Shock-induced reaction synthesis of cubic boron nitride

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Here, we report ultra-fast (0.1–5 μs) shock-induced reactions in the 3B-TiN system, leading to the direct synthesis of cubic boron nitride, which is extremely rare in nature and is the second hardest material known. Composite powders were produced through high-energy ball milling to provide intimate mixing and subsequently shocked using an explosive charge. High-resolution transmission electron microscopy and X-ray diffraction confirm the formation of nanocrystalline grains of c-BN produced during the metathetical reaction between boron and titanium nitride. Our results illustrate the possibility of rapid reactions enabled by high-energy ball milling possibly occurring in the solid state on incredibly short timescales. This process may provide a route for the discovery and fabrication of advanced compounds. Published by AIP Publishing. https://doi.org/10.1063/1.5017836

A shockwave passing through a porous material results in a drastic increase in both pressure and temperature, which can induce solid-state polymorphic phase transformations and shock-induced chemistry. Detonation of a solid explosive is the most common example of shock induced chemistry, where a shock wave propagates at a steady velocity and reaction travelling a short distance behind the shock sustains the propagation though acoustic feedback from the gas phase products. This rapid reaction is typically only possible in gas producing systems of energetic compounds; however, there has long been interest in whether a reaction can occur within a shockwave for a condensed phase reaction and form useful solid products.

Shock-induced reaction synthesis (SRS), which involves a combination of self-sustained, high-temperature (2000–3000 K) reactions and a shock wave, represents a unique method to produce advanced materials. SRS has been applied to many reactive systems, resulting in the synthesis of a significant number of solid compounds including carbides, borides, silicides, and aluminides.

However, fundamentally, there are two distinguishing cases for SRS. In the first case, the shock wave heats the material enough that, after pressure release, the material reacts through a deflagration combustion wave with a characteristic reaction time on the order of several milliseconds. Numerous works have demonstrated the existence of such a route through recovery experiments, showing product formation after shock loading. In the second case, a gasless reaction takes place directly in the shockwave within several microseconds. In general, two methods have been suggested to prove the existence of such ultra-fast gasless reaction. The more common approach involves an in-situ measurement and comparison of the shock Hugoniot for reactive and inert mixtures which allows an inference of reaction occurring on the timescale of the shockwave.

The second approach is through the synthesis and recovery of a metastable phase, which can form only under high-pressure conditions. Throughout the history of SRS studies, this second approach has not been applied. The precise reaction conditions become even more intriguing for reactive systems with an adiabatic combustion temperature (Tad) below the melting points of all precursors, intermediates, and final products, a class of reactions known as the solid flame. For such systems, solid-state mechanisms of mass transport are suspected to govern the reaction process. The boron (B)-titanium nitride (TiN) system, investigated in this work, leads to the formation of boron nitride (BN) and adheres to the prerequisites for the solid flame class of reactions.

The high pressure behavior of boron nitride (BN) has fascinated researchers since the middle of the last century. Being the second hardest known material, cubic BN (c-BN) possesses superior chemical and thermal stabilities (stable up to 1650 K), as compared to diamond (stable up to 950 K), is rarely found in nature, and forms only under high-pressure and high-temperature (high P/T) conditions. As a result, c-BN does not form below 6 GPa in quasistatic conditions and is not expected below 12 GPa under shock loading. It is important to note that a single shock loading of the hexagonal phase of BN (h-BN) results in a martensitic transformation to wurtzitic BN (w-BN) and not c-BN. The thermal stability of c-BN makes it less susceptible to reversion to the graphitic form due to residual heat upon unloading as compared to diamond. This feature makes it a promising phase to use as an indicator to determine if reaction and product phase formation occur during the shock.

In this work, we provide direct evidence for the formation of c-BN as a result of shock-induced reactions using TiN as the nitrogen source for B. By this observation and
taking into account that c-BN can be formed only at high P/T, we support the claim that under certain conditions, solid-sate reactions (solid flame) may occur at ultra-fast rates in the time span range of 0.1–5 µs.

