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Transformations of Condensed Substances under Shock-wave Compression in Controlled Thermodynamic Conditions

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The development of dynamic methods of acting on matter is reviewed, with special emphasis on isentropic shock-wave compression methods, which minimise the thermal contribution to the pressure. The effect of pressure, temperature, micro- and macro-plastic deformations, and of pressure relief waves is discussed. Problems arising in studies of the low-temperature compression of condensed gases under dynamic conditions and of chemical synthesis by shock-wave compression of solid-gas systems are examined. 53 references.

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I. INTRODUCTION

The aim of this paper is to examine the possibility of exploiting various regions of the p,T phase diagram of substances (where p is the pressure and T is temperature) and of obtaining high levels of compression under different heating regimes in dynamic experiments. Dynamic interactions include various types of compressive load: from compression by a single or a multiple shock wave (SW) to dynamic isentropic (or, more exactly, nearly isentropic) compression (DIC). Shock waves are generated in condensed substances under dynamic conditions by the detonation of an explosive substance (ES) in contact with the sample, or by impact from a body accelerated to a high velocity by the products of an explosion.

The dynamic approach to the physics and chemistry of high pressures includes: a) studies of the state of substances during shock-wave compression (measurement of the compressibility and construction of the equations of state, study of the visco-elastic characteristics and of the optical and electrical properties, study of the low-temperature plasma generated by the pressure relief following a shock wave in a porous substance), and b) studies of the physicochemical transformations of substances contained in strong vessels (sample preservation bulbs) after shock-wave compression. The latter approach has attracted a great deal of interest during the past two decades because of the possibility of its direct practical application in synthetic work under SW conditions.

Some aspects of high-pressure physics and chemistry are related to the physics of high energy densities.

A generalised p,T diagram (Fig.1*a*) shows (as cross-hatched areas) the regions of high static or dynamic pressure which have so far been exploited. In order to simplify the diagram the regions of ~10^3 GPa and 10^4–10^5 K (explored in compression experiments[1]) and of a few hundred GPa at 10^3–10^4 K (in experiments with preservation of the sample[2]), mainly involving an axially symmetrical loading geometry, have not been included.

The static method has one undeniable advantage: it allows the sample to be exposed to high pressures and temperatures for long times, and therefore the two parameters can be varied in the desired sequence (Fig.1*b*). The initial substance is usually first compressed, then heated, and at the end of the experiment the temperature is lowered before the pressure. This allows metastable states to be preserved under normal conditions. A general review of the thermodynamics and kinetics of reactions under static compression conditions is given in Ref.3.

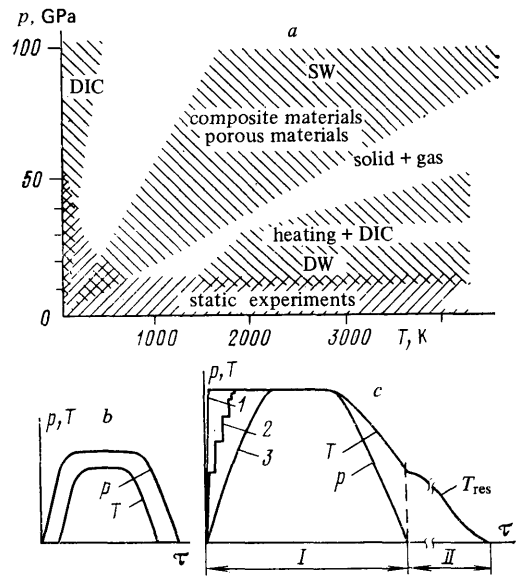


Figure 1. Generalised p,T diagram showing the regions of high static or dynamic pressure application (*a*), and idealised plots of p and T against time under static (*b*) and under dynamic conditions (*c*); DIC is the dynamic isentropic compression region, SW is the region of shock-wave compression of composite or porous solid materials, and of gas–solid systems, DW is the region of high p and T values generated in a detonation wave; *1*), *2*), and *3*) are the wave fronts for single and for multiple shock compression, and for DIC, respectively. Cooling rate ~10^8 K s^{-1}; the durations of processes I and II are ~10^{-5} s and ~1 s respectively.

Shock compression does not offer these advantages. Both the pressure and the temperature rise in a narrow zone (the SW front) in times of 10^{-12}–10^{-9} s, after which the pressure relaxes in ~10^{-6} s through isentropic pressure relief waves, while the temperature falls to some intermediate value (T_{res}, see Fig.1c) owing to the irreversibility of the shock compression. The whole process is completed in ~10^{-5} s: the final cooling of the depressurised sample follows the normal heat conduction laws. Obviously, high-pressure phases can be eliminated by high residual temperatures unless special precautions are taken (e.g., the back-graphitisation of the diamond formed by shock-wave compression).

Nevertheless, the shock interaction method has a number of specific features and advantages, including the ease with which ultra-high pressures and temperatures can be achieved, the generation of extremely high shear strains on the SW front (which give anomalously high rates of physicochemical reactions in the solid state), extremely fast cooling rates, strict control of the development of pressure, etc. All these advantages have been exploited in studies of physical and chemical changes in experiments with preservation of the sample, and shock compression has been shown to lead to defect formation, complex chemical reactions, polymorphism, etc.

This review will deal with the basic problems in the development of the SW method, and with the results obtained in diagnostic experiments on the factors (temperature, pressure, microscopic or macroscopic plastic deformation, pressure relief waves) responsible for various processes. The problem of achieving low-temperature compression under dynamic conditions will be examined in detail.

