;
t – test time, min.

Fig. 1. **Tested specimen in the holder**

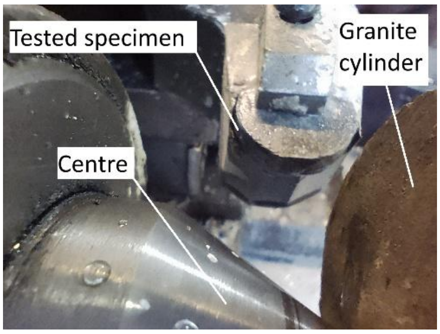

Fig. 2. **Specimen during the wear test**

Results and discussion

The values of the modulus E, measured for the tested compositions and shown in Table 1, differed in the range of less than 10%. However, other parameters, important form the applicational perspective, exhibited more significant differences. In particular, the compressive strength R_c is a crucial characteristic for the cutting edges. In turn, the load transfer mechanism contributes to the increased strength of the material. Rigid and thermally stable Al_2O_3 and ZrO_2 particles absorb part of the external load, reducing stress concentration in the metal bonds between carbide grains. This leads to a more uniform stress distribution throughout the material and slows the initiation and development of cracks. This effect can be seen in the diagram in Fig. 3 presenting the compressive strength of the specimens numbered according to Table 1.

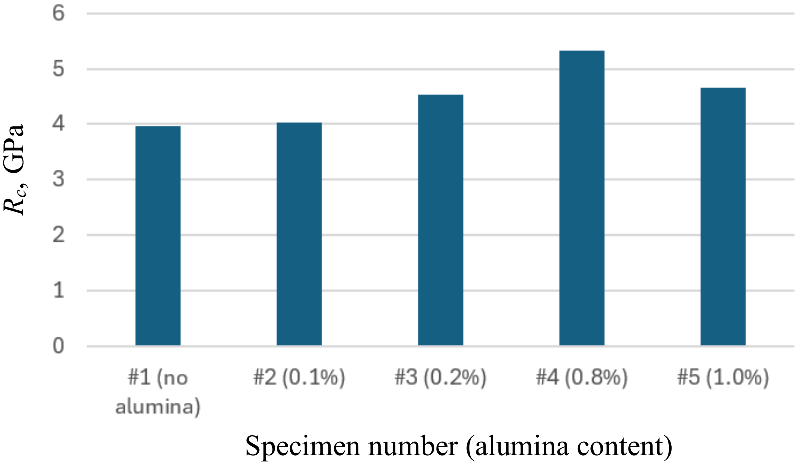

Fig. 3. **Dependence of the compressive strength R_c on the alumina content**

Among the compositions specified in Table 1, #4 with 0.8 wt% of alumina exhibited the highest compressive strength R_c = 5.320 GPa. It appeared to be by ca. 34% higher than that of the reference composite #1 with no alumina added. Notably, further increase of Al_2O_3 content was not favourable, since the compressive strength dropped back to the level represented by the material #3 with only 0.2 wt% of alumina.

Since the hardness of alumina is higher than that of tungsten carbide, its addition increased the overall hardness of the composite. More importantly, boundaries between the phases were enhanced, including the areas between diamond and matrix, significantly increasing the mechanical properties and wear resistance. The use of nanodispersed Al_2O_3 is a fundamental element of the proposed approach, since the nanodimensional particles can effectively interact with the matrix, improve sinterability of the powder mixture, and provide additional strengthening mechanisms. As a result, wear resistance of the composites with alumina nanoparticles significantly increased. It can be seen from the diagram in Fig. 4, where the results for the wear rate W_s are presented.

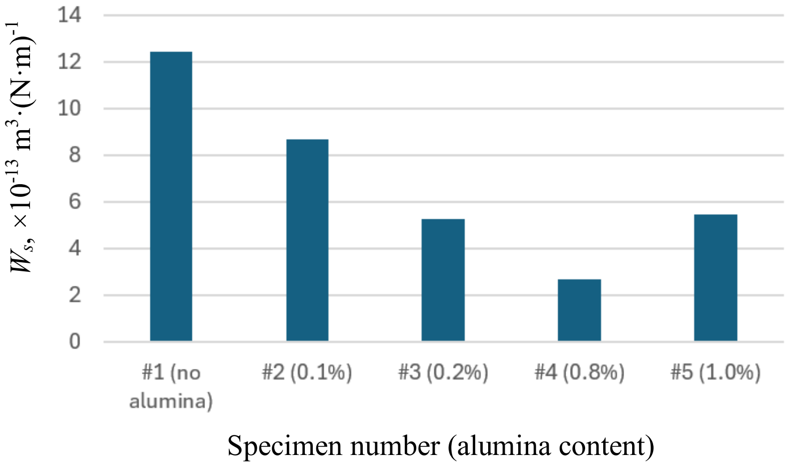

Fig. 4. **Dependence of the specific wear rate W_s on the alumina content**

Again, a similar trend can be seen as in the case of the compressive strength R_c. Namely, the wear resistance improved with the increase of alumina content, which corresponded with the reduction of the wear rate W_s. The wear rate for material #4 was the smallest, exhibiting reduction by ca. 79% from $W_{s1} = 12.45$ to $W_{s4} = 2.67 \times 10^{-13}$ $m^3 \cdot (N \cdot m)^{-1}$. Further increase of alumina content worsened the wear resistance of the composite, so the corresponding wear rate increased up to the level close to that of material #3 with only 0.2 wt% of alumina. In combination with the compressive strength data from Fig. 3, the composition #4 can be considered the optimal one from the perspective of application typical for the drill bits. As such, the composition was patented [17].

One of the key mechanisms responsible for improved wear resistance in the tested composite is transformation strengthening associated with the presence of the tetragonal zirconia phase (t-ZrO_2). Under external mechanical load, the phase transformation of $t\text{-}ZrO_2 \rightarrow m\text{-}ZrO_2$ takes place particularly in the crack tip region, accompanied by volumetric expansion of the monoclinic zirconia. As a result, the localized compressive stresses emerge in the crack vicinity, effectively suppressing its further propagation.

Another strengthening mechanism and favourable microstructure modification can be attributed to the presence of CrB_2. In particular, it promoted reduction of the grain sizes of the WC phase, contributed to disappearance of pores, and improved the interphase boundaries, supporting appearance of inhibitor phase clusters. Synergy of the strengthening mechanisms of zirconia and chromium diboride with alumina nanopowder effects provided the overall improvement of the mechanical properties of the composite.

Conclusions

1. Nanodispersed alumina significantly enhanced the $C_{diamond}$–(WC–Co)–CrB_2–ZrO_2 composite.
2. Synergy of toughening and strengthening effects of the three additives was reached.
3. The composition with 0.8 wt% alumina exhibited the highest compressive strength 5.320 GPa and the lowest specific wear rate 2.67×10^{-13} $m^3 \cdot (N \cdot m)^{-1}$, very important for the drill bit material.

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Author contributions

Conceptualization, B.R.; methodology, E.H. and M.R.; software, B.R.; validation, M.R; formal analysis, B.R.; investigation, V.M. and E.H.; data curation, E.H.; writing – original draft preparation, M.R.; writing – review and editing, B.R., V.M., and E.H.; visualization, V.M. and E.H.; project administration, B.R.; funding acquisition, V.M. All authors have read and agreed to the published version of the manuscript.

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