Mechanical response of ZrB$_2$–based ultra-high temperature ceramics to shock pulse loadings in a wide temperature range

V V Skripnyak, V A Skripnyak, E G Skripnyak and I K Vaganova
National Research Tomsk State University, 36 Lenin Ave., Tomsk, 634050, Russia

E-mail: skrp2006@yandex.ru

Abstract. The multiscale approach was used for 3D computer simulation of deformation and failure of porous nanostructured ZrB$_2$-B$_4$C composites. It was shown strong influence of ZrB$_2$-B$_4$C nanocomposites microstructure on dynamic fracture at temperatures (295-473 K). The fracture of ZrB$_2$-UHTC is caused by nucleation and coalescence of micro cracks. Cracks are formed near voids and in space between the strengthening particles at the mesoscale level. It was shown the transition of brittle to ductile fracture in ZrB$_2$-B$_4$C composites depends on strain rates. Thus, the strength threshold of nanostructured ZrB$_2$-B$_4$C composites depends on strain rates in temperature range (473-2200 K). The dynamic strength of ZrB$_2$-B$_4$C composites sharply decrease at temperature above 1773 K. It was shown that the dependence of normalized strength of ZrB$_2$-B$_4$C composites on the logarithm of normalized strain rates can be described by the power law.

1. Introduction
Mechanical response of ultra-high temperature ceramics (UHTC), located at elevated and high temperatures on intensive pulse loading is of interest in connection to protection of the wing leading edges and nose tips of future hypersonic flight vehicles, long term resistance to oxidation at extreme high temperatures, good electrical conductivity, and high strength at high temperatures.

The results of experimental studies of ZrB$_2$-based ceramics showed excellent and unique combination of high melting point, high electrical and thermal conductivity, chemical inertness against molten metals or nonbasic slags, and superb thermal shock resistance [1]. The crystal structure of ZrB$_2$ is AlB$_2$-type transition metal diboride with the space group symmetry $P6/mmm$ [2]. In a hexagonal lattice, in addition to densely packed layers, graphite-like layers are present. Thus ZrB$_2$-based ceramics refers to the isomechanical group of UHTC materials with a hexagonal lattice, combining materials TiB$_2$, ZrB$_2$, HfB$_2$, CrB$_2$, Mo$_2$B$_6$, W$_2$B$_6$, and LaB$_6$ [3]. The patterns of deformation, damage and fracture of hexagonal ceramics under thermal and mechanical influences have a similarity. Mechanical behavior of these ceramics at $T/T_m\leq0.3$ ($T_m$ is melting temperature) is determined by nucleation and growth of damages. Using of nanopowders allows reducing the sintering temperature of ceramics, but complicates the problem of providing the required physical and mechanical properties of new nanostructured ceramic materials due to the formation of defect structures on different scale levels. The resulting nanostructured ceramic materials have a number of specific features of the microstructure that affect the physical and strength properties of ceramics.

Data of elastic modulus, fracture toughness and strength of refractory ceramics in the temperature range from 297 to 2200 K and strain rates from $10^{-3}$ to $10^6$ s$^{-1}$ are required under designing of
structural elements from nanostructured UHTC ceramics. An important difficulty is the prediction of deformation, damage and destruction of brittle ceramic materials, taking into account their structure. The prediction of the behavior of nanostructured refractory ceramics at elevated temperatures, the shock wave loadings, impulse impacts are essential for evaluating accident consequences in the design of nuclear reactor control elements.

The aim of the work is to obtain predictions of the mechanical response to impulse responses over a wide range of temperatures.

2. Model for prediction of dynamic fracture of ceramic materials under intensive dynamic loads in a wide temperature range

The relationship between Young’s modulus and temperature is assumed to satisfy the following relationship [4, 5]:

$$E = E_0 - B_0 T \exp(-T_m/T) + B_1 (T - B_2 T_m + |T - B_3 T_m|) \exp(-T_m/T),$$  \hspace{1cm} (1)

where $E_0$ is Young’s modulus at 273 K, $T_m$ is the melting temperature of solid phase, and $B_0$, $B_1$, $B_2$ are material constants. The Young’s modulus of ZrB$_2$-25 vol.% B$_4$C was predicted in the temperature range from 297 K to 2200 K using $E_0$=500, $B_0$=2.54 GPa K$^{-1}$, $B_1$=1.9 GPa K$^{-1}$, $B_2$=0.363 K$^{-1}$, $T_m$=3500 K.