II. THE SHOCK-WAVE COMPRESSION REGION

Most of the work on the dynamic aspects of high-pressure physics and chemistry so far reported refers to the SW region (Fig.1a). Studies of the properties of matter under the influence of shock compression have been discussed in many monographs and reviews (see, for example, Refs.4–12). Studies of the properties retained after compression have shown[13–16] that the very short duration of the shock compression process is not a serious obstacle to the widespread use of the method. The products can be preserved after relief of the pressure if the residual temperature is not too high (a condition easily satisfied by the enormous cooling rates (~10^8 K s^{-1}) accompanying the decrease in pressure). However, many processes can take place as a post-effect, i.e. after relief of the pressure, if the residual temperature of the material activated by the SW front is relatively high. This unique situation is never encountered except in SW systems.

1. Planar Loading Scheme

SW application from one side only in the planar variant (Fig.2a) allows the development of pressure to be calculated with high precision. Macro-plastic deformation of samples in bulbs, mainly during pressure relief, is usually less than 10% at moderately high pressures. Low-density substances can easily be compressed to 50 GPa by repeated SW, reflected from the denser metallic walls of the bulb. By using a flat bulb design the samples can be pre-cooled to 4.2 K: a very important facility for studies of thermally unstable states[17]. The retention of these states is assisted by fast heat transfer from the experimental region towards the bulb walls at the end of the shock compression process. Even more marked effects are obtained by rapidly cooling the bulb at the end of the experiment (for example, to 77 K [17]).

Systematic comparative studies of organic reactions initiated by SW (in particular, the shock polymerisation of acrylamide[18]) have revealed a strong dependence of the final state of the sample on the initial temperature (T_0). At T_0 = 77 K the reaction products are found (by ESR) to include a fairly high concentration of paramagnetic active centres (AC): 10^{20}–10^{21} kg^{-1}. Furthermore, the presence of these centres gives rise to post-polymerisation even within the thermal explosion period, but no post-polymerisation is observed for T_0 = 293 K.

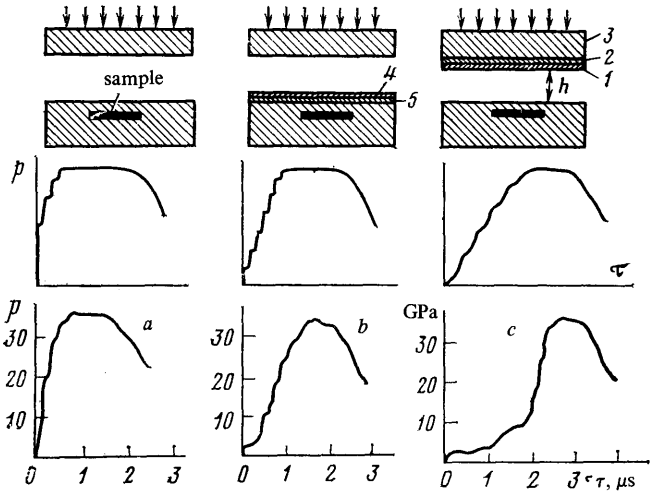


Figure 2. Schematic diagrams of the generation of multiple shock compression (*a*) and of dynamic isentropic compression (*b* and *c*), with idealised and experimental compression wave profiles: *1*), *2*), and *3*) are Perspex, aluminium, and copper plates; 4) and 5) are copper and Perspex plates.

Gamma-irradiation of many monomers at low temperatures is known to lead to the formation of stabilised ACs, which cause polymerisation if the temperature is raised. The combined effect of γ-radiation and SW on acrylamide samples has been studied[19] at 77 K. After pre-irradiation with 5–6 Mrad doses, shock compression was found to increase the yield of polymer to a level higher than the sum of the contributions from the separate agencies. This observation can be ascribed to the transition of the polymerisation process to the thermal explosion regime owing to the high rate of heat evolution produced by the simultaneous radiation-chemical and mechanical initiation of ACs.

We should note that studies of defects in materials exposed to shock compression have shown that the changes in the sample are not equivalent to simple thermal dissociation, and that the final product is often similar to the product of radiation-induced decomposition[14].

A comparative study of the thermal decomposition of ammonium perchlorate samples previously exposed to γ-radiation (1 Mrad dose) or to shock compression (1.5–20 GPa) has been reported[20]. Differential thermal analysis of these samples has shown a substantial decrease in thermal stability in both cases: decomposition begins at 490–500 K, whereas the initial sample of ammonium perchlorate begins to decompose at 563 K. The extent of decomposition in the low-temperature stage of the process increased more than three-fold.

Increasing the amplitude of the SW to 20 GPa causes 96% decomposition of the sample in a single step at 490 K. Thus, irradiation and SW treatment of ammonium perchlorate give very similar results.

We should stress that samples exposed to shock treatment develop defects similar to those found in irradiated samples[14]. In particular, Lisin points out[21] that irradiation of solids by powerful beams can give rise to localised SW, but this hypothesis needs to be confirmed experimentally.

2. Cylindrical Loading Scheme

Bulbs having a cylindrical geometry are most often used in experiments with preservation of the sample after shock compression. The creation of a three-impact configuration in a sample contained in a cylindrical bulb by a glancing detonation wave allowed the pressures to be calculated[2] and thus greatly advanced the development of the physics and chemistry of high dynamic pressures. The proof[2] that the detonation velocity of the explosive surrounding the bulb is equal to the rate of propagation of the three-impact configuration justifies the calculation of pressure in the sample without special direct measurements (if the shock-wave adiabatic curve of the sample is known).