The reactive mixture of B and TiN at a 3:1 molar ratio was selected to synthesize c-BN under shock loading. Thermodynamic calculations show that BN and titanium diboride (TiB₂) are the equilibrium products for this exothermic reaction

\[ 3B + TiN \rightarrow BN + TiB_2. \] (1)

The calculated \( T_{ad} \) for the system is 1903 K, which is lower than the melting points of B (2353 K), TiN (3203 K), and TiB₂ (3503 K), as well as the dissociation temperature of BN (3246 K). This suggests that the considered 3B + TiN mixture may behave as a solid flame system. Studies of this system have shown that, under locally initiated impulse heating, the reaction front exhibits oscillatory propagation, and the analysis of the product phase through XRD shows h-BN and TiB₂ to be the reaction products.²⁹

It was previously shown that direct SRS of BN from a virgin mixture of commercially available micron size beta-rhombohedral (β-r) B and TiN powders is essentially impossible due to the high effective activation energy associated with mass diffusion kinetics for this solid-state reaction.²⁹ To overcome these difficulties, the reactivity was enhanced by the preparation of nanostructured composites through high-energy ball milling (HEBM) (see supplementary material for material preparation).

XRD performed on the powder produced by this intensive mechanical treatment [Fig. 1(a)] reveals only TiN and β-r B phases, indicating that no other crystalline phases formed during the HEBM process. Electron micrographs show that the produced powder consists of micron scale composite particles [Fig. 1(b)], which consist of nanoscale (5–500 nm) crystallites of B suspended in a fine (10–100 nm) TiN matrix [Fig. 1(c)]. These nanostructured B/TiN composite particles are highly reactive due to the significant increase in the interfacial contact area and reduced diffusion distance as a result of the milling process [Fig. 1(d)]. The parameters

\[ \frac{\sqrt{A}}{l_{C24}} = 0.8–1.0, \quad \frac{C_{24}}{l_{C24}} = 0.8–1.0, \quad s = 4–5 \text{ µs} \]

The pulse width \( \Delta t \) is estimated to be \( \Delta t = 5s = 4–5 \) µs. This result is in line with the 1–2 µs pulse width observed in the simulations (Fig. S2).

Both XRD and SEM/TEM data confirm the formation of c-BN as a result of SRS. We examined the crystallographic parameters (d-spacing, Miller indices, reflection angles, and relative intensities) of the initial compounds (β-r B and TiN) and possible phases (TiB₂, TiB, h-BN, and c-BN) resulting from the reaction (1) (Table S3). The detected strong TiB₂ peaks indicate that reaction occurred as a result of the shock-wave. In addition to TiB₂ peaks, there are two peaks that can be attributed to the formation of BN phases, including c-BN [inset of Fig. 2(a)]. These peaks were found within samples taken from multiple cross-sections across several experiments at locations along the length of the recovery capsule.
indicating repeatable formation of c-BN. However, due to the low intensities of the BN peaks, further characterization was required to verify the formation of c-BN. It should be noted that the low intensities of B and BN peaks are associated with their low scattering factors and weight fractions as compared to the Ti-based phases and the small size of the synthesized crystals. As can be seen in the XRD of the initial material, despite the large volume fraction, the B peaks are substantially weaker than TiN peaks [Fig. 1(a)]. As a result, detailed structure and composition analyses of the materials were performed by electron microscopy based methods to verify the composition of the recovered material.

Figure 2 shows typical SEM (b and c) and STEM (d) images of a reacted particle. The particle has been cross-sectioned using the focused ion beam (FIB) slice and view technique to observe its structure in the reflection mode. Based on the SEM contrast, one can suggest the presence of four phases in the product material where light phases (B and BN) appeared with darker contrasts, while the phases with higher average atomic mass (e.g. TiN and TiB₂) have lighter contrasts. EDS analysis with nm scale spatial resolution in the STEM mode (Fig. S4) confirmed the elemental composition of the phases (Table S4).

