Obtained Heteromodulus Composites Based on Zirconium Carbide

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Abstract. The article is devoted to the impact of carbon additives on densification and mechanical properties of ZrC/C heteromodulus composites. In case of addition of small amount of carbon to ZrC residual porosity decreases, whereas higher carbon content leads to more than 3 vol.% increase in residual porosity. Moreover, increase in carbon content in ZrC/C composites boosts toughness of sintered materials. For example, $K_{IC}=4.3 \text{ MPa}\cdot\text{m}^{1/2}$ for ZrC and $K_{IC}=7 \text{ MPa}\cdot\text{m}^{1/2}$ for 3 vol.% C. For 15 vol.% of C, toughness is the lowest and equals 5.3 MPa\cdot\text{m}^{1/2}. The extrapolation of the dependence of toughness on the non-porous state of materials is $K_{IC0}=13.2 \text{ MPa}\cdot\text{m}^{1/2}$.

1. Introduction
High melting point, oxidation resistance, chemical inertness and thermal conductivity make zirconium carbide (ZrC) a promising material for a wide range of applications. However, ZrC has a very low fracture toughness, $K_{IC}=3-4 \text{ MPa}\cdot\text{m}^{1/2}$ [1,2] and, consequently, uncontrolled material damage accumulation significantly restricts its application field. Improvement of fracture toughness in brittle ceramics can be achieved by creation of internal dissipative structures restricting crack propagation [3]. One of the most effective mechanisms of internal dissipative structure creation and composite fracture toughness improvement is the formation of relatively weak internal interfaces between the matrix and the reinforcing component in ceramic composites. These mechanisms were described by J. Cook and J.E. Gordon [4] and their main feature is that crack tips experience branching on the matrix/particle interface under condition that particle/matrix adhesion energy is lower than that of the matrix cohesion energy. It means that the required composite structure is to be made of components with sufficiently different elastic modulus. Such materials are commonly classified as heteromodulus composite materials in which matrix and reinforcement particles possess significantly different elastic modulus [5–7]. It is suggested that ZrC-based composites may obtain a lower elastic modulus in case of technical-grade carbon addition. Zirconium carbide and carbon have $E_{ZrC}=420-480 \text{ GPa}$ [8], and $E_C=2-4 \text{ GPa}$ elastic modulus [9] respectively.

2. Experimental
The aim of this article is to study the effects of carbon addition on porosity and mechanical properties of ZrC/C composites. Commercial powders of zirconium carbide with particle mean size of 1.4 µm and standard deviation of 1.2 µm as well as technical-grade carbon $<d>=1.2 \mu$m, $\sigma=1.5 \mu$m were used in the
research. According to X-ray diffraction analysis ZrC has almost stochiometric composition with \( X = 0.98 \). Carbon concentration varied from 1 to 15 vol.%. Mixing of ZrC and C powders was performed in ethanol solution in the ball-milling mixer. Samples were obtained by hot pressing in argon atmosphere at 25 MPa pressure and 1800 °C temperature during 15 minutes. The composite structures were studied using X-ray diffractometer with filtered CuKα radiation and TESCAN Vega 3 scanning electron microscope at accelerating voltage of 20 or 30 kV. Hardness was measured using Berkovich pyramid nanoindentation at loading of 500 mN by NanoIndenter G200 nanoindenter according to Vickers indentation pyramid. Elastic modulus has been calculated by measuring ultrasound velocity in ceramic samples using TDS 220 test equipment.

3. Results and discussion

Addition of carbon has ambiguous impact on ZrC densification. Residual porosity of ZrC samples obtained by hot 1800 °C pressing at 23 MPa pressure during 15 minutes was 10 ± 4 %. Carbon addition in low concentration results in a better sintering behavior of ZrC and, thus, decreases the residual porosity. Porosity of ZrC/C composites with 1 and 3 vol.% carbon concentration is 5 ± 4%. On the contrary, carbon addition in higher than 3 vol. % concentration leads to increase in porosity. ZrC/C heteromodulus composites with 5 and 10 vol.% carbon concentration demonstrate slightly lower porosity than those of ZrC ceramics (8 ± 4%). For samples of ZrC/C composites with free carbon concentration of 15 vol. % porosity reaches 18 ± 4 %.

Densification of ZrC ceramics and ZrC/C heteromodulus composites demonstrates dual effect of free carbon addition. Positive influence of low carbon concentration on ZrC densification is connected with the removal of adsorbed oxygen [10]. More than 3 vol.% increase in porosity of ZrC/C heteromodulus composites with C concentration may be attributed to reduction of diffusion mass transfer due to filling of carbon vacancies. Similar discoveries concerning influence of free carbon concentration on ZrC sintering behavior were made by X.G. Wang [11].

Significant difference between ZrC ceramics’ hardness and its elastic modulus calculated by various methods is discovered. For ZrC/C composites the difference is considerably lower Fig. 1. For ZrC ceramics hardness \( H_{Berk} \) is found to be 21 ± 2 GPa and \( H_v = 13 ± 2 \) GPa, while elastic modulus \( E_{Berk} \) is 420 ± 30 GPa. Elastic modulus \( E \) calculated by ultrasound transmission velocity is 220 ± 30 GPa.