Under these conditions pressures of several hundred GPa can easily be obtained. Thus, by using explosives having detonation velocities of $\sim 8 \times 10^3$ m s^{-1}, pressures of ~500 GPa have been obtained in monolithic tungsten samples, and ~60 GPa in sodium chloride[2]. The pressure in the salt can be raised to 100 GPa or higher simply by mixing the salt with tungsten powder. By using a low salt content, and by making the sample denser by repeated SW compression, pressures as high as 500 GPa can be obtained, accompanied by very high temperatures (10^3–10^4 K). The compression conditions generated in the cylindrical loading scheme are convenient for chemical syntheses (which are also favoured by the very strong macro-plastic deformations).

3. Shock Compression of the Solid–Gas System

The simplest system of this type is a low-density substance with pores filled with water at atmospheric pressure. If the solid particles are small, shock compression in these systems can be assumed to cause pressure equalisation, but not thermal equilibrium. Because of the small mass of the air its contribution to the temperature is insignificant, and the average temperature of the mixture will not differ substantially from that of the solid component, in spite of the much stronger heating of the air in the micro-pores in the initial stage of compression.

Under powerful shock compression a porous medium experiences a strong deformation than a continuous medium, and as a result its entropy increases by a greater amount than that of the continuous medium compressed to the same final pressure[7] (Fig. 1*a*). Shock compression under vacuum can produce temperatures of tens of thousands of degrees, and convert part of the sample into the plasma state[23]: this can give rise to thermionic electron emission[24].

Shock compression of porous substances does not cause special difficulties in the preservation of the compression products. Complications arise only if the sample decomposes, or reacts with the large volume of gas evolved, or if the pores are previously filled with gases compressed to high pressures or condensed. Under these conditions the bulbs usually burst as a result of the high internal pressures developed. A special bulb design is needed to prevent bursting. Obviously, partial (or complete) reaction of the evolved gas to form a solid helps the preservation of the sample.

We have recently carried out a systematic study of the design of sample preservation bulbs of the planar and of the cylindrical type for the shock compression of solid–gas mixtures in various chemical investigations[25,26], and we have developed a bulb for the planar loading (up to 40 GPa) of porous substances mixed with gases for initial temperatures of $T_0 \cong 300$ and 77 K.[25] The gas (for example, hydrogen) is admitted under pressure to the working volume of the bulb through a thin connecting tube from a standard or a special gas storage cylinder. These bulbs are not fractured by the shock compression of their contents, and the solid products of the transformation can be examined. On the other hand the excess of gas is lost through the open vent provided.

Cylindrical bulbs offer an extended pressure range and substantial macroplastic deformations, with their associated heating effects, which assist chemical reactions. This feature allows the required gas to be produced during the experiment by compression of a "donor" of this gas (for example, a source of oxygen) either mixed with the sample or separately located[26]. As in the planar variant, the design of these bulbs allows the addition of gases from cylinders as well as cooling of the sample to 77 K. With a solid sample having a high dynamic stiffness the pressure in the mixture can reach 100 GPa or more. Unlike the planar variant, however, this variant allows the bulb to remain sealed during the compression, giving a product at some intermediate (residual) pressure.

We have used these bulbs to study the interaction of various substances with nitrogen, solid carbon dioxide, oxygen, and hydrogen. In particular, we have demonstrated the formation of niobium nitride and carbide by shock-wave compression of a mixture of niobium powder and liquid nitrogen or carbon dioxide[25]. In an attempt to prepare solid CO_2 under normal conditions we have studied[26] the oxidation of SiC under shock compression of a bulb containing a mixture of powdered SiC and gaseous or liquid oxygen. The products were examined by X-ray diffraction and i.r. spectroscopy, and oxidation of the SiC with formation of a non-molecular lattice structure was detected. Heating the oxidised SiC to 800–1300 K produces oxides of carbon.

The interaction of various metals with hydrogen yielded hydrogen compounds of titanium, manganese, and other substances. Saturated hydrocarbons, or water, can be used as hydrogen sources in these reactions.

III. METHODS OF CONTROLLING THE THERMODYNAMIC PARAMETERS DURING DYNAMIC COMPRESSION

Because pressure and temperature in the SW front are closely interrelated, the scope for achieving high pressures without a correspondingly high level of heating is very limited (DIC region in Fig. 1*a*). The possibility in principle of minimising the self-heating of the sample during shock compression by a stepped application of the pressure has been exploited, for example, in measurements of the compressibility as well as in experiments with preservation of the sample. Various experimental schemes for sample preservation under industrial conditions can be used to apply either single or multiple shock loading with variable final pressures, initial temperatures, etc.

By using multiple shock compression the entropy can be decreased very substantially (as compared with one-step compression to the same final pressure). However, in the multiple SW compression of very compressible condensed substances the amplitude of the first SW has to be very high in order to reach a high pressure, and its contribution to the

final temperature rise is predominant. For example, in the multiple shock compression of Perspex to pressures of 50 and 100 GPa the amplitude of the first SW must be ~10 and 20 GPa respectively, corresponding to maximum temperatures of 770 and 1570 K and residual temperatures of 520 and 860 K respectively[9].

Obviously, in order to achieve low-temperature dynamic compression we must lower the amplitude of the first SW and increase the number of compressions. In our work these requirements were met by using layer systems[27]. Clearly, a "smooth" dynamic compression could be achieved also by other methods: some of these are described in Refs. 28–30. However, magnetic accumulation generators[30] seem hardly likely to be compatible with experiments requiring preservation of the sample.

