Modeling of shock-wave loading of carbides as mixtures of components

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Abstract. The results of numerical experiments on the modeling of shock wave loading of solid and porous carbides with various stoichiometric compositions are presented. The model is based on the assumption that all the components of the mixture, including gas, have similar pressure, velocity and temperature. The model allows describing the behavior of porous materials and mixes in a wide range of porosity and pressures with precision of experiment. The behavior of complex materials such as carbides is considered as a mixture. The model accurately describes the behavior of the carbides with equal shares of the components of WC, TiC, TaC, NbC and the behavior of boron carbide B4C. Comparison for data of calculation and experimental data was held for carbides with different porosity.

1. Introduction
High-temperature composite materials are the most effective for solving a large number of tasks in various high-tech industries. Samples based on oxide-free refractory compounds of borides, carbides, and nitrides are being intensively investigated at the present time. Composite materials can be created from these refractory compounds for various practical applications, using the principles and capabilities of powder and ceramic technology [1]. Many investigations have focused on studying carbides and materials with them as components, for example, [2–21]. Boron carbide B4C is of great interest among carbides, which is second only to diamond in terms of hardness [3–13]. Despite the fact that studies shock compression on B4C have been going on for a long time, starting from the first articles [3–5], the question of the presence of a phase transition in the pressure range from 10 to 100 GPa remains a subject of discussion. It is noted that B4C is and probably will remain one of the most mysterious materials among ceramics studied by shock-wave methods [9].

Carbides are characterized by a high melting point in addition to their high hardness. Refractory carbides are the basis for the production of high-temperature materials, have high hardness values and are resistant to corrosion. Understanding the properties of uranium-carbon systems is important not only in connection with their potential candidate for using in the nuclear industry, but also from the point of view of fundamental science. However, very few experimental and theoretical studies exist in the literature on the behavior of UC at high pressure [15-19]. The same situation is about other refractory carbides, in particular with tantalum carbide TaC and hafnium carbide HfC, as well as their mixtures, which have abnormally high melting temperatures of about 4000 K, while maintaining high strength and durability under extreme thermal loads [20]. One of the possible options for modeling the behavior of carbides under shock wave loading is shown in [21], where carbides were considered as a
mixture of components that make up the test sample and the mixture model was used. In this model it is assumed that the components are compressed in the mixture in the same way as pure materials, which allowed reliably describing the data of shock-wave experiments of solid carbides with an equal stoichiometric ratio of the components WC, TiC, TaC, NbC, SiC, ZrC. The thermodynamic equilibrium components model was considered in [22–25] for the description of porous materials and mixtures of complex compositions, including carbides [23]. The model served to describe the values of pressure, compression, and temperature of loaded samples, including mixtures whose components undergo a polymorphic phase transition under shock wave loading [24].

2. Model

The TEC model, which is used to describe the shock-wave loading of carbides as a mixture of components, is based on the assumption that all components of the mixture, including the gas in the pores, are in thermodynamic equilibrium, which assumes the equality of velocities, pressures and temperatures. Mic-Grüneisen equation of state is used to describe the behavior of condensed phases in the model. The equations that determine the state of the condensed component are written as follows:

\[ P(\rho, T) = P_c(\rho) + P_T(T), \]
\[ P_T(\rho, T) = \Gamma \rho E_T(T), \quad E_T(T) = c_v(T - T_0). \]

Here \( P_c \) is the potential component of pressure; \( P_T \) and \( E_T \) are the thermal components of pressure and specific energy; \( c_v \) is the specific heat capacity; and \( T_0 \) is the initial temperature. Then the equation of state (EoS) for the condensed component with the current density \( \rho \), initial density \( \rho_0 \) and the corresponding coefficients \( A \) and \( n \) has the form:

\[ P(\rho, T) = A\left(\frac{\rho}{\rho_0}\right)^n - 1 + P_T, \]

the values of pressure and internal energy under normal conditions \((\rho = \rho_0, T = T_0)\) in the model under consideration are assumed to be zero. To describe the behavior of materials with different porosity, the function \( \Gamma = P_T V/E_T \) is introduced in the equation of state, which determines the contribution of thermal components, depending on the temperature in the following form [22].

