

The Role of Multiple Polytypes in Determining the Catastrophic Failure of Boron Carbide at High Shock Velocities

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ABSTRACT

The absence of a plastic phase in boron carbide and its failure at shock impact velocities just above the Hugoniot elastic limit (H_{EL}) has been a puzzle for a long time. In the present work, using self-consistent field density functional simulations we are able to account for many experimental observations by noticing that several boron carbide polytypes [(B₁₁C)C₂B, (B₁₂)C₃, etc ...] coexist without significant lattice distortions. Our analysis also indicates that above a threshold pressure all the candidate microstructures are less stable than a phase involving segregated boron (B₁₂) and amorphous carbon (a-C) but the energetic barrier between boron carbide and B₁₂ + 3C, is by far lower for the B₁₂(CCC) microstructure, requiring the lowest atomic displacement for a transformation B₄C → 3B + a-C, occurring at pressures of 6 GPa ≈ P(H_{EL}). For such a configuration, segregation of free carbon occurs in layers orthogonal to the (113) lattice directions, in excellent agreement with recent transmission electron microscopy (TEM) analysis

INTRODUCTION

The performance of ceramic armor must be fail proof since it determines the survival and safety of people. Boron carbide [1] is the ideal material for such an application. It sits at the third position on the hardness scale, just below diamond and cubic boron nitride, and it possesses the highest dynamic elasticity, its Hugoniot elastic limit (H_{EL} = 17-20 GPa) surpassing by a factor two all of its competitors, such as silicon carbide and alumina, which are 50% denser [2]. Nevertheless, the use of boron carbide in lightweight armor is not possible now because of a lack of residual plastic strength above the H_{EL} , a compulsory issue for armor survival upon damage. No one has been able to elucidate the physics of such a catastrophic failure [1], a unique behavior in dynamically elastic materials finding counterparts at much lower stress values (<1 GPa) in dynamically inelastic ionic insulators, such as quartz and glasses [1].

Only recently, some efforts have proven which are not the causes of failure. Voegler *et al* [3] show that it cannot be a phase transition, which they found only above 40 GPa.. A phase transition explaining the failure at the H_{EL} must occur at pressures $P \approx P(H_{EL}) \approx 7-8$ GPa, corresponding to the pressure occurring behind the shock wave at the Hugoniot conditions for $H_{EL} \approx 17-20$ GPa. On the other hand, Chen *et al* [4] prove that the reasons of the crash are not intrinsic since the material, except for a few 2-3 nm wide bands which become amorphous, preserves integrity of its crystalline lattice. This rules out any explanation in terms of local melting, rebonding or influence of twinning and dislocation defects for the collapse. The same work, however, also showed that failure always occurs

as these tiny amorphous bands, shock-induced in well defined lattice directions. More recently Ge *et al.* [5] have shown that similar structures can be produced also under quasi-static conditions, hence they are not an exclusive result of a kinetic process, and they contain free carbon, at least partly in graphitic, sp^2 hybridization.

Furthermore, even though the boron carbide microstructure has been widely accepted to be formed by 12-fold icosahedra and 3-fold chains, the actual location of the carbon sites in such microstructure is not yet clear. Duncan et al [6] proposed fully boron icosahedra and fully carbon chains, i.e. $B_{12}(CCC)$. Theoretical works have generally suggested that a phase formed by icosahedra containing one carbon atom at one polar site, i.e. $B_{11}C(CBC)$, is more favored [7]. However, all the simulations also found that the differences in ground state energies between the two polytypes, and many other ones, such as, for instance, a combination of $B_{10}C_2(CBC)$ and $B_{12}(CBC)$ polytypes are small, so that the coexistence of many polytypes must be assumed, as corroborated by some experiments [8-10]. Nevertheless all these calculations, though qualitatively significant on the strong sensitivity of the boron carbide microstructure to limited amount of disorder, bear a little practical meaning. Indeed, it is the Gibbs free energy at the formation temperatures in determining the coexistence of multiple phases and polytypes, and not the zero-point energy as directly provided by DFT calculations which is simply one of the components of the Gibbs free energy.