1. Layer Systems

The simplest experimental schemes for the planar leading variant (though they are applicable in principle to axially symmetrical loading) are shown in Fig. 2 for: (*a*) multiple shock compression, (*b*) compression by a SW transmitted through a system of screens having different dynamic stiffnesses, and (*c*) compression by successive impacts from an assembly of striker plates made from high dynamic stiffness materials moving towards the target at different times. By using the layer system in scheme (*b*) it has been possible[31] to lower the amplitude of the first SW to 3 GPa while achieving multiple shock compression to 50 GPa of organic substances having densities of ~10^3 kg m^{-3}.

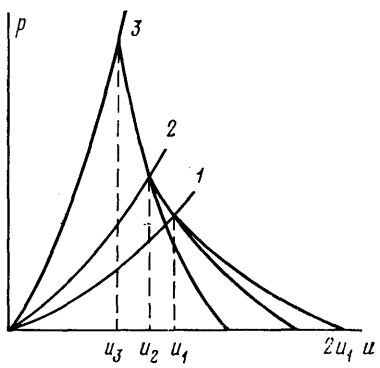


Figure 3. Shock compression adiabatic curves for Perspex (*1*), aluminium (*2*), and copper (*3*), and pressure relief adiabatic curves for the same materials plotted as pressure against mass velocity.

Loading by scheme (*c*) produces a complicated compression pattern, due to the possibility of interaction between the strikers after reflection from the target, spallation phenomena, etc.[32] Therefore it is advisable to plot the true loading profiles produced by the compression waves (using Manganin pressure sensors[27]). The principle of operation of scheme (*c*) is illustrated in Fig. 3. The planar detonation of the explosive charge sends a shock wave through the system of striker plates (e.g. copper, aluminium, and Perspex) whose shock-wave adiabatic curves are shown in the Figure in *p*,*u* coordinates (where *u* is the mass velocity of the material behind the SW front). When the shock wave reaches the free surface the Perspex plate is accelerated to a velocity approximately double the mass velocity of Perspex (since the velocity upon removal of the load is equal to the mass velocity); the aluminium (and especially the copper) striker will have lower speeds. Load is applied to the target containing the sample by successive impacts from the striker plates, the final pressure being determined by the impact of the copper plate (of thickness greater than the combined thicknesses of the aluminium and the Perspex plate).

A qualitative analysis of this method suggests that by varying the relative dynamic stiffness of the plate materials, their thickness, and the distance from the layered striker to the target (*h*), it should be possible to produce compression waves with different profiles: from a pressure increasing monotonically with time to a "saw-tooth" profile with gradually increasing pressure plates. The method allows the time of application of the pressure to be increased to 10 μs or more in large-scale applications. If the damping law which applies to the collision of the first (thin) striker in the target is known, the geometry of the experiment can be designed so as to make the amplitude of the SW reaching the sample during the first compression step negligibly small.

Because of their low thermal stability, organic substances can be used as "thermal indicators" in the search for suitable low-temperature compression conditions. Large differences in the final state of the sample were noted in comparative experiments on the dynamic compression of organic compounds with sample preservation by the schemes of Fig. 2*a*, *b*, and *c* with constant (50 GPa) final pressure and initial (room) temperature. Whereas conventional multiple SW compression of acrylamide caused full thermal degradation of the sample, compression by schemes (*b*) and (*c*) did not degrade the material, nor was degradation observed during the structural transformation in polypropylene. On the other hand compression by scheme (*a*) to 20 GPa or above converts any propylene structure into a microspherulitic phase, because the polymer activated by the SW front is exposed to a relatively high residual temperature.

These results suggest the possibility of achieving a substantially isentropic condition in dynamic experiments.

2. Dynamic Isentropic Compression of Condensed Substances at Low Initial Temperatures

The solution of many problems such as metallisation of dielectrics (including compressed gases) requires high degrees of compression, as well as low temperatures in the case of compressed gases. For a given compression, the temperature on the isentrope is proportional to the initial temperature of the samples. Hence, in order to achieve the lowest possible temperatures in dynamic experiments the interaction with isentropic compression waves is carried out after pre-cooling the sample to temperatures as low as 4.2 K.

We shall discuss below the results obtained for multiple shock compression and DIC of acrylamide samples in copper bulbs at pressures up to 40 GPa and initial temperatures of 10, 77, and 293 K.[17] After the experiments the bulbs were cooled back to 77 K in order to determine the relative amount of products formed.

The compression conditions of samples loaded in different ways can be determined, and their temperatures estimated, by using data on the compressibility of Perspex, whose density is similar to that of acrylamide and which has been fully investigated at high pressures. Under the multiple collision compression conditions used in Ref. 17 most of the

heat is generated by the first SW, which has an amplitude of ~8 GPa, and the subsequent compression waves (up to 40 GPa) can be treated as isentropic. The Grüneisen coefficient was assumed to depend on volume only, and the specific heat on temperature[33]. The calculated results (Table 1) show that the heating effect under DIC conditions is much weaker (especially for $T_0 = 10$ K) than under shock compression. It is also clear that under shock compression the residual temperature effect is substantially lowered for $T_0 < 77$ K, and the residual temperature of the bulb wall can be made even lower with $T_0 = 10$ K.

Table 1. Sample temperatures (K) calculated for different compression conditions ($p = 40$ GPa).

T_0	T_{DIC}	T_{SW}	T_{res}	T^*_{res}
10	24	545	320	30
77	124	565	330	90
293	480	765	445	310

*Residual temperature of the bulb.

