Self-propagating high-temperature synthesis of high-porous boron nitride

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Nitrogen pressure and gravity conditions were found to affect the density, sample elongation and microstructure of foam boron nitride synthesized from borane hydrazine.

The self-propagating high-temperature synthesis (SHS) of highly porous compounds is of current interest.[1,2] The synthesis is more efficient in the presence of gasifying agents that form an intermediate melt layer in the combustion wave. The evolution of gas promotes the formation of a high-porous end-product. For the first time, the effect was observed for the Ti–B system.[3,4] By this technique, TiB with a porosity of 97% (so-called foam titanium carbide) was synthesised[5] under microgravity conditions (during parabolic flights).

In this work we performed SHS to obtain highly porous boron nitride. Borane hydrazine, a well known blowing agent, was used which decomposes according to the scheme:

$$BH_3N_2H_4 \longrightarrow BN + 0.5N_2 + 3.5H_2,$$

yelding BN, the only condensed product. The evolving gas (4moles per mole of $BH_3N_2H_4$) strongly frothes up the condensed product and, in this case, there is no need for a gasifying additive. Selected physical properties for $BH_3N_2H_4$ are as follows: molecular weight, 45.88; melting point, 58–60 °C; density, (20 °C) 0.962 g cm^{-3}; yield of BN, 0.541.

Burning velocities in $BH_3N_2H_4$ (at a pressure of 20–100 atm) were determined earlier by Manelis and co-workers.[7,8] We focused mainly on the formation and characteristics of BN prepared over a wider range of nitrogen pressure (50–3000 atm).

Cylindrical samples with a density 0.8–0.9 g cm^{-3} (7 mm in diameter, 10 mm long) were placed into a silica tube (8–9 mm in diameter, 450–500 mm long). Combustion was initiated using an electrically heated spiral wire at the end of the sample. The ignited end was rigidly fixed to the tube and remained immobile during combustion. The sample expanded outwards along the tube. In this case, the expanding combustion zone shifted the charge rather than the combustion product. This ignition geometry was most suitable because it did not restrict expansion of the sample. Tubes were placed vertically. To determine the effect of gravity on the process,[9] combustion was initiated either from the top or from the bottom of the sample. Experiments were carried out in sealed vessels ($V = 4$ dm^3; $P = 50$–3000atm). The following parameters of the burnt sample were mesured: length, diameter, density, porosity and weight loss. In some cases, the composition and structure of the combustion product were also determined.

We observed a drastic increase in the sample volume upon combustion (up to a factor of 30). In this case, the sample diameter remained unchanged and its length markedly grew. The silica tubes with the charge and combustion product are shown in Figure 1 (combustion occurred at $P = 50$ atm; at $P < 50$atm the combustion was unreliable and a continuous layer of combustion product did not form, therefore most of the experiments were performed at $P > 50$atm). Figure 2 shows the relative elongation $\varepsilon = (L_{pr} - L_0)/L_0$ (where L_{pr} and L_0 are the lengths of the final and starting sample, respectively), product density ρ_{pr} and its porosity Π_{pr} as a function of nitrogen pressure P. The values ε and Π_{pr} decrease, while ρ_{pr} increases with increasing P. Unusual values of these parameters deserve special mention: for $P = 50$atm, $\varepsilon = 28$, $\rho_{pr} = 0.011$–0.012gcm^{-3}, $\Pi_{pr} = 99.54$–99.46%; at $P = 3000$ atm, $\varepsilon = 3$–4, $\rho_{pr} = 0.085$–0.095 g cm^{-3}, $\Pi_{pr} = 96.25$–95.86%. Even at high pressures, the samples expanded markedly. At $P \leq 1000$ atm, the parameters of the combustion product were identical. When the process was carried out at $P = 1000$–3000atm, the parameters were slightly different. Weight loss was virtually independent of pressure: upon ignition from the top, it was 0.38–0.55 (average 0.465) and upon ignition from the bottom, it was 0.32–0.45 (average 0.38) (theoretical value is 0.46). The combustion product did not have uniform density.

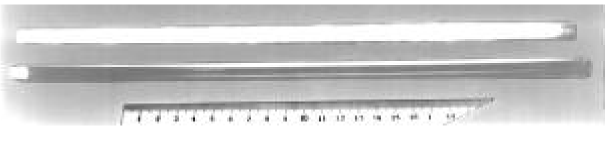


Figure 1 Silica tubes with the charge (below) and the combustion product (above) at $P = 50$ atm (N_2).

