STUDY ON PROPERTIES OF ZIRCONIA REINFORCED REFRACTORY MATRIX COMPOSITES

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Abstract. The research was performed in the context of examinations of refractory matrix composite feasibility for such applications as plow blades or mining drill bits. In the experiments, the WC matrix was used with Co binder, and zirconia played the role of the particulate filler. ZrO_2 is known and appreciated for its wear resistance, high fracture toughness, and high hardness. It forms the tetragonal metastable phase *t*-ZrO_2 and the termodynamically stable monoclinic phase *m*-ZrO_2. The WC–Co–ZrO_2 composite samples were made of the powders using an innovative, energy-saving, field activated vacuum hot-pressing unit. The alternating current passing through the graphite mold and the sample was the sole heat source, providing high heating rates up to 300 °C/min and a relatively short sintering time of several minutes. As a result, nanoscale features were preserved in the composite structure ensuring high hardness and wear resistance. In particular, during microindentation, the work of elastic deformation was W_e = 0.162 μJ, while the work of plastic deformation was W_p = 0.484 μJ, which showed that the elastic part of indentation work was η_{IT} = 26.58%. This can be explained by transformation toughening phenomena, which take place when tetragonal zirconia *t*-ZrO_2 transforms to the monoclinic phase *m*-ZrO_2, which is accompanied by the changes of the specific volume. This, in turn, generates compressive mechanical stresses suppressing crack propagation, improving elasticity of the composite. At the next stage of the investigations, it is planned to perform tribological tests.

Keywords: sintering, refractory matrix composite, particulate reinforcement, powder metallurgy.

Introduction

This report is a continuation of the research program on the composites based on refractory WC–Co matrix [1], which can be used both in agriculture and in mining industry. Since the systems used in these processes must be highly reliable and safe [2], all types of degradations that may affect the lifetime and reliability of the systems, where those composites are used, should be thoroughly investigated [3].

In order to strengthen composites, usually nanosize structural features are kept making a nanocomposite [4], or hard coatings, including nanoscale thin coatings, can be applied [5-7]. Spark plasma sintering (SPS) techniques allow obtaining nanocomposites due to the controlled grain growth [8]. Lower sintering temperatures and holding times shorter than that in conventional processes make this technique greener, which is extremely important considering the environmental issues emphasized by the European Commission and other institutions [9], as well as the increasing ecological attitude in society [10]. Thus, this study is a continuation of the research on fabrication of a stronger, wear resistant tool material feasible for plow blades or drill bit inserts, with greener, resource saving technology that allows for retaining submicron structures.

It is widely recognized that WC-6%Co cemented carbide tools fabricated using powder metallurgy methods exhibited improved performances [11]. In the previous study [12], it was found that sintering of WC-Co powders without additives caused formation of large cobalt matrix areas that weaken the composite, or areas with weak direct boundaries between WC grains. After addition of zirconia to the WC-Co compounds, formation of thin cobalt interlayers took place, which was found even between very small tungsten carbide grains. This structural feature was found to alter the properties of the composite with increasing ZrO_2 content from 0 to 10 wt.% as follows [13]: modulus E gradually decreased by almost 40% from 650 GPa down to 400 GPa, microhardness HV decreased by ca. 25% from 29 GPa down to 22 GPa, but plasticity index H/E increased by 30% from 0.43 up to 0.56, resistance to plastic deformations H^3/E^2 increased by 33% from 0.056 GPa up to 0.075 GPa, while resistance of the material to abrasive wear $1/E^2H$ increased more than 2.5 times from 0.75×10^{-7} GPa^{-3} up to 2.75×10^{-7} GPa^{-3}. The latter index was found the most promising, since the abrasive wear is among the main factors in the applications like plow blades and mining drill bit inserts.

The objective of the present study was to evaluate elastic and plastic deformation work of the WC-Co ceramic sintered with addition of zirconia. The novelty of the work is twofold. First of all, zirconia is known for its brittleness [14] and thus is not considered as strengthening additive to the WC-Co composites [15]. And the second novel aspect is the original sintering technique, which proved successful in the previous stage of the research [12].

Materials and methods

In the experiments, the WC matrix was used with cobalt binder (6 wt.%), and zirconia powder shown in Fig. 1 played the role of the particulate filler. Zirconia powder (delivered by NANOE, France) was added in amount of 4 wt.%, based on the previous research results [12]. The mixture was carefully prepared, since the mixing parameters may affect the mechanical characteristics of the nanocomposites [16]. Submicron particulate inclusions are distinguishable in the sintered specimen presented in Fig. 2.