These experiments revealed large differences in the yield of polymer from acrylamide and in the rate of the polymerisation process. Shock compression at $T_0 = 10$ K gives 10% of acrylamide polymer during the compression or within a few seconds. The concentration of growing polymer chains is high, and thawing the sample to 293 K results in strong polymerisation with a final yield of 40%. Evidently, the rapid removal of heat from the sample towards the bulb wall (Table 1) helps to retain the ACs. At 77 K the yield of polymer is 30%, and post-polymerisation does not take place on thawing the sample because the ACs are lost by annealing at the relatively high residual temperatures. Shock compression of acrylamide at $T_0 = 293$ K causes only thermal decomposition of the sample.

Under DIC conditions and $T_0 = 10$ or 77 K the yield of polymer does not exceed 2–3%, and no polymerisation takes place on thawing the sample, because of the small number of ACs resulting from the relatively modest pressure gradients at the SW front; DIC at $T_0 = 293$ K gives a higher yield of polymer (20%), but no thermal degradation is observed. From the above comparison of SW compression and DIC we may conclude that polymerisation under shock compression is initiated by the SW front.

Studies of the low-temperature compression of gases and of gas systems were stimulated by the growing interest in the transition of hydrogen to the metallic state. Clearly, the only suitable experimental region in this case was the DIC region (Fig.1*a*). As we have already pointed out, the procedure used in our experiments for realising these conditions in practice relied on the use of conventional explosives. Most of the work was carried out with gases and gas systems frozen at 77 K. Special bulbs were designed to preserve the samples after dynamic compression to 50 GPa. Immediately after the experiment the bulb with its charge were cooled back to 77 K, opened at that temperature, and the physicochemical properties of the products were studied at and above 77 K.

Carbon dioxide, chlorine, water, a mixture of water and carbon dioxide, and a mixture of n-heptane and chlorine were also investigated. Changes in state of these substances at low temperatures were monitored by the radiothermoluminescence (RTL) method[34]. Compression was found to affect the RTL spectra of many substances. For example, new peaks appear in the glow-curve of CO_2 after compression. After DIC, a mixture of C_7H_{16} and Cl_2 can no longer react rapidly at 153 K, unlike the initial mixture. Other similar results were also reported.

The most important outcome of this type of experiment so far has been the demonstration of the possibility of working with condensed gases under dynamic compression with preservation of the products and direct observation of their properties.

3. Dynamic Isentropic Compression of Condensed Substances at High Initial Temperatures

The main difference between shock compression and DIC lies in the leading edge of the compression wave (Fig.4*a* and 4*b*). In the case of DIC the microscopic shear deformations and the excess temperatures at the front are smaller even than in multiple shock compression. On the other hand the time of exposure to high pressures, the rate at which the pressure relaxes, and the amount of macroscopic plastic deformation of the bulb and sample after relief of the pressure are practically the same for shock compression and for DIC.

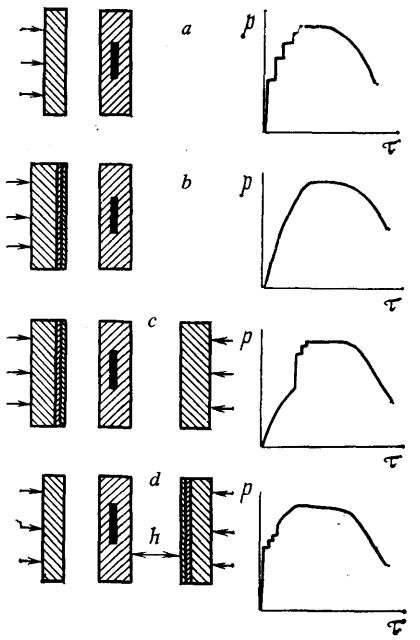


Figure 4. Main loading schemes and idealised profiles of the compression wave: (*a*) multiple shock compression, (*b*) dynamic isentropic compression, (*c*) combination of DIC and shock compression, (*d*) combination of shock compression and DIC.

As has already been stated, DIC of acrylamide samples at $T_0 = 293$ K does not cause thermal degradation: the concentration of ACs is small, and no post-polymerisation is observed. These observations suggest that the SW front is

responsible for the initiation and development of polymerisation during shock compression. However, the DIC experiment alone cannot distinguish the relative roles of micro-shear deformation and of the temperature factor, since any decrease in the effect of the former is invariably accompanied by a decrease in the temperature of the substance at the compression front. Preliminary heating of the sample under DIC conditions should yield p,T conditions identical to those of the conventional multiple shock compression arrangement, but without substantial micro-shear deformations, thus revealing the effect of the SW front in a "pure" form.

With that aim, we have studied the effect of pre-heating in conjunction with DIC on two quite different processes under shock compression: the chemical polymerisation and the structural transformation of graphitic boron nitride (g-BN) into the dense, wurtzite-like modification (w-BN).[35]

The main experimental arrangements and the corresponding idealised pressure profiles are shown in Fig.4*a* and 4*b*. Planar multiple shock compression at pressures up to 20 GPa of samples 2×10^{-3} m thick contained in a bulb was applied by impact from a copper plate 7×10^{-3} m thick; DIC to approximately the same pressure (Fig.4*b*) was achieved by layered Perspex, aluminium, and copper strikers 1×10^{-3}, 2×10^{-3}, and 7×10^{-3} m thick respectively. A more detailed description of the experimental arrangements is given in Ref.35.

Table 2. Yield of polymer (W), concentration of polymer chains (N), and increase in the final and in the residual temperature (ΔT (K) $= T - T_0$) under shock compression and DIC conditions for high initial temperatures.