In order to model the catastrophic failure of boron carbide at high impact pressures our work has been divided in two parts. First, we performed *ab-initio* density functional theory (DFT) simulations in order to consider the role of disorder in boron carbide and calculate the Gibbs free energies of a number of polytypes, showing them to coexist in the actual material. Afterwards, we focused on the consequences of our disorder model to the dynamic mechanical properties. Specifically, we have investigated the stability of B_4C against transitions into icosahedral boron (B_{12}) and free carbon. We show that the catastrophic failure and the related experimental data are consistent with the conversion of one of the coexisting polytypes, $B_{12}(CCC)$ into B_{12} and a-C, while the other polytypes experience similar transformation, if any, only upon much higher impact pressures. In other terms, the critical activation energy for the catastrophic failure is strongly polytype-dependant, as we will discuss in some detail.

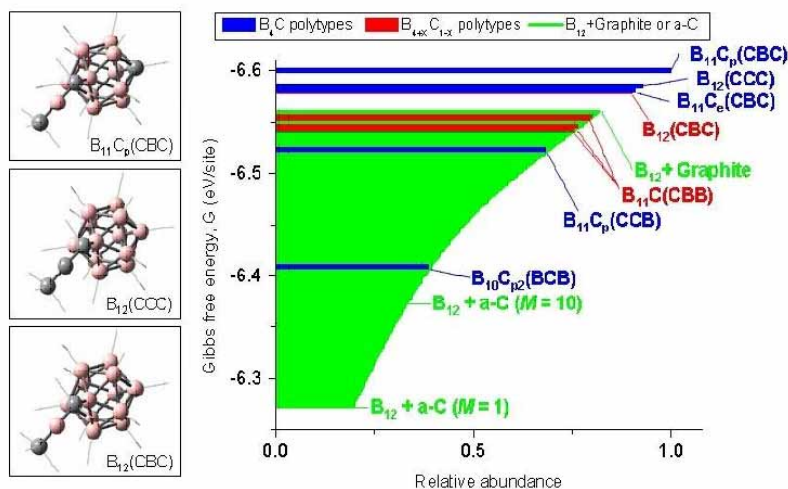


Figure 1. Some examples of Boron Carbide polytypes (left) and their relative abundance (right)

THEORY

Kohn-Sham DFT simulations were carried out using the Gaussian03TM. We used the PBE generalized gradient approximation for the exchange-correlation term, as proposed by J.P. Perdew *et al.* [11]. From the total energies per atom (E_0), we calculate the Helmholtz free energies per site F_i for a number of i -polytypes of $B_{4-x}C_{1+x}$:

$$F \approx E_0 + U_0 + F_{\text{vib}}(T) \quad (1)$$

where U_0 is the zero-point energy, and F_{vib} the temperature-dependent vibrational energy within the quasi-harmonic approximation. For both, we have used a Debye approximation of the vibrational density-of states. From that, the relevant quantity to test a polytype stability, the Gibbs free energy

$$G_i = F + P \cdot V_i, \quad (2)$$

can be easily extracted, where V_i is the unit cell volume divided per number of atoms in the unit cell. Let us notice that, at room pressure, it is almost irrelevant to deal with G and F_i , while the $P \cdot V_i$ term becomes important at high pressure.

Unlike the previous theoretical works, we have used a multi-polytype approach, accounting for the coexistence in the same lattice of different polytypes within a disorder potential. This approach is a rigorous quantification of the empirical chemical laws generally known as (a) Ostwald and (b) Ostwald-Volmer rules [13] indicating that a multi-phase system (a) will pass through all the metastable phases before reaching the ground state, and (b) in presence of several phases, either stable and metastable, the less dense phase is formed first.

RESULTS AND DISCUSSION

Room pressure behavior

In the solid state systems, the Ostwald rules are generally difficult to quantify since phases “interact” in the sense that each one involves some lattice mismatching into others. Therefore, the partition function of the system is very difficult to express. In boron carbide however, important simplification arises from the similarity in lattice constants of all the polytypes allowing them to be treated as a “non-interacting” system.