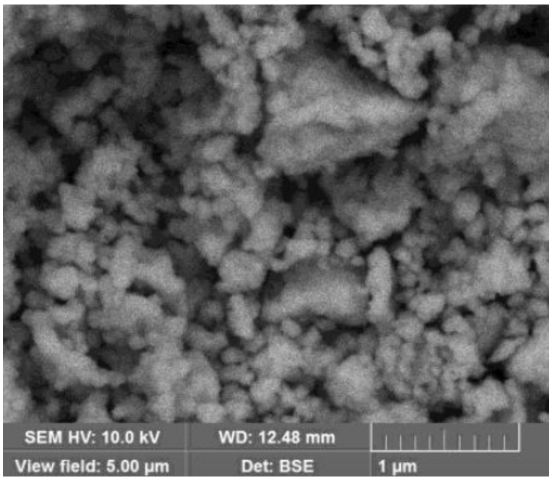

Fig. 1. **Submicron zirconia ZrO_2 powder**

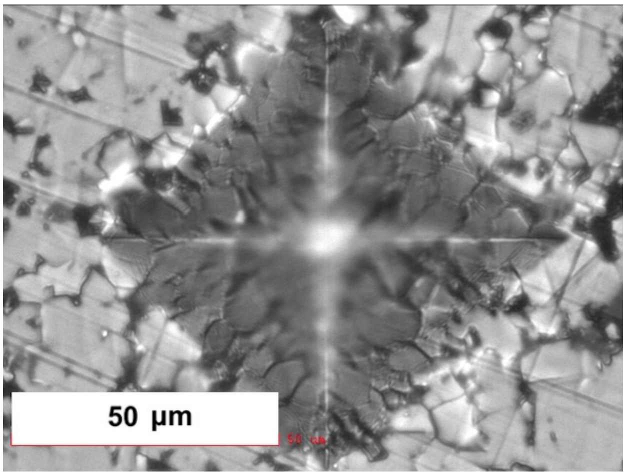

Fig. 2. **Submicron inclusions seen in sintered specimen**

The WC-Co-ZrO_2 composite samples were made of the powders using an innovative, energy-saving, field activated vacuum hot-pressing unit shown in Fig. 3.

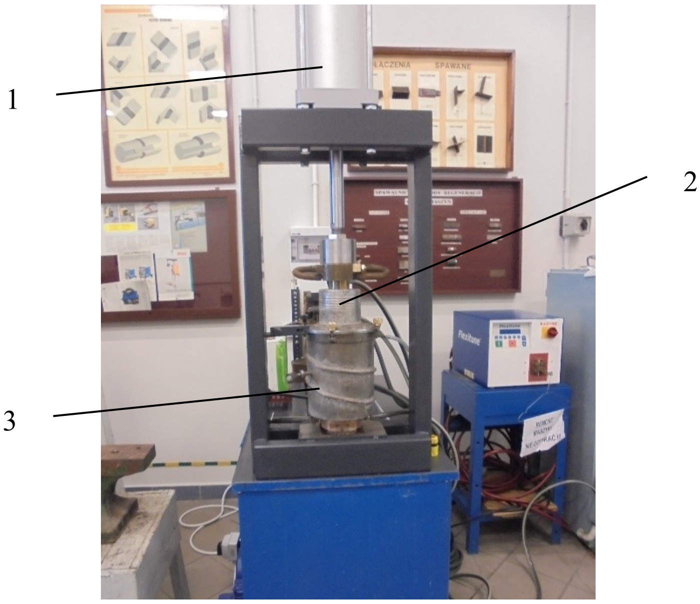

Fig. 3. **Modified SPS device used in experimental research:** 1 – pneumatic press; 2 – mould; 3 – vacuum chamber

The applied powder metallurgy method can be classified as a Spark Plasma Sintering (SPS) or Field Activated Sintering technique (FAST). The SPS group of techniques makes it possible to fabricate binderless WC structures [17] and provide ceramic-metal fusion through the specific necking and strengthening mechanisms [18]. Moreover, SPS ensures a high heating rate and relatively low sintering temperature, which combined with extremely short sintering time make is very suitable for mass production [19]. In the modified version used in this study, direct electrical current passed through the powder and mould, therefore we rather use “elecrtoconsolidation” term to distinguish it from typical SPS [20]. The sintering parameters were as follows: maximal temperature 1300 °C, mechanical pressure 45 MPa, holding time 5 min.