T_0, K	W, %	$10^{-20}N$, kg^{-1}	ΔT_{fin}	ΔT_{res}
293	30	$\frac{SW}{4.7}$	220	120
293	2	$\frac{DIC}{1.7}$	75	0
323	7.5	1.7	135	0
348	13	1.7	170	0

Polymerisation of acrylamide. The polymerisation process requires both the presence of ACs and heating, since activation energy must be supplied to allow the chains to grow. Under shock compression the SW front satisfies both these requirements. As Table 2 shows, shock compression of acrylamide at 293 K gives the polymer in 30% yield. The concentration of polymer chains under these conditions is 4.7×10^{20} kg^{-1}. The yield of polymer under DIC conditions at 293 K is an order of magnitude less, with a concentration of polymer chains three times smaller and unaffected by an increase in the initial temperature almost to the melting point of the monomer. The increase in the yield of polymer (to 13%) is due to the higher residual temperature.

Since the pressure and the residual temperature for shock compression at $T_0 = 293$ K and for DIC at $T_0 = 323$ K are not very different (according to calculations of the residual temperature similar to those used in Table 1), the formation of a greater number of polymer chains under shock compression conditions suggests that the SW front plays a dominant role in the generation of ACs and in bringing about the polymerisation reaction during shock compression. In the present example the concentration of Acs was 10^{20} kg^{-1}, and their time of formation was 10^{-6} s or less, corresponding to the strikingly high rate of generation of 10^{26} kg^{-1} s^{-1}.

g-BN–w-BN *transformation.* Shock compression of graphitic boron nitride to pressures higher than 12 GPa is known to cause irreversible transformation into a dense wurtzite-like modification. Two explanations have been put forward to account for the high speed of this transformation[36,37]: 1) strong shear deformations and 2) a martensitic type of transformation, proceeding athermally and under the influence of pressure alone.

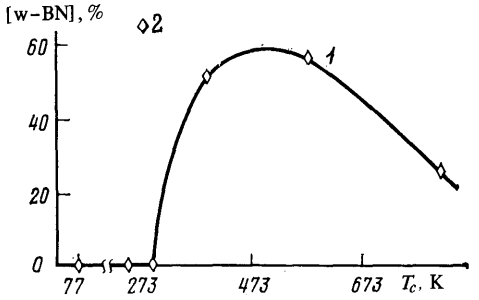


Figure 5. Yield of dense boron nitride phase against initial temperature: *1*) dynamic isentropic compression, *2*) shock compression.

By exploiting the application of almost isentropic compression in dynamic experiments at different initial temperatures we can distinguish between these alternative explanations. The results show (Fig.5) that if multiple shock compression is replaced by DIC at low or at normal temperatures the phase transformation in boron nitride is inhibited. However, a preliminary heating of the sample is sufficient to restore the transformation, even under conditions close to isentropic compression. Stronger pre-heating of the sample causes partial annealing of the dense boron nitride phase after removal of the pressure.

These results suggest[35] that a simple increase in pressure is insufficient to cause the g-BN–w-BN transformation in times of $\sim 10^{-5}$–10^{-6} s. An increase of temperature is also required in order to overcome the substantial activational barrier.

About 20 years ago, when structural transformations by shock compression were first reported[52,53], the possibility of SW generation in the deeper layers of the Earth by the sudden movement of rock formations was considered in relation to the generation of dense phases and to the initiation of earthquakes. Of course, these conditions are possible, but the generation and more sustained existence of strong and smooth pressure waves seems more likely (for example, after the passage of a SW). Because of the uneven temperature distribution in the Earth's core (varying by hundreds of degrees over distances of 100 km), and noting the above experimental results, we can expect transformations over large volumes in the depth of the Earth not only in regions which can support shock waves but also at greater depths, where the SW is transformed into a smooth compression wave.

Bridgman[38] recently suggested that SW pressure could be applied to a sample already under static compression. Our simple method of generating almost isentropic compression in dynamic experiments can be used to produce conditions in which a sample which has been compressed "smoothly" and with negligible heating (especially at low initial temperatures)

is subsequently subjected to shock compression (Fig. 4*c*). The opposite situation can also be arranged: isentropic compression of a shock-compressed sample (Fig. 4*d*).

Modern explosive handling techniques allow very precise synchronisation of the detonation of the charges used for launching the strikers. The required distance from the striker to the target (shown as *h* in Fig. 4*d*) and the corresponding pressure can be calculated from the *p*,*u* diagram if the shock-wave adiabatic curves of the materials and the striker velocities are known. For small sample thicknesses the pressure due to the reflected SW is equal to the pressure in the bulb material.

Frontal collision of compression waves has been used so far only in studies of compressibility and electrical conductivity by shock compression[39,49]. The above discussion shows that both shock waves and isentropic compression waves can be used (in their various combinations) to generate frontal collisions. In other words, we can now apply different types of controlled dynamic loading to a sample, and we can monitor changes in the state of the sample both during its compression and by direct analysis of the preserved sample.

IV. EFFECT OF PRESSURE RELIEF WAVES ON THE PHYSICOCHEMICAL TRANSFORMATIONS OF CONDENSED SUBSTANCES

After shock-wave compression the sample invariably experiences pressure relief waves which have the effect of removing both the pressure and the excess temperature in times of $\sim 10^{-5}$ s. Let us examine the planar loading scheme, which offers a simpler variant of sample compression. In the experiments with sample preservation the sample is located outside the disruptive load region formed by the interaction of opposing pressure relief waves. Therefore the sample is exposed to the pressure relief waves, and its pressure can fall to atmospheric (in most cases). With very short SW, generated by the impact of a thin (2–3 mm thick) plate, the pressure in the sample is relieved by overtaking relief waves from the direction of the free surface of the striker. The extent of macro-plastic deformation for moderate pressures is not very great in this case (1–2%). When the SW is generated by impact from a thick plate, or by the contact detonation of an explosive charge, the residual deformation of the bulb and sample can be as high as 10%.

