ANALYSIS OF WC-Co AND ZrO_2-WC MATRICES FROM PERSPECTIVE OF WEAR RESISTANCE OF DIAMOND-REINFORCED COMPOSITES

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Abstract. Both zirconia and tungsten carbide are known for hardness, fracture toughness, and wear resistance. However, when joined together by means of powder metallurgy, the mutual influence of both substances may lead to enhancement of the refractory matrix, which can be used for a special composite additionally reinforced with diamond. The research involved an elecrtoconsolidation apparatus for sintering at relatively low temperatures and nanopowders to keep submicron structural features of the sintered composites. In this work, the results for WC addition up to 50 wt.% to zirconia are presented demonstrating increase of fracture toughness by 63% compared to pure zirconia and by 2% compared to pure binderless WC. On the other hand, addition of few per cent of zirconia to WC-Co system increased the fracture toughness by 9%, which was by 63% higher than for pure zirconia. In the case of hardness, it decreased by 9% when 10 wt.% of WC were added to zirconia, which was by 49% smaller than that of pure binderless WC. In turn, addition of ZrO_2 to the WC-Co matrix reduced its hardness by 6% only, keeping it at the level of pure zirconia hardness. After preliminary tests, a matrix was selected to produce a composite reinforced with diamond grits, and wear tests for this material were carried out. The results of specific wear rate were of the order of 10^{-13} $m^3 \cdot (N \cdot m)^{-1}$ corresponding with the range of anti-wear materials. High wear resistance may be attributed to the known phenomenon of the stress-induced phase transformation of zirconia, but also to zirconia-promoted better densification of the WC-Co powder system during the sintering process.

Keywords: mining, drilling, refractory matrix composite, particulate reinforcement, powder metallurgy.

Introduction

Tungsten carbide-based nanocomposites are widely used in hard rock cutting [1], mining [2; 3], or production of agricultural machinery [4], due to their high strength, potential of wear reduction, and ability to optimize the working conditions of the machinery. Tungsten carbide WC is known for its superior characteristics, including high hardness reaching 22 GPa and a high melting point of 2750 °C [5]. When cutting very hard rock with strength above 100 MPa, high temperatures of 1000 °C and more occur in the drilling area, which decrease wear resistance of the WC tipped picks reducing the efficiency of the rock cutting [6].

Among the WC-based composites, WC-Co compounds with variable metal/ceramic ratio are well-established and widely applied materials in engineering and tooling applications [7]. The advantageous combination of toughness, strength, and wear resistance in WC-Co composites is attributed to the properties of their two interpenetrating phases of a hard, brittle carbide phase and a soft, ductile metal binder [8]. Composites of this group allow for tailoring the properties according to the critical requirements, primarily hardness and toughness when wear-resistant demanding or rupture-limited applications are considered [9]. Some additives may further improve the desired properties. For instance, introduction of 2 wt.% of CrB_2 additive to the 25%$C_{diamond}$-70.5%WC-4.5%Co composite caused reduction of the wear rate by 50% [10]. Li with co-authors reported application of solid solutions $(Cr_{0.9}, V_{0.1})_2(C, N)$ and $(V_{0.9}, Cr_{0.1})_2(C, N)$ as grain growth inhibitors to produce WC-10Co cemented carbides with narrower grain size distributions [11]. Megret with the team used boron-doped cobalt additions to improve the characteristics of a recycled WC-Co composite [12]. However, cobalt is not able to withstand elevated temperatures, limiting the range of applications of WC-Co composites.

