INVESTIGATION OF THE STRUCTURE OF SHOCK WAVES IN BORON NITRIDE AND GRAPHITE IN THE REGION OF POLYMORPHOUS TRANSFORMATION

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Investigations of shock compressibility and of the products of shock compression of graphitoid boron nitride [1-4] and graphite [5-8] have shown that these substances in a shock wave undergo transformation to close-packed modifications with a tetrahedral coordination of atoms. The purpose of this paper is to show the feasibility of investigating the kinetics of these transformations. If the characteristic relaxation time of the process is comparable with the loading time of the sample, then the kinetics of the process can be determined by analyzing a series of pressure profiles p(t) or the mass velocity inside the sample during shock compression [9]. The diagram of the experiments for recording the growth of a pressure pulse in boron nitride and graphite under conditions of single and multistage shock compression is shown in Fig. 1. A shock wave with an initially rectangular pressure profile passes in the sample 1 in the direction shown by the arrows through an aluminum or Perspex screen 2. Multistage compression of the sample was effected by the shock waves having passed through and then being reflected from a copper or aluminum barrier 3. Manganin probes 4 [10], located at the screen–sample and sample–barrier interfaces, and also in the center section of the sample, were used for recording the pressure profiles. The samples had a diameter of 120 mm and an overall thickness of 5-15 mm. The density of the boron nitride samples varied from 1.57 to 1.80 g/cm^3 and that of the graphite samples from 1.80 to 1.97 g/cm^3. The probes were prepared by etching from manganin foil with a thickness of 30 μ and had an area of $\sim 7\times 7$ mm^2 and a resistance of 2.5 to 3.5 Ω. The probes were separated from the surfaces of the sample, screen, and barrier by insulating Teflon inserts. The overall thickness of a probe with its insulation did not exceed 0.17 mm. The samples were loaded by the impact of an aluminum plate of thickness 7-10 mm. Explosive propellant devices [11] were used to accelerate the plates. In a number of the experiments with boron nitride samples of increased thickness, a compression pulse with an approximately rectangular profile was formed in the Perspex screen during retardation at its surface of the detonation products of an explosive charge, located at a certain distance from the screen. The geometrical layout of the shock-wave generator in this case was similar to that described in [12], but the dimensions were increased. By varying the mass of the explosive charge, the amplitude of the shock wave entering the sample was varied from 55 to 90 kbar, and the pressure drop behind the shock front did not exceed 15% for a time of 6 μsec.

Recording of the readings of the three Manganin probes were carried out by a bridge circuit, using two OK-33 double-beam oscilloscopes. Typical oscillograms are shown in Figs. 2-4. The number 1 on the oscillograms denotes the pressure profile recorded by the probe located between the screen and the sample, the number 2 denotes that recorded by the probe inside the sample, and the number 3 denotes that for the probe between the sample and the barrier. The arrows denote the times of origin of the phase transition in the monitored sample layer. The pressures behind the shock front and the shock-wave velocities were determined from the processed oscillograms by the time intervals between the instants of arrival at the probes; the

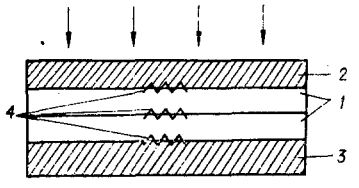

Fig. 1

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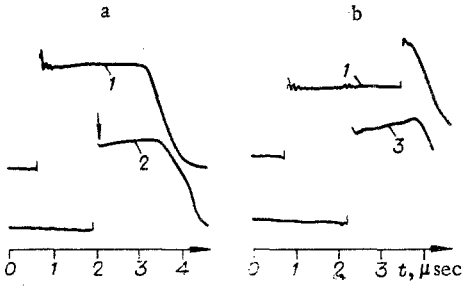