There are no estimates so far in the published literature of the temperatures produced by deformation, nor is there any evidence on the formation of defects or on structural transformations by the pressure relief waves during the fall of the pressure to atmospheric levels. We shall attempt to answer these questions by using the results of comparative studies of substances subjected to shock-wave and to dynamic isentropic compression respectively, given in sub-section 3 of the previous Section.

Comparison of the two sets of results for acrylamide at 293 K (Table 2) shows that the combined effect of micro-plastic deformations and high temperatures, characteristic of shock compression, increases the yield of polymer by a factor of 10 and the number of ACs (assuming the concentration of polymer chains to be proportional to the concentration of ACs) approximately 3-fold. Hence we may conclude that the number of ACs formed by pressure relief waves and by macro-plastic deformations during shock compression is one-third of the total. The relative proportions of ACs formed by pressure relief and by deformation respectively cannot be estimated at present. Since the character of the pressure relief and the extent of macro-plastic deformation are very similar in SW compression and in DIC it would appear that the contribution of the pressure relief waves to the initiation of polymerisation is negligible in comparison with the contribution of the SW front.

Let us examine a different type of transformation: the formation of dense phases by shock compression. Multiple shock compression of g-BN samples to 20 GPa gives the dense w-BN phase in ~70% yield (Fig. 5). If DIC is used at initial temperatures in the range 77–293 K the dense phase is not formed, in spite of the increased macroplastic deformation produced by the "discharge" of material into the free volume of the bulb.

The conversion of g-BN into the dense phase under shock compression occurs at 12–20 GPa pressures in the presence of high temperatures. If the temperature rise produced by the presssure relief waves and by the resulting macro-plastic deformations in this pressure range were sufficient to bring about the transformation, a dense phase would be detected in the boron nitride samples preserved after DIC. The absence of w-BN is evidence that the macro-plastic deformations have failed to raise the temperature of the g-BN sufficiently. The results obtained for DIC with high initial temperatures (Fig. 5) show that the temperature rise of the sample under these conditions is not very marked.

A third example can be taken from Ref. 41, which describes a metallographic study of copper single crystals and of nickel and brass polycrystals exposed to DIC conditions (changing to shock compression within the sample). The DIC was produced by multiple reflection of SW in an intermediate layer (between the striker plate and the target, see Fig. 2*b*) consisting of a low-density material: liquid hydrogen, which also acted as a coolant. The density of deformations and the micro-hardness were found to be lower in the region affected by the DIC than in the shock compression region.

These examples show that the effect of the pressure relief waves on the formation of defects in the sample is very small. When a planar loading scheme and moderately high pressures are used the macro-plastic deformations generated during pressure relief make a negligible contribution to the final residual temperature rise.

We should also mention a report[42] of phase transformations induced by shock compression and giving less dense structures: these are most probably caused by the expansion stresses arising during load removal. However, the exact stage during pressure relief corresponding to these changes is still not clear: they could take place during the decrease of pressure to atmospheric values, or they could require negative (disjoining) pressures. The results[42] are a good illustration of the wide scope of scientific and practical applications of shock waves.

V. DIRECT APPLICATION OF THE HIGH PRESSURES AND TEMPERATURES DEVELOPED DURING THE DETONATION OF EXPLOSIVES

Detonation is the propagation (at supersonic speed) of an exothermic chemical reaction front through a substance capable of sustaining the reaction without the participation of the surrounding medium. The hydrodynamic theory of detonation treats the detonation wave as a shock front followed by a zone of chemical reaction and a zone in which the reaction products are ejected. The detonation wave is propagated at a constant speed because any loss in energy of the SW is immediately replaced by the energy evolved by the chemical reaction in new regions of the sample. The passage of a detonation wave converts solid or liquid compounds into a mixture of gaseous products (CO_2, CO, H_2O, H_2, N_2, etc.) whose density at the end of the reaction zone is $\sim 2 \times 10^3$ kg m^{-3}.

The size of the stationary zone (a) and the duration of the chemical reaction (τ) in the explosive substance depend on a number of factors, such as the power of the explosive and the density of the charge. For example, if the density of TNT is changed from 1.0×10^3 to 1.6×10^3 kg m^{-3} the parameter a changes from 1.6×10^{-3} to 1.0×10^{-3} m, and τ from 0.5 to 0.2 μs. The pressure at the end of the chemical reaction zone changes from 6.5 to 18 GPa. For Hexogen a change in density from 1.0×10^3 to 1.72×10^3 kg m^{-3} changes the a value from 1.4×10^{-3} to 0.7×10^{-3} m, the τ value from 0.4 to 0.1 μs, and the pressure from 9.5 to 30 GPa. These results were obtained[43] by an electromagnetic method. The temperature of the detonation in condensed explosives is 2000–5000 K (Fig.1, DW region).

Several recent publications have described the direct application of the high pressures and temperatures and of the products of the detonation in physicochemical studies of a sample mixed with the explosive. The products were preserved by carrying out the experiments in strong, sealed containers, able to withstand the pressure of the detonation products.