The binderless tungsten carbide ceramics exhibit a very high modulus above 700 GPa, higher than other transition metal carbides, and exhibit excellent resistance to elastic deformation [13]. Due to poor sinterability, Grasso et al. developed a new spark plasma sintering (SPS) method to obtain fully consolidate binderless tungsten carbide with diamond powders [14]. In order to improve the fracture toughness, WC-MgO-ZrO_2 composites were developed and reported [15]. Addition of zirconia was proposed also in the report [16], while zirconia itself is an excellent material for fabrication of ceramics. The performance of ZrO_2 ceramics is dependent on the quality of the initial powder and its phase composition. Zirconia can have three forms: monoclinic-phase ZrO_2 (m-ZrO_2), tetragonal-phase (t-ZrO_2), and cubic-phase (c-ZrO_2), and crystal transformation between m-ZrO_2 and t-ZrO_2 is vital for the stability of zirconia ceramic powders [17]. Exceptional fracture toughness of zirconia ceramics is closely related to the stress-induced phase transformability and the stability of the tetragonal phase, which mostly is obtained with addition of 3 mol% Y_2O_3 stabilizer.

In the present study, different WC-ZrO_2 systems with increasing WC content, starting from pure yttria-stabilized zirconia, were compared in terms of hardness and fracture toughness. On the other hand, the effect of zirconia additions to the WC-Co composite was considered.

Materials and methods

In the research, an electroconsolidation apparatus was used for sintering of the composites out of powders [18]. The "pure" matrices were sintered using tungsten carbide WC with no additives, the microstructure is shown in Fig. 1. WC-Co compounds are able to build an extensive number of microstructural assemblages and to manufacture various combinations of interdispersed ceramic and metal phases [19]. For the current research, mixture of tungsten carbide with 6 wt.% of cobalt binder was used. Its sintered microstructure is shown in Fig. 2. And the third group of specimens were produced using ZrO_2 powder stabilized with 3 wt.% of Y_2O_3. The microstructure of sintered yttria-stabilized zirconia specimen with no other additions is shown in Fig. 3.

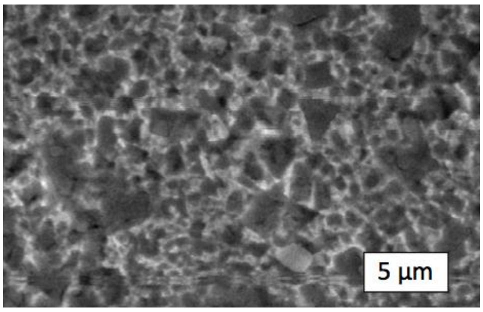

Fig. 1. **Microstructure of sintered WC-6wt.%Co**

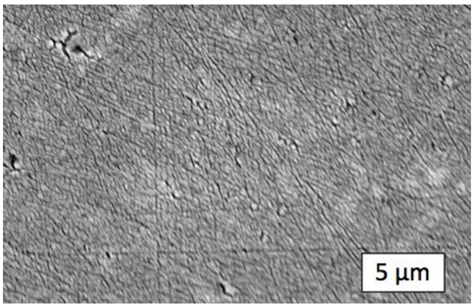

Fig. 2. **Microstructure of sintered binderless WC**

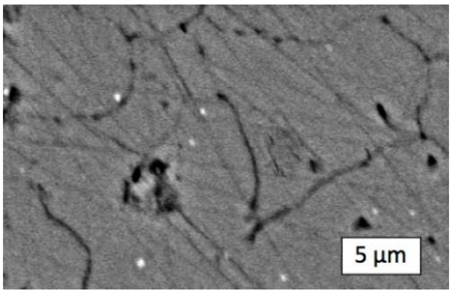

Fig. 3. **Microstructure of sintered ZrO_2-3wt.%Y_2O_3**

To visualize the mutual influence of the abovementioned component, the mixtures were prepared as follows. One the one hand, zirconia powder was mixed with tungsten carbine added in proportions of 10 wt.%, 20 wt.%, 30 wt.%, and 50 wt.%. On the other hand, zirconia was used as additive to the WC-Co system in proportions of 2 wt.%, 4 wt.%, and 10 wt.%. The amounts of powders were measured using the Radwag weight model AS82/220.R2 (Radwag, Radom, Poland) with a precision declared in the technical specification of 0.01 mg. The obtained materials were compared in terms of hardness and fracture toughness.