Fig. 2

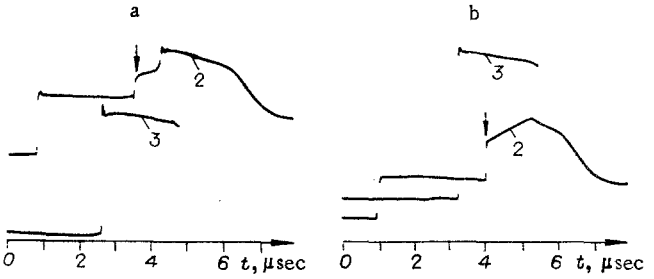

Fig. 3

corresponding values of the mass velocities and the specific volumes were then calculated from these data. The pressure was determined by the relative change of resistance of the probe, using the empirical relation [13]

$$p = (340\Delta R/R_0 + 70(\Delta R/R_0)^3) \text{ kbar.}$$

The validity of using this relation in the case of pressure measurements with multistage compression is also verified in [13].

Figure 2a shows the oscillogram of one of the experiments on recording the characteristics on the pressure profile in the progressive shock wave due to phase transition. The amplitude of the shock wave in the boron nitride sample was 132 kbar in this experiment. The pressure profile, recorded by the second probe, consisted of a jump to 120 kbar and, following behind it, a region of smooth pressure rise (over a period of $\sim 1\,\mu$sec) to the end. Then, before the arrival of the rarefaction wave, the pressure remains constant for a certain time. In these experiments, splitting up of the shock wave with the formation of a two-wave configuration [13] was not recorded. It is obvious that the region of smooth rise behind the shock front in the pressure profile corresponds to a phase transition. In order to verify this, an experiment was set up to record the pressure profile at the boundary with a rigid (copper) barrier for the same amplitude of the shock wave incident on the boron nitride sample.

Based on the results described, the degree of transformation to the dense modification immediately after the first pressure jump is equal to zero, but with increase of the distance from the shock front, it increases smoothly. It can be verified that in this case, because of the different curvature of the shock adiabats of the secondary compression of the initial and dense phases, the rate of rise of the pressure at the boundary with the rigid barrier must increase disproportionally after the first compression shock. The oscillogram of this experiment is shown in Fig. 2b. It can be seen that the special features of the pressure profile were expressed more clearly. The first compression shock at the boundary with the copper barrier amounted to 190 kbar, and then over a period of $\sim 1\,\mu$sec the pressure increases up to 213 kbar.

Thus, at least with pressures in the shock wave of 120-132 kbar, transformation of boron nitride into the dense modification proceeds with a completely measurable rate. The relaxation nature of the transformation also must be revealed on the pressure profile, recorded by the first probe, in the form of a characteristic peak. This feature of the pressure profile at the screen–sample boundary describes the "prompt" compression of the original material up to a metastable state with a pressure which is higher than the pressure of the onset of transition and subsequent transition to the equilibrium state, accompanied by a reduction of volume and unloading [14, 15].

It can be seen from the oscillograms shown in Fig. 2 that the peak on the pressure profiles recorded by the first probes are actually recorded, but their duration is close to the limit of resolution of the procedure,

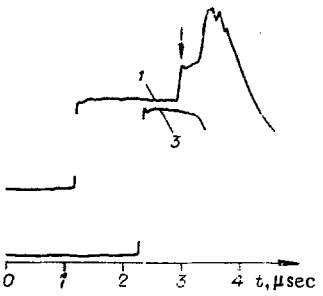

Fig. 4

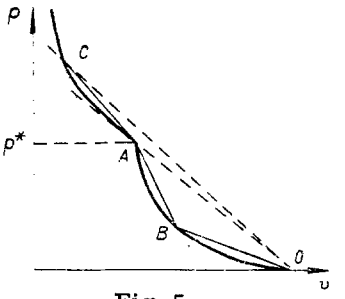

Fig. 5

TABLE 1

p, kbar	55	74	92	120	198
$v, \frac{cm^3}{g}$	0,392 ±0,005	0,384 ±0,005	0,377 ±0,005	0,360 ±0,005	0,300 ±0,01