Eq. (1) can be used for calculating of the Young’s modulus at temperatures below $\sim 0.25$ Tm [4-6]. Temperature dependence of Poisson’s ratio can be described by the linear relationship (2):

$$\nu(T) = v_0 - K(T),$$  \hspace{1cm} (2)

where $\nu$ is the Poisson’s ratio, and $v_0$=0.1037, $K_1$=1.3389 $10^{-6}$ K$^{-1}$ correspond to condensed phase of ZrB$_2$.

Temperature dependence of the shear modulus $\mu(T)$ and the bulk modulus $B(T)$ were calculated by equations:

$$\mu(T) = E(T)/2(1 + \nu(T)),$$  \hspace{1cm} (3)

$$B(T) = E(T)/3(1 - 2\nu(T)).$$  \hspace{1cm} (4)

The temperature dependence of ZrB$_2$ specific heat capacity was calculated by the relation:

$$C_p(T)=c_0+c_1 T+c_2 T^2+c_3 T^3,$$  \hspace{1cm} (5)

where $c_0$, $c_1$, $c_2$ are constants of material, $T$ is a temperature.

Specific heat capacity $C_p$ (J·g$^{-1}$·K$^{-1}$) of ZrB$_2$ was calculated by (4) at $c_0$=−3.916 J·(g·K)$^{-1}$, $c_1$=233.34 J·g$^{-1}$·K$^{-2}$, $c_2$=−196.082×$10^{-6}$ J·g$^{-1}$·K$^{-1}$, $c_3$=−0.545 $\times$ $10^3$ J·g$^{-1}$·K$^2$ [7].

The temperature dependence of flexural strength $\sigma_f(T)$ was described by Eq. (5) [5]

$$\sigma_f(T) = \sigma_f(0) (E(T)/E_0)^{1/2} \left[ \int_0^T C_p(T)dT / \int_0^{T_m} C_p(T)dT \right]^{1/2},$$  \hspace{1cm} (6)

where $\sigma_f$ is the fracture strength at the reference temperature, $E_0$ is the Young’s modulus at the reference temperature and $E(T)$ is the temperature-dependent Young’s modulus, $C_p(T)$ is the specific heat capacity for constant pressure, and $T_m$ is the melting temperature.

The dependence of the thresholds stress on the normalized strain rate at temperature $T/T_m < 0.3$ was considered by Grady and Kimberley [8, 9]:

$$\sigma_f / \sigma_0 = 1 + (\dot{\varepsilon}/\dot{\varepsilon}_0)^{2/3},$$  \hspace{1cm} (6)

$$\sigma_0 = 2.4 K_{IC} / R\eta^{1/4}, \quad \dot{\varepsilon}_0 = 2.4 K_{IC}\eta^{1/2} / R(pE)^{1/2}, \quad \eta = [6\alpha/(\pi d_0^3)]^{2/3},$$
where \( \sigma_f/\sigma_0 \) is the normalized macroscopic stress of the ceramic under compression, \( \varepsilon = \varepsilon_t/\varepsilon_0 \) is the normalized strain rate, \( \dot{\varepsilon} = (2/3)\dot{\varepsilon}_t \) is the equivalent strain rate, \( R \) is the average pore size, \( \alpha \) is the relative pore volume, \( \rho \) is the effective mass density, \( K_{IC} \) is the fracture toughness, \( E \) is the Young's modulus, \( d_p \) is the average pore size.

The computational model of mechanical behavior of structured quasi-brittle materials under dynamic impact was used for prediction of the stress properties of nanostructured ceramic materials based on ZrB₂ [10-12]. The kinetic model for the fracture proposed by Johnson-Holmquist was used for damage accumulation [13]. The fracture criterion \( D=1.0 \) was used for nanostructured UHTC ceramic.

The damage parameter \( D \) at the mesoscopic structural level was determined by the relation:

\[
D = \int_0^{\varepsilon_f^n} \frac{\varepsilon_{eq}^n}{\varepsilon_f^n} \, dt, \quad \varepsilon_{eq}^n = (2/3)\varepsilon_t \varepsilon_0^{1/2}, \quad \varepsilon_f^n = D_1 (P^* + T^*)^{D_2},
\]

where \( \dot{\varepsilon}_{eq}^n \) is the intensity of the rate of inelastic deformation; \( \varepsilon_f^n \) is the threshold inelastic deformation; \( D_1, D_2 \) are parameters of the material; \( P^* = \rho \sigma_{HEL}; T^* = \sigma_{eq}/\sigma_{HEL} \); \( \sigma_{HEL}, \sigma_{eq} \) are pressure and the value of the main stress at the elastic limit shows that Huguenot, respectively.