Finally, the diamond-reinforced composite was sintered using 4 wt.% of zirconia added to the WC-Co system, and then 25 wt.% of diamond powder was added with an average diameter ca. 0.45 mm. This matrix was chosen for the wear tests due to the highest fracture toughness from the tested group with small loss of hardness, compared to other specimens. It exhibited relatively high modulus

E = 550 GPa and hardness H = 27.2 GPa, so that its resistance to abrasive wear could be calculated as $1/(E^2H)$ = 1.3 GPa^{-3}. The index of tolerance to damage $1/(E^2H)$ is used for assessment of the resistance of materials to abrasive wear [20]. The surface of the specimen before the wear test is shown in Fig. 3. The worn surface of the diamond-reinforced composite is shown in Fig. 4.

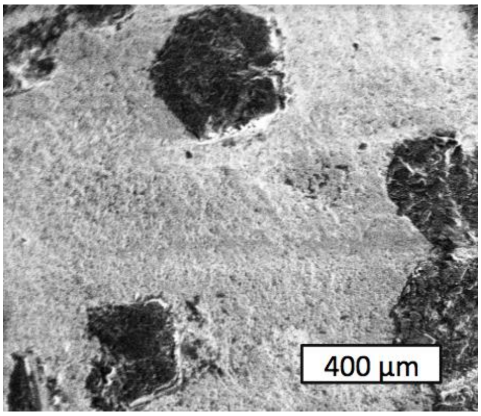

Fig. 4. **Composite before wear test**

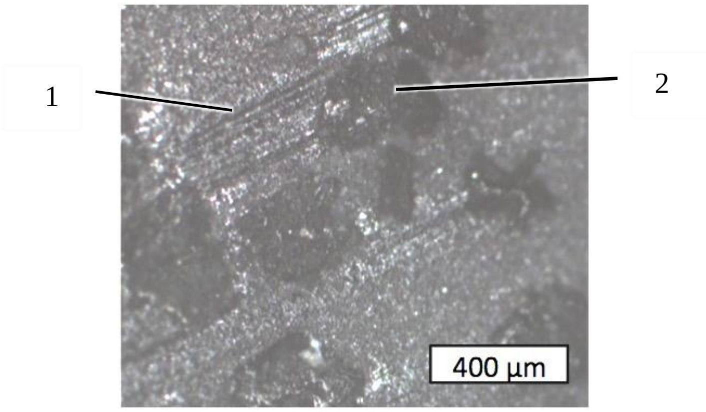

Fig. 5. **Composite after wear test:** 1 – abrasive wear traces; 2 – diamond reinforcement

The methodology of calculation of the fracture toughness K_{IC} and hardness HV has been described in detail in [21]. Each value was based on 5 measurements, providing the average result with dispersion between 3% and 5%.

Results and discussion

Figures 6 and 7 present dependences of the fracture toughness K_{IC} and hardness HV, respectively, on the composition of the matrices. Notably, the lowest value of toughness K_{IC} corresponded with the sintered yttria-stabilized zirconia, which did not exhibit the highest hardness, though. The highest hardness among the tested materials HV = 26.4 GPa was in the case of binderless WC. General observations can be made, as follows.

- The row of WC-Co matrices exhibited higher fracture toughness than that of ZrO_2-WC systems.
- Addition of ZrO_2 increased the fracture toughness of WC-Co matrices.
- Even though binderless WC exhibited higher hardness than that of zirconia, addition of WC to ZrO_2 matrix decreased its hardness. The hardness increased above that of zirconia only when the content of WC became 50% and higher.

