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Phase Transformation of Turbostratic BN by Shock Compression

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Using two kinds of turbostratic BN (tBN) powders with different degrees of turbostratic disorder, the shock-induced phase transformation has been investigated through recovery techniques in a pressure range 12−36 GPa. Recovered specimens were investigated by X-ray diffraction and electron microscopy. It is shown that the temperature plays an important role in promoting the tBN→cBN (zincblend-type BN) transformation and that the transformation efficiency depends strongly upon the degree of turbostratic disorder of the starting tBN. It is deduced from the results that the mechanism of the shock-induced phase transformation of tBN to cBN is a direct conversion through diffusion process and that tBN is most likely the intermediate phase via which shock-induced phase transformation of rBN to cBN proceeds under relatively low shock pressures (<50 GPa).

Introduction

Boron nitride (BN) obtained under atmospheric pressure has a graphite-like layer structure. Two kinds of layer polymorph are known with different stacking sequence of layers. One is hexagonal BN (hBN) which is thermodynamically stable with a two-layer sequence; the other is rhombohedral BN (rBN), which is metastable with a three-layer sequence.[1] Under high shock pressures (>50 GPa), hBN and rBN are converted with high yields into their high-pressure phases, namely, wurtzite BN (wBN) and cubic BN (cBN), respectively.[2,3] These transformations are believed to be a diffusionless type (martensitic transformation). However, recent experiments with static high pressures and also relatively low shock pressures (≤20 GPa) indicated that hBN and wBN are produced from rBN.[4−9] Thus the transformation process is not as simple as has been believed.

tBN may be considered as an intermediate form between the amorphous and the crystalline states. Compared with hBN and rBN, the stacking of layers of tBN is less periodic and interlayer distances are less uniform. Layers of tBN may be random in translation and may be tilted and/or rotated about the *c* axis. Depending upon the synthetic method employed, the degree of turbostratic disorder can be significantly different. Since tBN has no corresponding high-pressure phase, it is expected that tBN is converted into the therodynamically stable high-pressure phase, i.e., cBN, with rearrangement of B and N atoms under high pressures. In this case, the transformation would have to be diffusional and should require relatively high temperature as compared with transformations of crystalline BNs through diffusionless processes.

It is generally believed that shock compressions cannot induce diffusional transformations effectively because of its short duration. It is interesting to see if the tBN→cBN phase transformation is induced by shock compression, and if it happens how the transformation efficiency depends upon various factors such as shock temperature, pressure, and turbostratic degree. If the transformation is of diffusion type, it is expected that the transformation efficiency of tBN to cBN should strongly depend upon the degree of turbostratic disorder. Under static high pressures, it is reported that the rate of the tBN → cBN transformation is faster than that of the BN_{ord} (ordered-layer lattice form)→cBN transformation.[10] It is also reported that the transformation yield of hBN→wBN under shock compression is a function of disorder of hBN.[11] It is worthwhile to study the transformation of tBN for elucidating the transformation mechanism of crystalline BNs because when a diffusional transformation such as rBN→wBN takes place, there must exist a disordered phase as an intermediate state.

In the present study, we prepared tBN from a B−N−C precursor obtained by reducing H_3BO_3 with urea and saccharose.[12] This tBN, designated as βtBN in the following text, is unique because there exists a relatively long-range ordering (>50 nm) with respect to the interlayer distance. The results of shock recovery experiments are compared with the previous results of

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Table 1. Shock-Recovery Conditions of 3 wt % tBN−97 wt % Cu

run[a]	impact velocity[b] (km/s)	bulk density (g/cm^3)	pressure[c] (GPa)	temp (°C)
368β	1.60	6.03	20	1600
369β	(1.85)	8.06	37	900
389β	1.27	5.39	12	1400
434β	(1.80)	7.05	30	1500
298α	(1.50)	8.31	31	600
281α	1.35	5.80	15	1500
334α	1.78	7.28	30	1400

[a] Starting material; β = βtBN, α = αtBN. [b] Values in the parentheses are estimated values. [c] First shock pressure.

ordinary tBN, designated as αtBN in the following text, which was prepared from a mixture of sodium tetrahydroborate and ammonium chloride.[13]

Experimental Section

To synthesize a B−C−N precursor, one part of boric oxide, 2.2 weights parts of urea, and various ratios of saccharose were mixed and heated in a Pyrex beaker at 240 °C for 2 h under a pressure of 1 kPa. The obtained B−C−N precursor was heated at 2200 °C under nitrogen atmosphere for 24 h and then carbon was removed by oxidation treatment. Finally B_2O_3 was removed by ethanol to obtain tBN. tBN synthesized this way contains approximately 1 wt % of carbon and 2 wt % of oxygen. Studies on the effects of impurities upon the transformations of BN under static high pressures have been reported.[14−17] The tBN powder was mixed with copper powder (97 wt %) and pressed into stainless steel containers (density 5.3−8.3 g/cm^3). The amount of saccharose (28−55 wt %) did not make much difference in the results.