Following parameters were used in calculations of mechanical behavior of ZrB₂-25 vol.% B₄C ceramics under shock pulse loading: for ZrB₂: \( E=495 \text{ GPa}, \rho=6.11 \times 10^3 \text{ kg/m}^3, K_{IC}=3.5 \text{ MPa·m}^{1/2}, \sigma_{HEL}=7.11 \text{ GPa}, \rho_{HEL}=3.07 \text{ GPa}, D_1=0.1, D_2=1, C_0=9.233 \text{ km/s}, \sigma_{eq}=0.5 \text{ GPa}, \sigma_{d} = 0.5 \text{ GPa}; \)

for B₄C: \( E=432 \text{ GPa}, \rho=2.52 \times 10^3 \text{ kg/m}^3, K_{IC}=5 \text{ MPa·m}^{1/2}, \sigma_{HEL}=16 \text{ GPa}, \rho_{HEL}=7.2 \text{ GPa}, D_1=0.1, D_2=1.0, C_0=12.8 \text{ km/s}, \sigma_{eq}=0.32 \text{ GPa}, \sigma_{d} = 13.2 \text{ GPa}.

Parameters were determined for the ceramic materials based on ZrB₂ within the parameters of the structure, \( K_{IC} \) and modules of elasticity. The average pore size \( d_p \approx 1.185 \text{ microns} \) and grain size \( a \approx 7.45 \text{ microns}, E=495 \text{ GPa}, \alpha = 0.07, \eta = 3.27 \times 10^{10} \text{ m}^{-2} \) was determined by the values \( \sigma_0 = 2.117 \text{ GPa}, \dot{\varepsilon}_0 = 6.96 \times 10^6 \text{ s}^{-1} \).

Equations (2)-(6) were used to determine the dependence of the compressive strength and the shear stress of the nanostructured ZrB₂ ceramics. In determining the coefficients, the Young's modulus, the fracture toughness parameter \( K_{IC} \) and the bending strength of the temperature were taken into account [4, 14].

For the prediction of mechanical behavior under compression over a wide temperature range of ceramic composite materials, the Armstrong-Zerilli [15] was used at temperature \( T/T_m \geq 0.3 \), according to which the yield strength \( \sigma_y \) is determined by the equation:

\[
\sigma_y = \sigma_{s} + C_3 (\varepsilon_{eq}^n)^{n_1} + C_4 \exp \left[ -C_5 T + C_6 T \ln(\dot{\varepsilon}_{eq}/\dot{\varepsilon}_{eq0}) \right],
\]

where \( \varepsilon_p \) is equivalent plastic strain; \( \sigma_{s}, C_3, n_1, C_2, C_3, C_4 \) are parameters of the model.

As the failure criterion is used coupled model of Johnson – Cook on the basis of the cumulative law of damage accumulation \( D \) at temperature \( T/T_m \geq 0.3 \):

\[
D = \frac{1}{\varepsilon_f} \sum \Delta \varepsilon_{p}^{i}, \quad \varepsilon_f = \left( D_1 + D_2 \exp \left( \frac{D_3}{\sigma_{eff}} \right) \right) \left( 1 + D_4 \ln \left( \frac{\varepsilon_p}{\varepsilon_0} \right) \right) \left( 1 + D_5 \frac{T - T_r}{T_m - T_r} \right),
\]

where \( \Delta \varepsilon_{p}^{i} \) is the increment of effective plastic strain; \( D_1, D_2, D_3, D_4, D_5 \) are material parameters; \( \sigma_{eff} \) is the effective stress; \( \rho \) is the pressure.

Following parameters were used in calculations [16] for ZrB₂: \( T_m=3270 \text{ K}, \sigma_{d}=120 \text{ MPa}, C_3=0.7, n_1=0.4, m=0.85, D_1=0.01, D_2=0.003, D_3=0.003, D_4=0.05, D_5=0.0; \) for B₄C: \( T_m=2620 \text{ K}, \sigma_{d}=261 \text{ MPa}, D_1=0.009, D_2=0.0, D_3=0.001, D_4=0.0, D_5=0.0 \). Model (1)-(9), was used as a user subroutine of WB ANSYS Autodyne to simulate the impulse impact on representative volume of ZrB₂-25 Vol. % B₄C.
3. Results and discussion