\[ \Gamma(T) = \left[\Gamma(T_0) - \Gamma(T_\infty)\right]^{-1} + C(T - T_\infty) \]
\[ C = \left[\Gamma(T_\infty) - \Gamma_\infty\right]^{-1} - \left[\Gamma(T_0) - \Gamma_\infty\right]^{-1}(T_\infty - T_0)^{-1} \]

At the wave front, the conditions for the conservation of mass, momentum, and energy, known as the Hugonio equations, are written out [26]. The conditions for the conservation of momentum and energy are considered for the mixture as a whole, and for the conservation of mass flow, the conditions for each component of the mixture are written out. EoS of an ideal gas is taken for a gas. For a mixture consisting of \( n \) condensed components having initial volume fractions of \( \mu_{i0} \), the following expression is obtained:

\[ P = \sum_{i=1}^{n} \frac{A_i \mu_{i0}}{\sigma_i} \left( h_i - k_i + 1 \right) + \frac{2k_i \sigma_i}{k_i - 1} - h_i - 1 \]

Here \( \sigma_i = \rho_i/\rho_0 \), \( \sigma_g = \rho_g/\rho_0 \) are the compression ratios of the corresponding component \( i = 1..n; \rho_0 \) and \( \rho_{i0} \) are the current and initial gas densities; and \( \gamma = 1.41 \) is ratio of specific heats. The resulting equation, together with the condition that the temperature values of the components are equal, and the
equations of state of each component allow constructing a shock adiabate for a multicomponent sample.

3. Results of simulation

The data obtained from the experiments allowed verifying the model and considering the possibility of using this model for materials the data on which is insufficient or missing. The adiabats of the components were used in the calculations for describing the shock-wave loading of carbides. For carbon, the adiabate of diamond was taken in a similar way [21]. The model parameters obtained on the basis of experimental data for the components of the researching carbides are shown in the table.

The author’s approach allows similarly describing the experimental data not only for solid carbides in [21], but also for porous samples. Porous carbide is considered as a porous mixture with the components of the corresponding carbide elements; while the ratio of the volume fractions of the condensed components decreases in proportion to the value porosity of the sample \( m \) (porosity \( m \) is the ratio of the density of the solid to the density of the sample). The simulation results for carbides of different porosity values are shown in figure 1. The behavior of porous materials within the limits of experimental accuracy is described for tungsten carbide with porosity value \( m = 1.101 \), tantalum carbide \( m = 1.125 \), and niobium carbide \( m = 1.07 \). The calculations and data are shown with a shift in the pressure value by 100 GPa for clarity.

\[
\begin{array}{cccccccc}
\text{Substance} & A \text{ GPa} & \rho_0 \text{ g/cm}^3 & n & c_v \text{ J/kg*K} & \Gamma(T_0) & \Gamma(T^*) & T^* \text{ K*10}^3 & \Gamma(T_\infty) \\
C & 200.0 & 3.515 & 2.6 & 500 & 1.10 & 0.55 & 20 & 0.500 \\
W & 101.8 & 19.235 & 3.105 & 140 & 1.61 & 1.35 & 23 & 0.400 \\
Nb & 52.0 & 8.586 & 3.2 & 280 & 1.68 & 1.2 & 23 & 0.500 \\
Ta & 54.18 & 16.656 & 3.45 & 140 & 1.69 & 1.15 & 23 & 0.667 \\
B & 115.0 & 2.340 & 1.7 & 816 & 1.10 & 0.90 & 23 & 0.500 \\
Be & 51 & 1.848 & 2.5 & 1824 & 1.17 & 070 & 23 & 0.500 \\
\end{array}
\]

**Figure 1.** Shock adiabats in the coordinates of pressure and compression ratio for porous carbides:
1 – WC \( m = 1.201 \), 2 – TaC \( m = 1.125 \), 3 – NbC \( m = 1.07 \).
Experimental points 4 are from reference [27], 5 [28], 6 [2].
The assumption on determining the volume of the components based on the stoichiometric ratio allows reliably describing the experimental data for boron carbide B₄C. Modeling results are shown in figure 2. The volume fractions are determined in a ratio of 4:1, according to the chemical composition for B₄C. This approach also provides a realistic description of the experimental data for porous B₄C samples as well [23]. The results prove the possibility to describe the dynamic parameters (pressure, compression) of solid and porous carbides with different stoichiometric ratios under shock-wave loading.