Characterization of the obtained samples was performed using a Micro Combi Tester produced by Anton Paar, UK. The diamond Vickers-type indenter was applied, the temperature in laboratory was kept 22.5 ± 1 °C. The load of 1.00 N was used, both loading and unloading was linear at the rate 1.00 N/min. Ten indentations were made, providing maximal and minimal values, and standard deviation of the results.

Results and discussion

As a result of the applied electroconsolidation process, the nanoscale features seen in Fig. 2 were preserved in the composite structure ensuring high hardness and wear resistance. Moreover, cracks after indentation are not linear, as it is seen in Fig. 2, which is important from the perspective of the crack growth resistance. Deviation and branching of cracks seen all around indentation contributed to higher energy dissipation during crack propagation [21]. For the investigated samples, the fracture toughness was $K_{Ic} = 15.8 \pm 0.86$ MPa·m$^{0.5}$, indicating increase by 14% after addition of zirconia in the amount of 4 wt.%. In the case of pure WC-Co composition with no zirconia, the fracture toughness was $K_{Ic} = 13.8 \pm 0.75$ MPa·m$^{0.5}$. It should be noted that increase of ZrO_2 proportion up to 10 wt.% resulted with a slightly lower fracture toughness of $K_{Ic} = 15.5 \pm 0.63$ MPa·m$^{0.5}$. Since the difference is smaller than the dispersion of the results, it can be considered negligible, and the mechanism of fracture resistance can be considered essentially the same for the composites with 4 wt.% and with 10 wt.% od zirconia.

Figure 3 presents the example of the indentation curve, while Figure 4 presents the registered penetration depth during microindentation. The results of the measurement with statistical data of standard deviation, and minimal and maximal values from 10 repetitions are collected in Table 1.

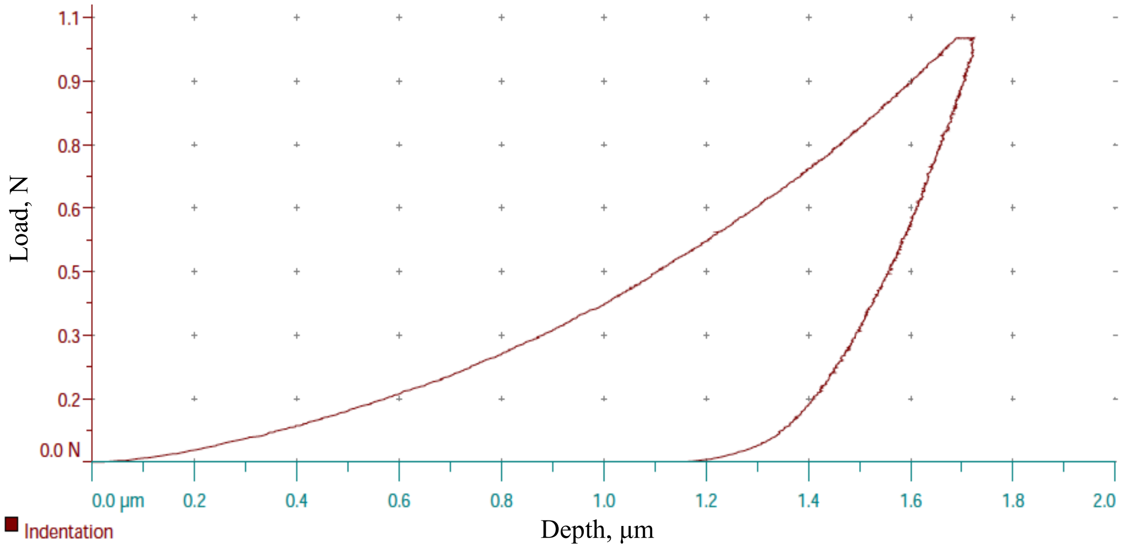

Fig. 3. **Example of the indentation curve of the tested specimen**

In particular, during microindentation, the work of elastic deformation was $W_e = 0.162 \pm 0.011$ µJ, while the work of plastic deformation was $W_p = 0.484 \pm 0.029$ µJ, which showed that the elastic part of indentation work was $\eta_{IT} = 26.58\%$. This can be explained by transformation toughening phenomena, which take place when tetragonal zirconia *t*-ZrO2 transforms to the monoclinic phase *m*-ZrO_2, which is accompanied by the changes of the specific volume. This, in turn, generates compressive mechanical stresses suppressing crack propagation, improving elasticity of the composite.