![Figure 1](image.png)

**Figure 1.** Effects of free carbon addition on hardness (a) and elastic modulus (b).
Needless to say, that free carbon concentration in a heteromodulus composite affects the composite’s mechanical characteristics. Adding free carbon in concentrations from 1 to 15 vol.% was accompanied by hardness and elastic modulus reduction from 15 to 5 GPa and 330 to 200 GPa respectively.

According to the Vickers hardness data it is possible to calculate the stress intensity factor, $K_{IC}$, for sintered composites Fig. 2, using the Niihara, Morena and Hasselman formula [12]:

$$K_{IC} = \frac{0.035(Ha^{0.5})(E_{eff}^{0.4} \cdot (\frac{L}{a})^{-0.5})}{\varphi}$$

where $H$ is the hardness, $E_{eff}$ is the modulus of elasticity, $a$ – $\frac{1}{2}$ of diagonal of impression, $l$ – crack length, $\varphi$ – constant ($\approx 3$).

Calculations conducted in accordance with the given formula allowed revealing that addition of free carbon to ZrC resulted in improved fracture toughness. For example, $K_{IC}$ of ZrC ceramics was 4.3 ± 0.2 MPa×m$^{1/2}$, while fracture toughness of ZrC/C samples with 3 vol. % free carbon concentration was 7 ± 0.5 MPa×m$^{1/2}$ Fig. 2a. However, $K_{IC}$ of these composites was dependent on free carbon concentration as well as other characteristics. ZrC/C composite fracture toughness with 15 vol.% carbon concentration was the lowest 5 ± 0.3 MPa×m$^{1/2}$ although this value is higher as compared to that of ZrC without carbon addition.

![Figure 2. Effects of free carbon (a) and porosity (b) on ZrC/C heteromodulus composites’ fracture toughness.](image)

Undoubtedly, fracture toughness, as well as hardness and elastic modulus of ZrC/C heteromodulus composites were influenced by two factors – porosity and free carbon inclusions. Presence of carbon in ZrC matrix provided an increase in fracture toughness, but porosity was a factor of $K_{IC}$ decrease. Extrapolation of $K_{IC} = f (P)$ to the non-porous state ($P = 0$) showed that the largest fracture toughness of ZrC/C heteromodulus composites was obtained with 1 to 15 vol.% free carbon addition: $K_{IC0} = 13.2$ MPa×m$^{1/2}$, Fig. 2b. Such a high value of $K_{IC}$ for heteromodulus composites can be provided by the Cook-Gordon implementation mechanism, when a crack interacts with ZrC–C interface. Therefore, we have replotted $H$, $E$ and $K_{IC}$ data as dependencies on porosity, as there are two factors influencing toughness, hardness and elastic modulus: carbon concentration and porosity. As it can be from these pictures after extrapolation for samples’ poreless states the results are $Hv_0 = 17.8$ GPa, $E_0 = 399$ GPa and $K_{IC} = 13.2$
Values of $H$ and $E$ are similar to those from scientific data on dense ZrC-based ceramics. Moreover, a linear dependence between $H$ and $E$ typical for brittle materials Fig. 3a has been obtained.

Fracture toughness for the given ZrC/C composites especially their extrapolated values is similar to those of other CMC and MMC ZrC-based composites. In some cases it exceeds $K_{IC}$ values of ZrC-containing multi-phase ceramic composites.

For ZrC/C heteromodular composites, a positive correlation between hardness and fracture toughness in the relative coordinates $H/H_0 - K_{IC}/K_{IC0}$ has been obtained, Fig. 3b. In ZrC/C heteromodular composites hardness increase and fracture toughness of the $H/H_0 - K_{IC}/K_{IC0}$ dependencies are observed with C volume concentration rise from 1 to 15%. It is suggested that correlation between hardness and fracture toughness in such composites with a wide range of free carbon concentration options might have two realizations: the increasing one with simultaneous increase in $H$ and $K_{IC}$ and decreasing one involving the decrease of $H$ along with increase in $K_{IC}$. Most likely, increase of ZrC/C composites’ hardness is connected with condition $H=H_0+K_{HP}\times L^{-1/2}$ [13], where $H_0$ is a variable corresponding to monocrystal hardness, $K_{HP}$ is the Hall-Petch coefficient, $L$ is the grain size. Previously, it was observed that addition of free carbon to ZrC reduces carbide grain growth [11]. Obviously, the carbide grain refinement leads to the observed increase in hardness with rising concentration of free carbon. Fracture toughness of ZrC/C heteromodulus composites increases due to the contribution of carbon fraction in accordance with energy dissipation mechanisms of crack branching at internal interfaces.

4. Conclusion
The research proves that in hot pressed ZrC/C composites an increased toughness up to 7 MPa×m$^{1/2}$ can be obtained in spite of porosity up to 10% and without decreasing hardness. It shows that in such composites increased hardness and toughness can be obtained simultaneously. It is probably due to realization of both the Hall-Petch behavior when carbon addition to ceramic matrix reduces carbide grains and the Cook- Gordon mechanism.

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