Shock pulse propagation was numerically simulated in representative volume of ZrB$_2$-B$_4$C at initial temperatures from 297 to 2200 K. The 3D model volume of ZrB$_2$-25 % vol. B$_4$C was loaded on the right side by a shock pulse with amplitudes from 5 to 7 GPa. The particle sizes of B$_4$C were assumed as $\sim$0.01 $\mu$m. Calculated equivalent stresses behind of shock front in ZrB$_2$-25 vol. % B$_4$C at time 0.767 ns after impact are shown in figure 1. Figure 1a-c shows stress distributions in section of representative volume element (RVE) of ceramics at initial temperatures 295, 1273, 2273 K respectively. The distribution of local stresses and strains reaches quasistationary states in 0.4 ns after the start of loading by a shock pulse at 297 K.

![Calculated equivalent stress in ZrB$_2$-25 Vol. % B$_4$C at time 0.767 ns after impact with amplitudes 5 GPa.](image)

**Figure 1.** Calculated equivalent stress in ZrB$_2$-25 Vol. % B$_4$C at time 0.767 ns after impact with amplitudes 5 GPa.

Particles of B$_4$C have higher strength characteristics and are the cause of the development of localized shear in the dynamic compression of ZrB$_2$-25 % vol. B$_4$C ceramics. Cracks are formed near voids and in space between the strengthening particles at the mesoscale level. The simulation results confirmed the assumption of voids healing in the front of the compression wave. It was found that in the structure of the material there are untreated pores after compression of the porous ZrB$_2$-B$_4$C ceramics by impact pulses with submicrosecond duration and amplitudes comparable to the Hugoniot elastic limit. These residual pores are the centers of formation of spalling microcracks in the zone of
action of tensile stresses formed by the interaction of rarefaction waves. Thus, at low homological temperatures \((T/T_m<0.3)\), porous ceramic materials based on ZrB\(_2\) have significantly different limits of dynamic compressive strength and tensile strength. Pulsed compression of boride ceramic materials can be accompanied by complete pore healing at elevated homologous temperatures. The resistance to deformation at high strain rates of the ZrB\(_2\)-B\(_4\)C ceramics increases as a result of structural changes caused by compression at \(T/T_m>0.3\). Time history evolutions of pressures and equivalent stress in ZrB\(_2\)-25 Vol. % B\(_4\)C under pulse loading are shown in figure 2. The solid lines (1) correspond to the calculated pressures, the dashed lines (2) show changes in the equivalent stresses behind the shock impulse front. The history of stress changes is shown for a Lagrangian material point \(G\) in the cross section \(z=h/2\) (\(h\) is the thickness of representative volume element) with coordinates \(x=2\ \mu m\) and \(y=1.14\ \mu m\) (See figure 1b,c). The oscillations of the stresses behind the front of the shock pulse are caused by the relaxation of shear stresses under the shear bands formation at elevated temperatures (see figure 1c) or formation of microcracks at low homologous temperatures.

![Figure 2](image-url)

**Figure 2.** Time history of pressures and equivalent stress in ZrB\(_2\)-25 vol. % B\(_4\)C under pulse loading; (a) – at the initial temperature of 1273 K, (b) – at initial temperature of 2273 K.

Both processes lead to an increase in damage in the structure of the material at high strain rates. The strength threshold of nanostructured ZrB\(_2\)-B\(_4\)C composites depends on strain rates in temperature range (473-2200 K) due to transition of brittle to ductile fracture.

### 4. Conclusion

The multiscale approach was used for 3D computer simulation of deformation and failure of porous nanostructured ZrB\(_2\)-B\(_4\)C composites. It was shown strong influence of ZrB\(_2\)-B\(_4\)C nanocomposites microstructure on dynamic fracture at temperatures (295-2273 K). The fracture of ZrB\(_2\)-UHTC is caused by nucleation and coalescence of micro cracks at low homologous temperatures \((T/T_m<0.3)\).

Cracks are formed near voids and in space between the strengthening particles at the mesoscale level. It was shown the transition of brittle to ductile fracture in ZrB\(_2\)-B\(_4\)C composites depends on strain rates.

Thus, the strength threshold of nanostructured ZrB\(_2\)-B\(_4\)C composites depends on strain rates in temperature range (473-2200 K). The dynamic strength of ZrB\(_2\)-B\(_4\)C composites sharply decrease at temperature above 1773 K.

It was shown that the dependence of normalized strength of ZrB\(_2\)-B\(_4\)C composites on the logarithm of normalized strain rates can be described by the power law.
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