and therefore their quantitative description is made difficult. In the case of transformation to the dense modification, the rectangular compression pulse with pressure peak at the front cannot be steady, and this pressure profile is characteristic only for the onset of the process at the boundary with the screen. During propagation through the substance, the shape of the compression pulse is transformed to a near-stationary form, and it becomes a profile with a sharp compression shock up to a magnitude p* (corresponding to the pressure at the start of transformation) and with a subsequently relatively smooth rise of pressure, accompanied by a further reduction of the specific volume, due to transformation to the dense modification. The final transformation step is determined by the final pressure and the time of action of the elevated (above p*) pressure. According to the available results (Fig. 2a), limiting estimates can be made of the degree of transformation of the boron nitride into the dense modification, at the instant of reaching the maximum pressure of 132 kbar. For the estimates, the region of the relatively smooth pressure rise was described either by a centered compression wave or by a stationary wave propagating with the same velocity as the shock front. For both cases, the values of the specific volumes v, corresponding to the state of the substance at the final pressure, and the position of the points obtained on the p–v diagram relative to the shock adiabats of the original and dense phases of the boron nitride were considered. The limiting estimates of the degree of transformation (on the assumption of additivity of the compressibility of the original and dense phases [16]) carried out in this way, show that in the case being considered, over a time of $\sim 1\,\mu$sec, from 30 to 60% of the boron nitride transforms to the dense modification. Meanwhile, the formation of a two-wave configuration is the most obvious and convincing demonstration of phase transition in the shock wave. As a result, the most favorable conditions are created for determining the transition parameters.

The conditions for division of the shock wave can be created during gradual compression of the sample. The shock adiabats of boron nitride with a density less than 1.8 g/cm^3 and of graphite have the form represented in Fig. 5. The region of mixed phases is located above the constant velocity beam OA. Therefore, all states are achieved with a single shock-wave compression. If, however, the substance is compressed previously up to a certain state B and then a shock wave with amplitude p_C is created in it, then the latter breaks up into two parts: In the first wave, the pressure is increased up to the pressure of the start of transformation p* and in the second wave, up to the pressure p_C (the slight difference between the shock adiabats of the double and single compression is neglected here).

The oscillograms of the experiments on the multistage compression of boron nitride and graphite are shown in Figs. 3 and 4, respectively. The thicknesses of the tablets of the compound sample were chosen so that the compression wave, originating as a result of the interaction with the screen of the shock wave reflected from the barrier, arrived at the second probe after the two-wave structure had been recorded by it. By evaluating the oscillograms, the pressure at the start of polymorphous transformation, the amplitudes of the entering and reflected shock waves, and their velocities were determined by the corresponding time intervals between the instants of arrival at the probes; then, from these data the corresponding values of the mass velocities and the specific volumes were calculated. For the experiments with increased wavelength, corrections for the small pressure drop before the arrival of the reflected shock wave were introduced.

The form of the pressure profile in the case of multistage compression of boron nitride is determined by the amplitude of the reflected shock wave p_2. With sufficiently high final pressures p_2, a clearly expressed two-wave structure is formed in the sample (see Fig. 3a, profile 2). With a reduction of the pressure p_2, the front of the second wave of the two-wave configuration is blurred (see Fig. 3b, profile 2). The smooth pressure rise observed on the oscillograms behind the front of the first wave of the two-wave configuration confirms the relatively slow development of the transformation process.

The oscillogram of the experiment on the multistage compression of graphite (see Fig. 4) has qualitatively the same form (see Fig. 4).

The comparatively large times after which partial polymorphic transformation is effected in boron nitride and graphite, in the case of multistage compression make possible, as in the case of the advancing shock wave, the investigation of the kinetic features of these transformations. An estimate of the initial rate of transformation in boron nitride behind the shock front gives a value of $(0.3 \text{ to } 0.5) \cdot 10^6 \text{ sec}^{-1}$ with a pressure rise of from 120 to 134 kbar. Completion of transformation takes place in the second wave front of the two-wave configuration at a higher rate. Judging by the steep drop of the front on the oscillogram, the time of completion of transformation does not exceed 0.1 μsec with a final pressure of the shock compression of $p_2 =$ 160 kbar.