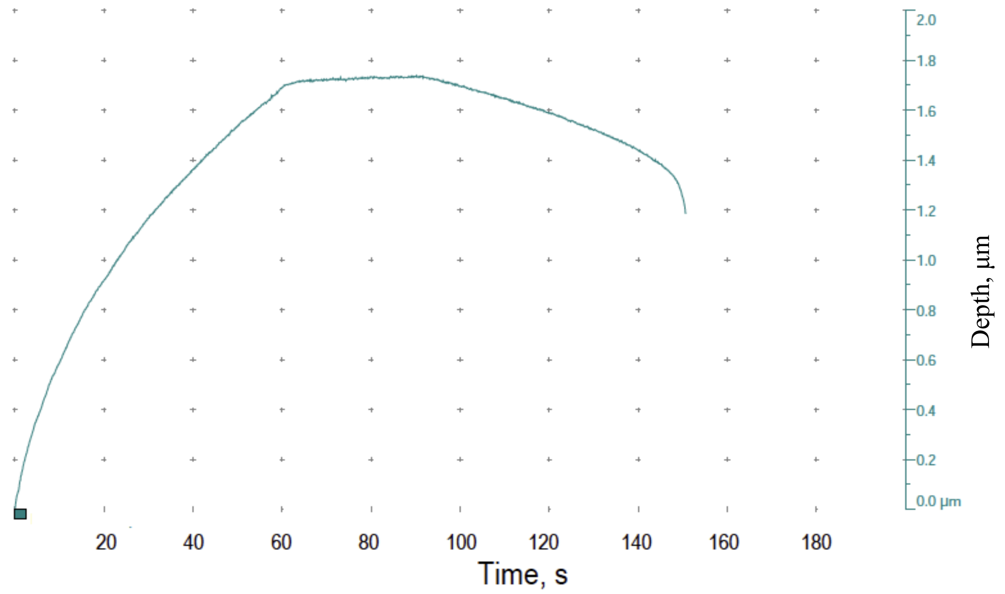

Fig. 4. **Example of the registered penetration depth**

Table 1

Results obtained from microindentation

Statistic	W_e**, µJ**	W_p**, µJ**	E_{IT}**, GPa**
Repetitions	10	10	10
Min	0.144	0.424	587.612
Max	0.176	0.513	922.189
Mean	0.162	0.484	667.15
Std.Dev.	0.011	0.029	109.949

There are large differences between the values of the elastic modulus obtained from each indentation E_{IT}, in the range between 588 and 922 GPa with standard deviation 109.9 GPa. The large dispersion of the results can be attributed to E_{IT} measurements performed in different areas with different components dominating, which have a significant effect in the microscale indentation. The obtained E_{IT} values from indentations are higher than that obtained for the overall modulus for WC-Co with 4 wt.% of zirconia addition, which was $E = 550 \pm 50$ GPa [13]. Even though the two ranges are overlapping, the E_{IT} values for WC-Co-ZrO_2 in this study are closer to the overall modulus $E = 650 \pm 50$ GPa for the same material reported in [13]. This observation may indicate that unlike the overall modulus, which decreased with increased addition of zirconia, the E_{IT} values may exhibit different or at least a modified trend. To check this observation and to make proper conclusions, additional measurement will be performed in the nearest future.

Moreover, at the next stage of the investigations, it is planned to extend the research on the mixtures with other proportions of the zirconia filler and to perform tribological tests.

Conclusions

1. Addition of zirconia nanopowder to the WC–Co matrix promoted toughening phenomena, presumably due to transition of tetragonal zirconia *t*-ZrO2 to the monoclinic phase *m*-ZrO_2.
2. The observed crack propagation in the samples with 4 wt.% of zirconia is non-linear, demonstrating increased crack resistance of the composite.
3. The elastic component of indentation work for the tested specimen was $\eta_{IT} = 26.58\%$.

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Author contributions

Conceptualization, B.R.; methodology, E.H. and V.M.; software, V.M.; validation, M.R. and E.H.; formal analysis, B.R. and V.M.; investigation, E.H., M.R., and V.M.; data curation, B.R.; writing – original draft preparation, M.R.; writing – review and editing, E.H., B.R., and V.M.; visualization, M.R.; 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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