Shock recovery experiments were carried out with a 30 mm bore propellant gun at NIRIM.[18] The shock pressure and temperature were estimated using the impedance match method from the measured impact velocity of projectile, assuming that the thermal equilibrium is reached within the mixture. The Hugoniot for the mixture was approximated by that of copper powder with the same density. Successfully recovered containers were cut open, and specimens were immersed in an acid mixture of HNO_3 and HCl to dissolve the copper matrix. The recovered BN specimens thus obtained were examined by powder X-ray diffraction and electron microscopy.

Results and Discussion

Experimental conditions are summarized in Table 1. The XRD patterns of the starting βtBN and a series of shock recovered specimens are shown in Figure 1. The XRD pattern of the starting βtBN shows a couple of features characteristic of the tBN employed in this study. The reflection peak at 41.6° has a long tail that corresponds to the two-dimensional lattice reflection t(10), the profile expected from a turbostratic structure.[19] The sharp feature of this peak and the reflection peak at ~53° (the second-order reflection of the interlayer distance) are not seen in XRD patterns of αtBN (see Figure 2). The full width at half-maximums (fwhm) of these peaks (Figure 1) suggest that *Lc*, *La* > 50 nm. Here *Lc* is the average stack height of a layer group and *La* is the average layer diameter.[20]

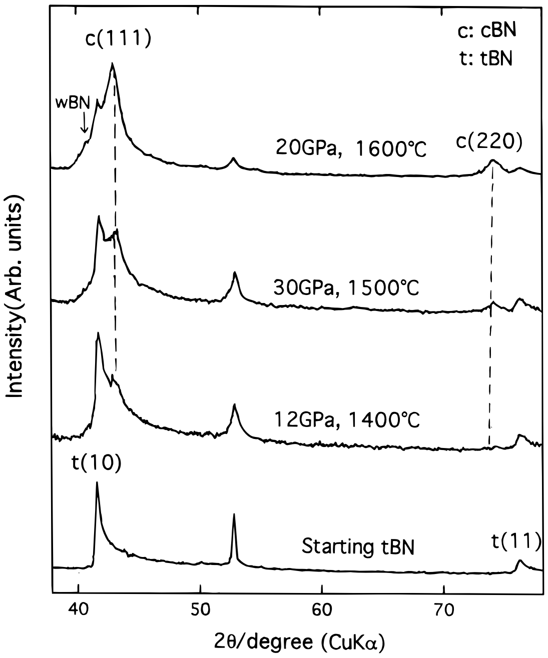

Figure 1. X-ray diffraction patterns of the starting βtBN and shock-recovered samples from various shock conditions (pressure: first shock pressure).

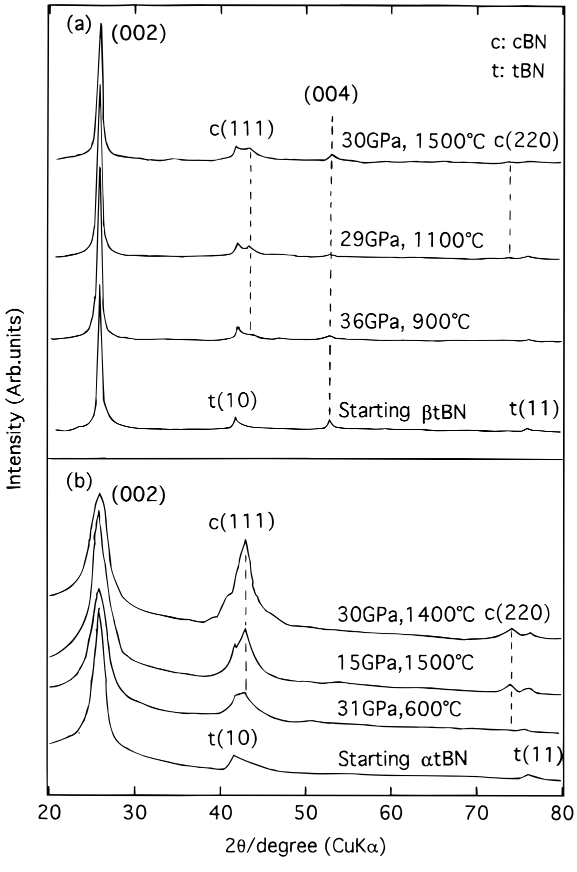

Figure 2. X-ray diffraction patterns of the starting tBN and shock recovered samples. (a) tBN with lower turbostratic degree (βtBN). (b) tBN with higher turbostratic degree (αtBN).