Figure 2. Shock adiabats in the coordinates of pressure and compression ratio: dashed line for diamond, dot-dash line for boron, solid line for B₄C. Experimental points 1 are from reference [28], 2 [29], 3 [3], 4 [12].

Figure 3. Shock adiabats in the coordinates of pressure and compression ratio: dashed line for diamond, dot-dash line for beryllium, solid line for Be₂C. Experimental points 1 are from reference [28], 2 [30], 3 [29].
Assumingly, using the same method, it is possible to model the thermodynamic parameters of carbides with different stoichiometric ratios, for which there are no experimental data. The similar calculations are performed for various carbides, in particular for beryllium Be\(_2\)C, which has high melting point, heat resistance, and specific nuclear properties. It is a component of structural materials and biological protection. The volume fractions for this carbide are determined to be in the ratio of 2:1. The simulation results for solid Be\(_2\)C and its components, as well as the experimental data of the components, are shown in figure 3.

It is of interest to compare the temperature value along the shock adiabate B\(_4\)C of different porosity with the results of [31], in particular, providing for the value of the melting temperature at a pressure of 70 GPa. This point is considered as the phase transition region. The model calculation and data from [31, 32] are shown in figure 4. The simulation results are shown additionally for porosity values \(m = 1.03, 1.07\). The temperature value at 70 GPa is below the temperature obtained in [31, 32] for solid carbide \(m = 1\). At the same time, the data of [31, 32] are located in the region between the adiabates corresponding to the porosity values \(m = 1.03, 1.07\). This location can be interpreted as the region of the shock adiabate of high-pressure phase. As it was shown in [33] for carbon, for which the high-pressure phase is diamond, the experimental values above the phase transition region are close to the shock adiabate of diamond of the same initial density as the investigating carbon samples. Thus, the shock adiabate of a carbide with a porosity \(m = 1.05\) with an accuracy of 0.02 can be considered as corresponding to the high-pressure phase of boron carbide, thereby indirectly confirming the possibility of a phase transition at this pressure value.

\[T, \text{K} \]
\[P, \text{GPa} \]

![Figure 4](image)

**Figure 4.** The temperature along the shock adiabate for boron carbide. Data 1 is from reference [31], 2 [32]. Calculation: solid line 1 for \(m = 1\), dashed line 4 for \(m = 1.03\), dot-dash line 5 for \(m = 1.07\).

The EoS (3) of this model uses a constant value of the heat capacity for the components. This assumption can be considered justified for compression values less than 2, as it was noted in [34]. It results in some overestimation of the temperature value of the investigating samples, however, a reliable description of the values of the dynamic parameters of nitrides, such as pressure and compression in the pressure range from 3 to 800 GPa, is obtained. The TEC2 model [35], which is a modification of the method under consideration, is designed to obtain more complete information, including on the temperature values along the shock adiabate. The coefficient depends on the temperature and volume. In this case, to determine the parameters of the equation of state of the components, it is necessary to have a dependence of the heat capacity value on the temperature for the components of the investigating material.
Conclusions
Thus, the proposed model describes the dynamic loading of carbides of different porosity values, considering them as a mixture of components corresponding to the chemical composition of carbides. A reliable description has been obtained both for carbides with equal fractions of 1:1 in the stoichiometric ratio, and for boron carbide, which, respectively, has a ratio of 1:4. This approach allows us to determine the thermodynamic characteristics of shock-wave loading of previously unexplored carbides. The method may be useful in numerical modeling of the behavior of complex materials, in particular carbides at high energy densities.