Under such a model, we get a number of metastable polytypes having Gibbs free energies lying within an energy range comparable to the kinetic energy $k_B T_s$ available at the synthesis temperature T_s . Of course, the synthesis temperature is neither instantaneously nor homogeneously reached. Thus, different regions of the material under synthesis experience energies E with a probability distribution

$$x_i(E) \sim \exp(-G_i/k_B T_s) \quad (3)$$

and a number of polytypes, including those listed in **Fig.1**, are synthesized during growth. The same calculations, coupled with a Debye model and a Birch-Murnaghan equation of states are also used to extract the elastic constants of the materials between room pressure and 40 GPa. They are found to be in agreement with those reported by Lee *et al.* [14] and experimentally measured by McClellan *et al* [15] with little dependence on the polytype.

Behavior under high pressures

Let us first observe that the connectivity of the icosahedral sites is very high, each one of them being connected with other 6 sites, 5 of them pertaining to the icosahedron. We therefore expect very high activation energy to extract an atom from the icosahedron. Our simulations show that the extraction energy is indeed higher for a polar site than for an equatorial one while only little activation energy is required to swap sites within a chain or an icosahedron. This sheds light on the transition path involved by the segregation of $B_{11}C(CBC)$ into separated phases of rhombohedral B_{12} and graphitic C. Quantification of the most energetically favored transition process, corresponding to the transition scheme in **Fig. 2** can be obtained.

For the sake of simplicity, let us divide it in four steps, each one requiring the overcoming of an activation energy barrier:

- i) Migration of the C site in the icosahedron from a polar to an equatorial site [$B_{11}C_{pl}(CBC) \rightarrow B_{11}C_e(CBC)$];
- ii) Migration of the B site position in the chain from the central to a boundary site [$B_{11}C_p(CBC) \rightarrow B_{11}C_e(BCC)$] with the formation of an electronic defect state;
- iii) Swapping of the equatorial icosahedral C-atom with the boundary B-atom in the chain [$B_{11}C_e(BCC) \rightarrow B_{12}(CCC)$] and finally,
- iv) Coalescence of the as obtained (CCC) chains on the (113) planes, through a rotation of their axis around the [001] vector. This eventually leads the (CCC) chains, already involving carbon planes to finally relax into a hexagonal, graphite-like lattice.

The energy minima between steps i-iv) correspond to the B_4C polytypes in **Fig. 2**. Due to their similarity in force constants, each step can be considered separately and the activation energy of the process will correspond to that of the highest step, hence to the extraction energy of the C_{eq} atom from the icosahedron (step iii). In order to be spontaneous, such an effect requires the icosahedron to become unstable. We stressed icosahedra of different composition at increasing pressures and we found the $B_{12}C_{eq}$ icosahedron, actually the less stable one, to be still stable at $P_1 = 40$ GPa.

We can therefore conclude that $B_{11}C(CBC)$, either with the C site in polar or equatorial position, is at least metastable up to 40 GPa, a value in agreement with the phase transition the experiments of Voegler *et al* [3] set above such values. In contrast, the $B_{12}(CCC)$ polytype does not require any change in the icosahedron structure in order to transform into separated B_{12} and graphitic phases. Its transition pressure P_2 will then correspond to the energy necessary to rotate the (CCC) chains along the [001] vector and align them on the (113) plane. This just requires quite little displacement of the boundary C-atoms in the chain, which may occur at much lower pressures than P_0 .

Actually, when stressing $B_{12}(CCC)$ at increasing pressures we find that it becomes unstable at $P_3(\infty) = 6$ GPa. Such a value is just a little lower than the pressures $p(H_{EL}) \approx 7-8$ GPa occurring behind the shock wave at the failure conditions. Furthermore, the free energy is found to very weakly decrease, from graphite to finite aromatic carbon islands of M rings [16]

$$G(M) \sim 1.62 - 0.29 \cdot M^{-0.2} \quad (4)$$

with little dependency on disorder or island amorphization [16]. Hence weak dependency of P_3 on the disorder is expected, until an almost complete disappearance of the $B_{12}(\text{CCC})$ polytype will occur and the free carbon phase is easily produced as an amorphous phase due to shear induced amorphization during the impact.