In particular, the diagram in Fig. 6 demonstrates that WC addition up to 50 wt.% to zirconia increased the fracture toughness by 63% compared to pure yttria-stabilized zirconia and by 2% compared to pure binderless WC. On the other hand, addition of few per cent of zirconia to the WC-Co system increased the fracture toughness K_{IC} by 9%, which was by 63% higher than for pure zirconia. In the case of hardness values shown in Fig. 7, HV decreased by 9% when 10 wt.% of WC were added to zirconia, which was by 49% smaller than that of pure binderless WC. In turn, addition of few per cent of ZrO_2 to the WC-Co matrix reduced its hardness by 6% only, keeping it at the level of pure zirconia hardness HV = 14.5 GPa.

In the above context, the WC-Co matrix with 4 wt.% of ZrO_2 appeared to be the most optimal one, and it was chosen then for the diamond-reinforced particulate composite to perform the wear tests. In Fig. 5 above, clear traces of abrasive wear are seen indicating domination of the abrasive wear mechanism [22]. At the same time, strong diamond-holding forces prevented the reinforcement from falling out. The specific wear rate was determined as $W_s = 4.27 \times 10^{-7}$ mm^3·(N·m)$^{-1}$, which corresponded with the range of anti-wear materials [23]. It appeared better than that of WC-Co-GO (graphene oxide) cemented carbides with the best reported result $W_s = 2.31 \times 10^{-7}$ mm^3·(N·m)$^{-1}$ [24].

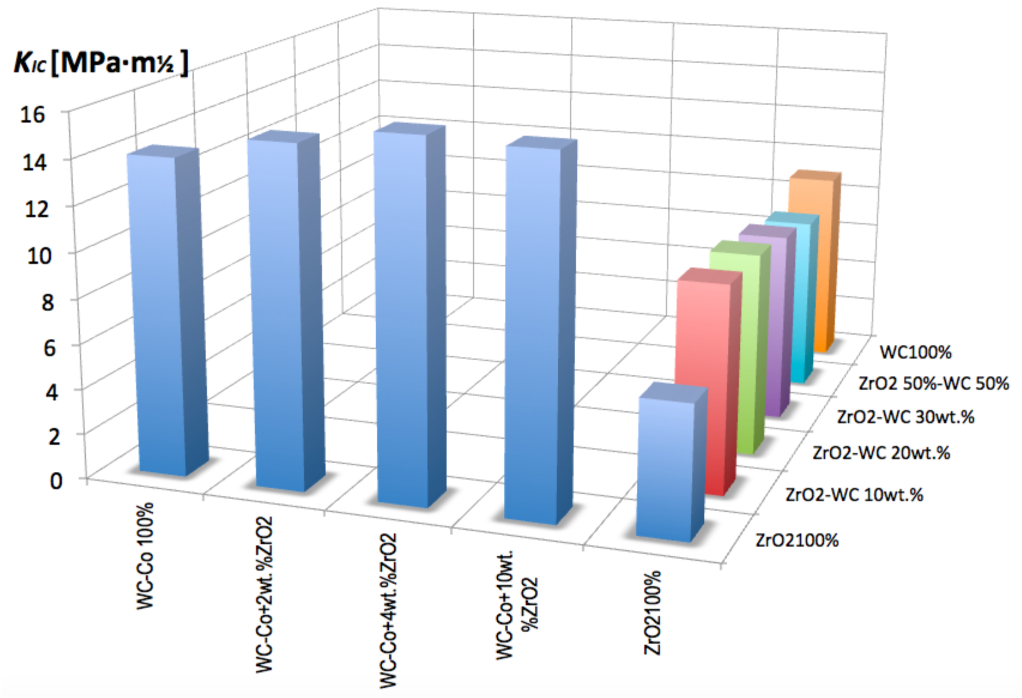

Fig. 6. **Diagram of the fracture toughness K_{IC} dependent on the proportion of the components**