Appendices
TEC – thermodynamic equilibrium components
EoS – equation of state

References
[1] Akopov F A, Adrianov M A, Amirov R Kh, Borodina T I, Borovkova L B, Val’yano G E, Dolgoroborodov A Yu, Tkachenko V V and Shavelkina M B 2017 Refract. Ind. Ceram. 57(5) 496
[2] Bakanova A A, Bugaeva V A, Dudoladov I P and Trunin R F 1995 Fiz. Zeml. 6 58 [In Russian]
[3] Pavlovskii M N 1970 Fiz. Tverd. Tela 12 2175 [In Russian]
[4] McQueen R G, Marsh S P, Taylor J W, Fritz J N and Carter W J 1970 The equation of state of solids from shock wave studies in High-Velocity Impact Phenomena, ed. by Kinslow R. (Academic, New York, Elsevier) 293–417
[5] Gust W H and Royce E B 1971 J. Appl. Phys. 42 276
[6] Grady D E 1994 Journal De Physique IV 4 385
[7] Vogler T J, Reinhart W D and Chhabildas L C 2004 J. Appl. Phys. 95 4173
[8] Zhang Y, Mashimo T, Uemura Y et al., 2006 J. Appl. Phys. 100 113536
[9] Grady D E 2015 J. Appl. Phys. 117 165904
[10] Dera P, Manghnani M H, Hushur A et al. 2014 J. Solid State Chem. 215 85
[11] Dyachkov S A, Parshikov A N, Egorova M S et al. 2018 J. Appl. Phys. 124 085902
[12] Fratanduono D E, Celliers P M, Braun D G et al. 2016 Phys. Rev B 94, 184107
[13] Molodec A M, Golyshiev A A and Shahray D V 2017 GETF 151(3)
[14] Savvatimsky A I and Onyfriev S V 2020 TVT 58(6) 865
[15] Sahoo B D, Joshi K D and Kaushik T C 2019 Computational Condensed Matter 21 e00431
[16] Olsen J S, Gerward L, Benedict U et al.1986 Comm. Metals 121 445
[17] Sahoo B D, Joshi K D and Gupta S C 2013 J. Nucl. Mater. 437 81
[18] Sahoo B D, Mukherjee D, Joshi K D et al.2016 J. Appl. Phys. 120 085902
[19] Dancausse J P, Heathman S, Benedict U et al.1993 J. Alloys Compd. 191 309
[20] Senchenko V N and Belikov R S 2019 J. Phys.: Conf. Ser. 1147 012011
[21] Trunin R F 2006 Investigation of Extreme Conditions of Condensed Matter by the Method of Shock Waves. Hugoniot Equations (Ross. Federal. Yadern. Centr-VNIIE’F, Sarov) 137–141
[22] Maevskii K K and Kinelovskii S A 2018 High Temperature 56 853
[23] Maevskii K K 2019 AIP Conf. Proc. 2167 020204
[24] Maevskii K K 2021 Mathematica Montisnigri 50 140
[25] Maevskii K K 2021 Tech. Phys. 66 791
[26] Zeldovich Y B and Raizer Y P 1966 Physics of shock waves and hightemperature hydrodynamic phenomena (New York: Academic Press)
[27] Trunin R F, Gudarenko L F, Zhernokletov M V and Simakov G V 2006 Experimental Data on Shock Wave Compression and Adiabatic Expansion of Condensed Matter (Ross. Federal. Yadern. Centr-VNIIE’F, Sarov) 411–5
[28] Marsh S P 1980 LASL Shock Hugoniot Data (Berkeley: Univ. of California Press)
[29] Pavlovskii M N 1970 Fiz. Tverd. Tela 13(3) 2175 [In Russian]
[30] Levashov P R, Khishchenko K V, Lomonosov I V and Fortov V E 2004 AIP Conf. Proc. 706 87
http://www.ihed.ras.ru/rusbank/

[31] Molodets A M, Golyshev A A and Shilov G V 2020 JETP Letters. 111 720
[32] DeVries M., Subhash Gh., Awasthi A 2020 Phys. Rev. B 101 144107
[33] Charakhchyan A A, Milyavskii V V and Khishchenko K V 2009 High Tem 47 235
[34] Ostrik A V 2018 Composite materials constructions 2 48
[35] Maevskii K K and Kinelovskii S A 2019 Tech. Phys. 64 1090