To analyze the morphology at the atomic level and crystal structure of the synthesized phases, high-resolution TEM (HRTEM) has been employed. Typical TEM images of a sample that has been subjected to the shock wave are shown in Fig. 3. The analysis of over ten regions, where complete reaction occurred, reveals that all consists of the three phases: TiB₂, h-BN, and c-BN. The h-BN nanosheets are present in between the randomly oriented TiB₂ crystallites, while c-BN nanocrystals are primarily observed on the surface of the TiB₂ crystallites [see the inset in Figs. 3(a) and 3(b)].

During TEM imaging, the TiB₂ crystallite has been placed in a low index orientation, e.g., close to the ⟨001⟩ zone. This low zone orientation has been critical for reliable identification of c-BN since other possible phases in the sample have d-spacings that are close (within 4%). HRTEM images have been used to identify the d-spacing with the required accuracy (down to 1%). It can be seen from Fig. 3(b) that 4-fold symmetry is recognizable.

It is known that the lattice parameters (d-spacing) of unstrained (perfect) crystals can be determined from HRTEM images with a relatively high accuracy of 0.2%. The procedure typically involves the analysis of intensity profiles taken from HRTEM images of the crystal structures. However, the accuracy of this method decreases in the case of nanocrystals. Figure 4 shows an HRTEM image of a nanocrystal in a low zone crystallographic orientation. The averaged intensity profiles were used to measure the d-spacing in both horizontal and vertical directions to increase the signal-to-noise ratio. To exclude the systematic error associated with some minor variations in magnification, the magnification for a particular HRTEM image with one of the nanocrystals in question was corrected by the measurements of the d-spacings of known crystal structures. In this work, h-BN and/or TiB₂ were used as reference crystals to determine the correction factor. For example, the (0002) d-spacing of h-BN crystallites, measured on the same HRTEM image for calibration, appeared to be 0.345 ± 0.039 nm, instead of 0.333 nm (the database value), yielding a calibration factor of 0.96. The corrected d-spacing value for this nanocrystal was estimated to be 0.183 ± 0.014 nm, which fits within 1% accuracy of 0.181 nm, the (200) d-spacing of the c-BN crystal structure.

In order to provide further confirmation that the crystallites are the c-BN phase, we used JEMS to simulate a HRTEM image and an atomic model of c-BN crystallites oriented in the ⟨001⟩ zone [Fig. S5(a)]. The simulated atomic
columns of B atoms [Fig. S5(b)], which correspond to the white contrast on the HRTEM image taken at Scherzer focus [Fig. S5(c)], fit well with the c-BN structure.

Thus, it is clearly shown through XRD, HRTEM, and TEM modeling that c-BN has been formed through reaction between B and TiN after the shockwave (15–20 GPa) was applied to the initial reactive nanostructured media. Since the formation of c-BN requires high P/T, there is no doubt that we have observed shock-induced reaction, i.e. the products were formed in the time span of several μs. A thorough discussion of the expected temperature limits and their method of calculation is given in the supplementary material with the limiting behavior summarized here. The equilibrium shock temperature at pressure can be estimated by calculating the energy deposited through shock loading, $\Delta E = 1/2$ $P\Delta V$, and finding the temperature through integration of non-constant specific heats. Using data for β-B and TiN from the NIST Webbook, the equilibrium shock temperature is found to be between 1600 and 2200 K. The lowest melting point in the B-TiN system is for B at 2350 K, which can be estimated for a perfect crystal of TiN based on their respective mass fractions, with G being the energy deposited through shock loading, $E/2(1 - \nu)$, the maximum shear strength in a perfect crystal of TiN is found to be between 3 and 3.3 GPa. This suggests that any residual stress would be below the necessary 6 GPa to drive formation of c-BN, particularly considering that this would be the strength of a dislocation-free crystal. These results show that HEBM enables ultra-fast chemical reactions, which take place on the timescale of several microseconds, resulting in the formation of a high pressure polymorph (c-BN).

See supplementary material for additional experimental and computational methods.

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