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Table 2. tBN→cBN Transformation Efficiency[a]

βtBN (more ordered; Lc, La >50 nm)		αtBN (less ordered; Lc ~4 nm, La ~ 8 nm	
$T-P$ conditions (first shock)		$T-P$ conditions (first shock)	
starting (ambient)	0 (22.4%)[b]	starting (ambient)	0 (14.4%)[b]
1400 °C, 12 GPa	4.7 (27.1%)	600 °C, 31 GPa	17.8 (32.2%)
900 °C, 36 GPa	6.4 (28.8%)	1500 7C, 15 GPa	21.5 (35.9%)
1500 °C, 30 GPa	25.8 (48.2%)	1400 °C, 30 GPa	62.8 (77.2%)
1600 °C, 20 GPa	36.6 (59.4%)		

[a] See text for the definition of transformation efficiency. [b] Values in the parentheses are the ratios $R = I(2\theta \sim 43°)/I(002)$.

In Figure 2, XRD patterns of the starting tBN and shock-recovered specimens with various shock loadings are shown for the two kinds of tBN. It is seen that the XRD patterns of starting tBNs have lines of the type ($00l$) and ($hk0$) only and the general lines (hkl) are missing. These facts indicate a random layer structure, i.e., turbostratic structure.[20] Here, in the figure, reflection lines with (002) and (004) are indexed in terms of hexagonal BN (hBN) and the index $t(hk)$ correlates with ($hk0$) of hexagonal BN. The peak positions of (002) lines of starting tBNs are shifted toward shorter angle (larger average spacing between layers) compared with that of hexagonal BN, which is expected when the stacking of layers become less ordered.[20] On the other hand, one of the main differences between αtBN and βtBN is that a relatively strong (004) reflection appears in the XRD pattern of βtBN, while the (004) reflection is very weak in the XRD pattern of αtBN. Furthermore, the (002) line of αtBN is much wider than that of βtBN (by a factor of >5), and the shape of the (002) line of αtBN is shaded toward shorter angle. These facts suggest that the spacings of layers of αtBN are more random than those of βtBN. Therefore the βtBN employed in this study is quite unique compared with the ordinary tBN (αtBN) in respect that the layers are well developed and there exists a long-range ordering with respect to the interlayer distance. The structural characteristics of βtBN may be stated as follows: Layers are arranged parallel and equidistant but random in translation parallel to the layers and rotation about the normal. On the other hand, the ordinary αtBN synthesized from a mixture of sodium tetrahydroborate and ammonium chloride consists of small grains and is believed more disordered in every respect, i.e., interlayer distance, translation parallel to the layers, tilt and rotation about the normal. *Lc* and *La* of this tBN are estimated to be around 4 and 8 nm, respectively.

It is seen in Figure 1 that the shock-induced transformation (tBN→cBN) increases with increasing shock loading, especially with shock temperature. If the shock-induced tBN→cBN transformation is of diffusion type, the transformation efficiency should also strongly depend upon the original atomic arrangement of the starting tBN, turbostratic degree in other words, in addition to other important factors such as temperature. Transformations of diffusion type involve a rearrangement of atoms (reconstruction of the original lattice) often with breaking some of the original bonds and creating new bonds. If the shock-induced transformation of tBN to cBN is diffusional, less-ordered tBN should have a higher transformation yield than more ordered tBN because when an ordered phase transforms to a different phase through a diffusional process, it must pass through some kind of disordered state on its way to the final phase. Less-ordered tBN with smaller grains should be more favorable for such a diffusional transformation than more ordered tBN with larger grains. This is in good accord with our experimental results which show that less ordered tBN (αtBN) is converted into cBN more efficiently than more ordered tBN (βtBN).