It should be noted that the proposed mode of splitting of the shock wave allows the parameters of the state in which polymorphic transformations are effected, for substances whose shock adiabats have a form similar to that shown in Fig. 5, to be determined more accurately and with smaller losses of time than by means of conventional methods.

The pressures at the start of polymorphic transformations, determined by the many experiments, amount to 120 kbar for boron nitride (the spread of the experimental data is $\pm$ 2 kbar) and 196 $\pm$ 5 kbar for graphite. The possible systematic error in the amplitude measurements is determined by the error of the calibration curve, which describes the relation between the relative change of electrical resistance of the manganin and the pressure. According to the data of [13], this error does not exceed $\pm$ 5%.

Table 1 shows the data on the shock compressibility of boron nitride, obtained as a result of processing the oscillograms described above. Within the limits of measurement error, these data are found to be in good agreement with the published data of [1-4]. The effect of the initial density and nature of the shock compression on the position of the points in p, v coordinates is not perceived.

It is interesting to compare the parameters of the start of polymorphic transformations in boron nitride and graphite, which are crystallochemical analogs, with the almost identical densities of the corresponding modifications. Comparison of the shock compressibility curves of these two substances shows that with a significant difference of pressures, the start of the phase transition is defined by almost one and the same value of the specific volume $v = 0.36 \pm 0.01$ cm^3/g, while for its completion we have the value $v = 0.29 \pm 0.01$ cm^3/g.

According to the measurement of the time of arrival of the unloading wave at the back surface of the striker, the velocity of sound in the singly compressed material was determined in specified sections of the sample. With a pressure of 70 kbar it is equal to 5.9 km/sec; with a pressure of 120 kbar it is 7.0 km/sec. In view of the indistinct appearance of the instant of the start of unloading on the oscillograms, the accuracy of the velocity of sound determination is not high, but the error still does not exceed 10%.

Thus, in this paper we have shown the feasibility of studying the kinetics of polymorphic transformations in boron nitride and graphite under shock compression. A new method of revealing the region of phase transitions in the shock adiabats has been achieved by creating the conditions for the splitting of the shock wave.

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GENERALIZED SHOCK ADIABATS OF THE ELEMENTS

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Shock adiabats are needed for the analysis of any kind of explosion processes. They are the main source of information on the equations of state of substances at high pressures and temperatures. This also explains the great interest in their experimental determination. At the present time, approximately 1000 shock adiabats are known, including about 200 shock adiabats of many of the elements of the D. I. Mendeleev periodic table, determined by various authors. This large number of data makes it possible to analyze them statistically and to bring out definite regularities.

Generalized forms of the shock adiabats of substances have been proposed repeatedly, for example, in [1-3]. Here the shock adiabats were assumed to be approximately linear in the coordinates mass velocity–velocity of shock wave. Below we discuss generalized shock adiabats of the elements which are free from this assumption.

§1. In the coordinates mass velocity–velocity of shock wave, experimental shock adiabats are usually approximated by simple analytical dependences, most frequently segments of straight lines:

$$D = a + \lambda u. \tag{1.1}$$

The quantity λ in (1.1) can be regarded as the derivative $\lambda = dD/du$ at some intermediate point of the shock adiabat. The value of λ varies, generally speaking, along the shock adiabat with an increase of the compression in the shock wave.

The distribution of the values of λ or of the derivatives with respect to the shock adiabat (shown in Fig. 1) was plotted on the basis of approximately 150 experimental shock adiabats, approximated by segments of straight lines, mainly taken from [4, 5] (but, in the case of hydrogen, from [6]). On the vertical axis with an

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