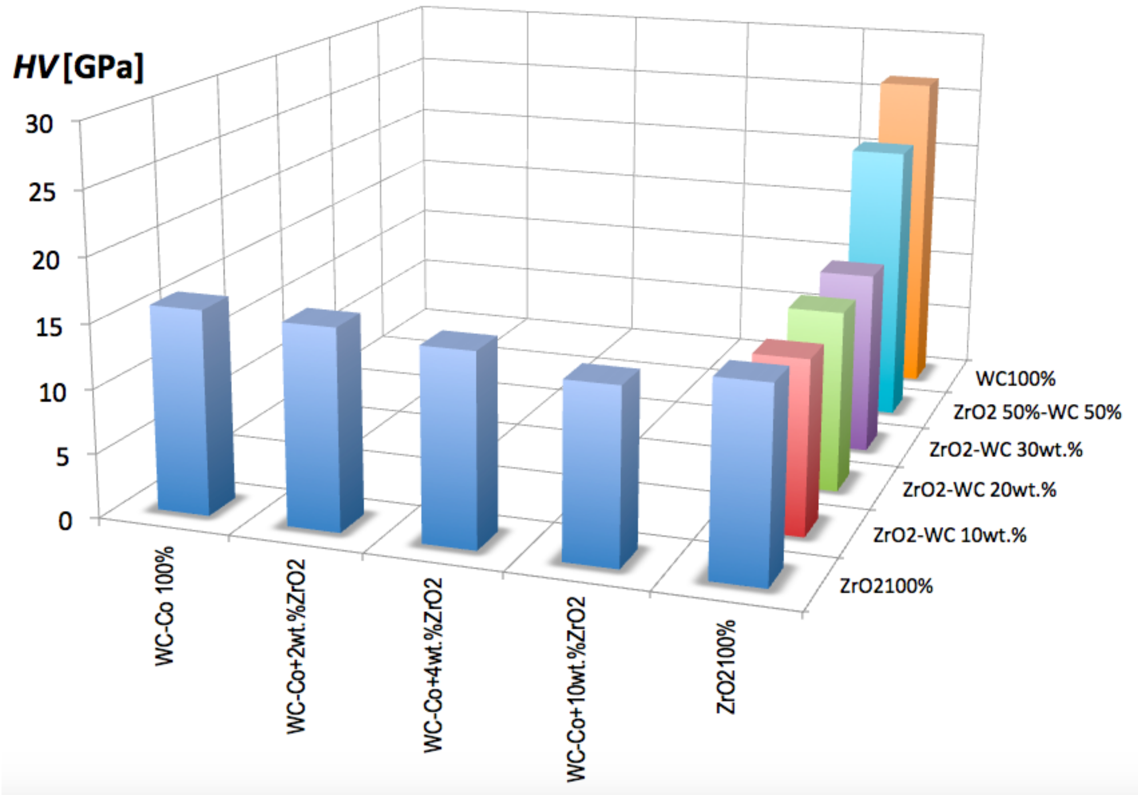

Fig. 7. **Diagram of the hardness *HV* dependent on the proportion of the components**

High wear resistance of the WC-Co matrix with 4 wt.% of ZrO_2 may be attributed to the known phenomenon of the stress-induced phase transformation of zirconia [25], but also to the zirconia-promoted better densification of the WC-Co powder system during the sintering process.

Conclusions

1. WC-Co matrices with zirconia additives exhibited better properties than ZrO_2-WC systems.
2. Binderless WC exhibited the highest hardness, keeping moderate fracture toughness.

3. Diamond-reinforced composite with the WC-Co matrix exhibited abrasive mechanism of wear with good retention of diamond grits.
4. The coefficient of abrasive wear resistance $1/(E^2H) = 1.3$ GPa^{-3} corresponded with the specific wear rate $W_s = 4.27 \times 10^{-7}$ mm^3·(N·m)$^{-1}$, placing the material among anti-wear materials, applicable in mining, rock drilling and other demanding work conditions.

Acknowledgements

This research was funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP23484450).

Author contributions

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

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