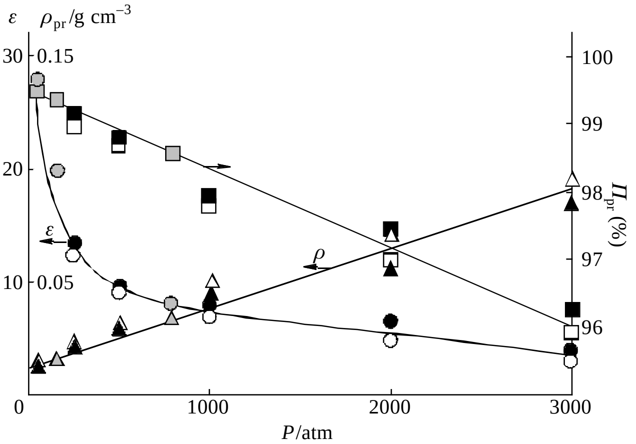


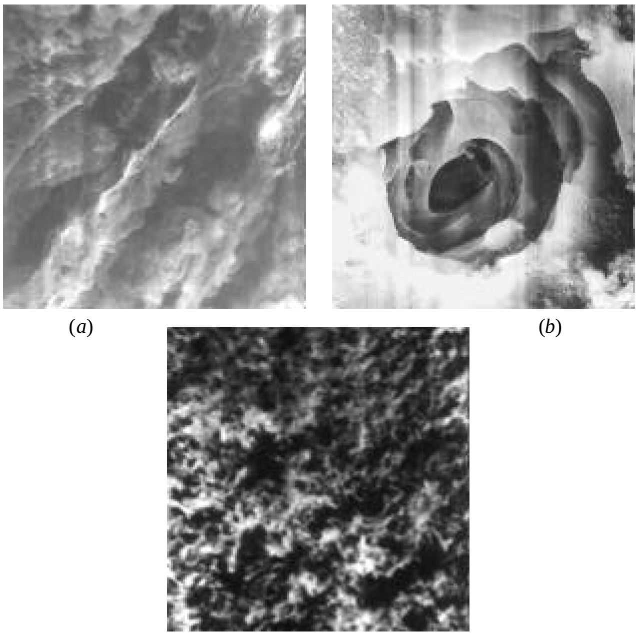
Figure 2 Values of ε, ρ_{pr}, Π_{pr} as function of P: ○ – initiation from the top; ● – initiation from the bottom; ◍ – data points were the same for both ignition geometries.

Investigations on the combustion processes accompanied by extremely high volume increments are in progress.

Chemical analysis shows that the final condensed product of borane hydrazine combustion is BN. Found (%): B, 42.01; N, 51.5; calc. (%): B, 43.5; N, 56.5. XRD data suggest that BN has an amorphous cotton-like structure. Electron-probe microanalysis (Superprobe-JEOL) showed that the combustion product is identical to the BN standard. The microstructure of BN was found to depend on ambient pressure. At $P > 500$ atm, the product was flocculent with fibres 3–10 μm thick and above 150 μm long. The foam surface of BN exhibited craters (80 μm in diameter) on the front of the sample. At $P = 1000$–3000atm, the structure was more compact and resembled solidified foam

Table 1 Density and porosity of the combustion product compared to sample length ($P = 50$atm, $L_{pr} = 290$mm).

Sample length/mm	Ignition from the top		Ignition from the bottom	
	ρ_{pr}/gcm^{-3}	Π_{pr}/%	ρ_{pr}/gcm^{-3}	Π_{pr}/%
0–80	0.0236	98.97	0.0199	99.13
80–160	0.00405	99.82	0.0112	99.51
160–290	0.00524	99.77	0.0071	99.69



(*a*) (*b*)

(*c*)

Figure 3 Surface relief of foam boron nitride: (*a*) $P = 150$atm N_2; (*b*) $P = 500$atm N_2; (*c*) $P = 1000$atm N_2.

with a pore size of 1 μm (Figure 3). Therefore, we managed to prepare BN with unique porosity (96–99.5 %) exceeding that of other well-known highly porous materials.

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