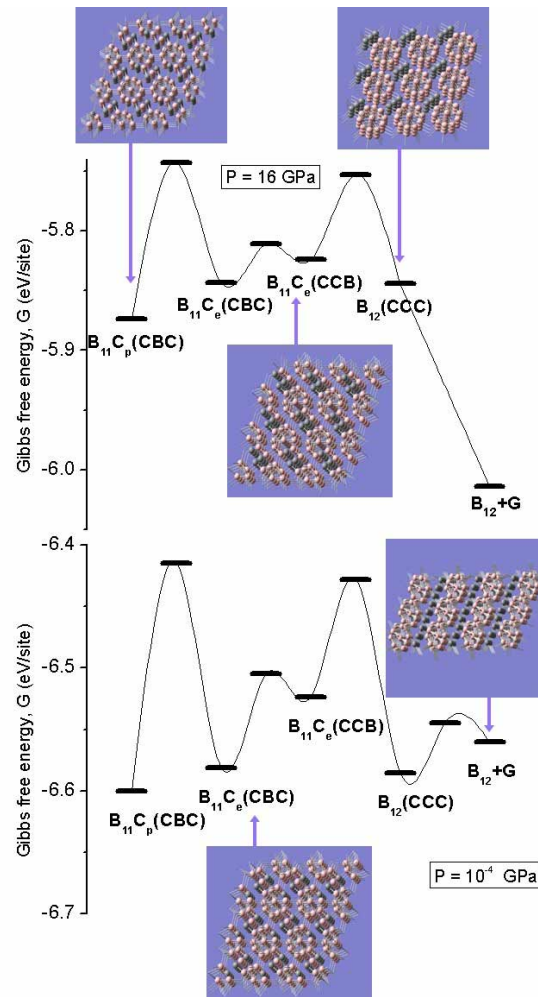


Figure 2. Sketch of the reaction steps i-iv) (see text) at room pressure (bottom) and 16 GPa (top)

Comparison with electron microscopy experiments

We have also investigated the most stable configuration of a segregated B_{12} -free carbon phase, finding that it consists in carbon layers oriented along the (113) plane mixed with layers of B_{12} icosahedra. This is in excellent agreement with the TEM images of Chen *et al* [4] (**Fig. 3**) and gives a full explanation of the relationship between the catastrophic failure of boron carbide and the appearance of an amorphous carbon amount as little as is the $B_{12}(\text{CCC})$ concentration in the starting material. Appearance of bands of segregated free carbon and icosahedral B_{12} , having little elasticity and no plasticity, immediately terminates the elastic range of boron carbide preventing additional plastic range even if the residual non-segregated majority portion of the material would allow it.

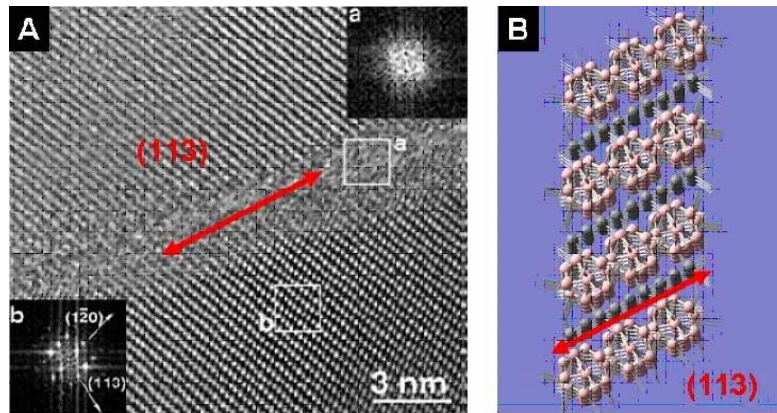


Figure 3. Comparison of (a) TEM image [4] and (b) simulated structure after shock.

CONCLUSIONS

In summary, our results solve the longstanding question on the failure of boron carbide just above the Hugoniot elastic limit. We have shown that little amounts of a minority polytype, $B_{12}(\text{CCC})$, is responsible for the instability of the whole material at 6 GPa which is close to that occurring below the shock wave at the Hugoniot conditions. Therefore, the absence of plasticity is *not* an intrinsic material property, but simply of the tiny bands of amorphous carbon and boron icosahedra in which $B_{12}(\text{CCC})$ transforms.

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