One of these publications[44] describes the synthesis of silicate crystals from a mixture of oxides; others discuss the interaction of the nitrogen formed during the detonation with metal powders to give aluminium, beryllium, boron, magnesium, and zirconium nitrides[45], and the preparation of boron oxide, nitride, and carbide by the reaction of boron with detonation products[46]. The possibility of inducing structural changes under these conditions has been demonstrated[47]: the density dependence of the detonation velocity of a mixture of TNT and quartz was found to include a break, which was interpreted as a phase formation in the quartz.

In the light of these results it is interesting to examine the state of additives affected by a detonation wave. There have been various attempts at describing the establishment of equilibrium between the particles of an inert additive and the detonation products during the chemical reaction period, i.e. during the equilibration of pressure and temperature[48]. Similar problems were considered in a study[47] of the effect of added aluminium on the parameters of the detonation of TNT, and in a calculation[49] of the parameters of detonation waves in mixtures of explosives and inert substances. The detonation of water-filled explosives has attracted much attention, and the addition of water has been shown to enhance the detonation parameters[50]. The water acts as an internal envelope, and it prevents the dispersal of the detonation products, thus increasing the time available for chemical reactions and leading to a more complete evolution of energy. This effect is observed only in explosives with a negative oxygen balance[51].

Let us examine the state of particles of inorganic additives having a density of $\sim 2 \times 10^3$ kg m^{-3}, i.e. close to that of the detonation products, in terms of published results[48–51] and of known features of the shock compression of condensed substances. Because the densities are so similar, the additive in the front will experience a single shock compression, and it will be heated by the SW compression and by the hot detonation products. Clearly, the state of a mixture of inert particles and dense gases in a detonation wave is determined by the reaction time, and by the physical properties (and size) of the particles. We shall take the average size of the chemical reaction zone to be $a \cong 0.5 \times 10^{-3}$ m, and $\tau \cong 10^{-7}$ s. In this case the size of the inorganic particles which are heated, $l \cong (\lambda\tau)^{1/2}$, is ≤ 0.5 μm (where λ is the thermal diffusivity of the material). Pressure equalisation between the detonation products and the particles of the additive will occur in time $\tau_1 \cong l/D$, where D is the velocity of propagation of the shock wave in the additive ($\sim 5 \times 10^3$ m s^{-1} at 20 GPa). In our case the pressure will be equalised for $\tau_1 < \tau$, i.e. for $l < 0.5$ μm. Thus, if the particle size of the additive is <0.5 μm we can expect temperature and pressure equalisation in a heterogeneous detonation zone.

The presence of high temperatures and pressures, and of chemically active products, in the reaction zone of the detonation should stimulate physicochemical changes in the additives. It is important to note that the cooling rate of the detonation products[43] and of the additive particles (or of the resulting compounds) is as high as during pressure relief after shock compression ($\sim 10^8$ K s^{-1}). The only difference is that after shock compression the sample in a preservation bulb remains in a densified state, whereas in the detonation products the particles fly apart: this helps to quench them and to preserve the compounds or the structural changes produced by the detonation.

We should also note that in a detonation wave the high pressures and temperatures can exist for times significantly longer than in the shock compression process. Some reactions probably occur when the detonation products are being ejected but while their temperature and pressure are still high.

In conclusion we should stress that the detonation parameter region (high temperatures and moderate pressures) is not easily accessible in SW experiments. These parameters can be achieved by DIC of previously heated samples (Fig.1*a*), but this approach does not offer the quenching conditions associated with the ejection of detonation products.

VI. CONCLUSIONS

We have shown that the wide range of methods recently developed for generating dynamic pressures can be applied to substances in the pressure range 10–100 GPa (or more) and the temperature range 4.2–10^4 K, and that the state of the sample after this treatment can be studied. The development of nearly isentropic dynamic compression methods is important, because it has allowed high levels of compression to be achieved by lowering the thermal contribution to the pressure generated by shock compression. By using DIC in conjunction with low initial temperatures it has been possible to work with compressed gases and to preserve the products thus obtained. Colliding pressure waves have been shown to create conditions in which an isentropically compressed sample can be additionally subjected to shock compression.

Comparison of the results obtained by shock compression and by DIC at high initial temperatures has established (by a direct experimental method) the role of the SW front in various processes. The conversion of boron nitride into a dense modification has been shown not to involve the strong microshear deformations generated at the SW front, and to be a thermally activated process. A chemical polymerisation reaction has been studied, and shown to be produced by the SW front.

By comparing shock compression and DIC results for moderately high pressures (using planar loading) we have shown that the pressure relief waves in the region of pressure falling to atmospheric levels do not contribute significantly to the creation of defects or to the final (residual) temperature rise of the sample associated with the macroplastic deformations.

Some very revealing experiments on the shock compression of systems including gaseous components have allowed new chemical syntheses to be performed. It appears that high residual temperatures convert a large proportion of the products (and possibly also some other unstable compounds) into the initial compounds. However, the resulting phases can be quenched by pre-cooling the sample. In principle it should be possible to establish conditions similar to those of

static experiments during the final stages of the shock compression (i.e. to cool the sample under high residual pressure). This requires a strong bulb, which will remain gastight after removal of the pressure. Our calculations suggest that samples can be retained under residual pressures of 1 GPa or more. This problem requires further study, and becomes even more complex when the compression products include gases.

We have shown that the region in the p,T diagram of a condensed substance which is not easily accessible in SW experiments (high temperatures at relatively low pressures) can easily be reached by applying dynamic isentropic compression to a pre-heated sample or by exploiting the high pressures and temperatures developed in a detonation wave.

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