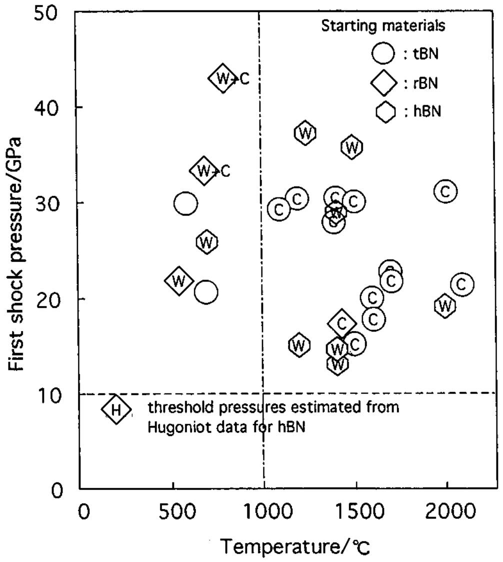

Figure 3. Relations between shock-induced $P-T$ conditions and obtained crystalline phases (C: cBN; W: wBN; H: hBN) from starting hBN, rBN, and tBN. For example, © means that tBN as the starting material was shock-compressed at the corresponding pressure and temperature with a significant amount of cBN found in the recovered sample.

Figure 2 shows that the width of the diffraction peak (002) was increased by shock compression which indicates that smaller grains were produced. It is clearly seen that the cBN yield is much more sensitive to the shock loading for αtBN (lower portion of Figure 2) than that for βtBN (upper portion). To see this point a bit more quantitatively, peak intensities of (002) and c(111) were compared. The ratio $R = I(2\theta \sim 43°)/I(002)$, contains information about the transformation efficiency (tBN→cBN) because the intensity increase of the peak at $2\theta \sim 43°$ is mainly due to cBN (Figures 1 and 2). Here I represents the area intensity of the peak and $I(2\theta \sim 43°)$ includes both t(10) and c(111) peaks. The quantity defined as the difference between R(shocked tBN) and R(starting tBN) should give a rough estimate of the transformation efficiency (Table 2). It should be noted that the estimates of transformation efficiencies defined this way are not absolute transformation efficiencies but relative transformation efficiencies. It is seen from Table 2 that, for similar shock loadings, the transformation efficiency is much higher (by a factor of 2−3) for αtBN than for βtBN, which is consistent with the expected trend from transformations of diffusion type.

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In Figure 3, the relation between the phases present in the shock products and estimated shock-induced P−T conditions is shown with our previous results of hBN and rBN. Whether or not appreciable amount of cBN exists in the recovered tBN was judged by observing the XRD (220) line of cBN at 74.2° because the most intense (111) line of cBN is overlapped with tBN(10), making it more difficult to identify the c(111) line than the c(220) line when the intensity becomes weaker. tBN indicated by circles is transformed into cBN in the temperature range above 1000 °C, but little crystalline phase was observed in the temperature range below 1000 °C. On the other hand, it is seen in the figure that hBN is converted into wBN even at a low temperature if the pressure is high enough, which is a characteristic of martensitic transformation. From these facts, it is understood that the temperature plays a more crucial role in promoting tBN→cBN transformation than the pressure, which also supports that the tBN→cBN transformation is of diffusion type.

In Figures 1 and 2, no crystalline phases other than cBN are observed for any shock-loading conditions except a trace of wBN. wBN is not converted into cBN unless intensively shocked.[21,22] This may suggest that tBN is converted into cBN without passing through intermediate crystalline phase(s) such as rBN.

In the previous paper on rBN by two of the present authors,[4] it was proposed that rBN is transformed into cBN through two paths: (i) direct conversion by relatively strong shocks (martensitic) and (ii) indirect, kinetically controlled conversion via intermediate phase(s) by relatively weak shock loadings ($P < 50$ GPa), possible intermediate phases being hBN, tBN, and wBN. It is known from both static[6] and dynamic[4] compression experiments that turbostratic structure is obtained from rBN at low pressures. From the present study, it was found that tBN is converted into cBN under relatively weak shock loadings, whereas it is known that hBN and wBN are not converted into cBN under such shock loadings.[4] Therefore, if the phase transformation of rBN to cBN involves an intermediate phase for shock loadings with relatively weak pressures, tBN seems to be the most probable candidate. It should be emphasized, however, that this does not mean that the path rBN→tBN→cBN is the only path to cBN from rBN under relatively weak shock loadings. The direct transformation of rBN to cBN (martensitic transformation) is probably taking place simultaneously.

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