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SHOCK-INDUCED MARTENSITIC TRANSFORMATION OF HIGHLY ORIENTED GRAPHITE TO DIAMOND

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ABSTRACT

Shock-wave profiles of highly ordered pyrolytic graphite shocked normal to the basal plane of the graphite crystal structure have been measured. For graphite with sufficient orientational order a martensitic transformation to a diamond-like phase is observed with a transition onset pressure 19.6±0.7 GPa, the stability limit of the graphite structure under shock compression. The minimum overpressure required for the transformation is not more than 6 GPa.

INTRODUCTION

Because of their great technological importance, the investigation of the carbon phases and how they transform from one to another under pressure is an important field of materials research. A significant part of this research is accomplished using shock-waves, since in these experiments uniform and accurately determined pressures can be applied over large sample volumes.

It is well known that diamond is formed by the shock compression of graphite. This process, which occurs in microseconds, happens naturally in the impact of meteors[1,2], within products of explosives[3,4], and by explosive compression of powders[5,6]. However, an important issue is whether the shock-induced phase transition of graphite to diamond is martensitic or diffusive. The relation between the crystal structures of graphite and diamond indicate that the phase transition should be fast and martensitic if shock pressure is applied perpendicular to the graphitic basal plane[7,8]. Since the lattice planes of graphite are loosely coupled, small amounts of shear stress naturally existing in the shock state are expected to induce displacive shear motion between the planes so as to produce the diamond stacking sequence.

Recently, several groups have measured the stability of the graphite lattice under *static* compression[9-12]. These studies all support that the graphite lattice is unstable above ~20 GPa and that the transformation to the new phase is reversible. However previous *shock* compression studies of graphite presented an inconsistent picture. A consequence of a martensitic transformation is a well-defined transition onset pressure. Shock studies[13-15] using pressed porous graphite samples indicate a phase transition near 20 GPa. In contrast, other studies using pyrolytic graphite (a quasi single-crystalline form) have observed phase transitions near 34 GPa[16], 45 GPa[13] or have failed to see it below 50 GPa[17]. Since pyrolytic samples are more ideal crystalline graphite than porous samples, this wide variety of transformation pressures previously seemed inconsistent.

Our preliminary measurements[18] on pyrolytic graphite of two different crystalline grades having different orientational order indicate a strong sensitivity of the transformation on graphite microstructure. Thus we believe the elevated transition pressures observed with pyrolytic samples of earlier studies were caused by insufficient order in their microstructure. Since porous samples are heated by shock compression significantly more than full density samples, we believe the porous samples underwent a thermally activated transformation[19], allowing a transition onset pressure near the crystalline graphite value.

Our studies are the first real-time shock wave-profile measurements using highly ordered full-density pyrolytic graphite.

EXPERIMENTAL TECHNIQUE

The locus of states achieved through shock is called a Hugoniot. Because the graphite-diamond transition involves a relatively large volume change, the graphite Hugoniot is expected to have a pronounced kink at the transition onset. This will cause the shock-wave transiting the specimen to bifurcate into two waves[20], producing a "two-step" structure in the shock pressure and mass velocity profile. This is illustrated in Fig. 1.

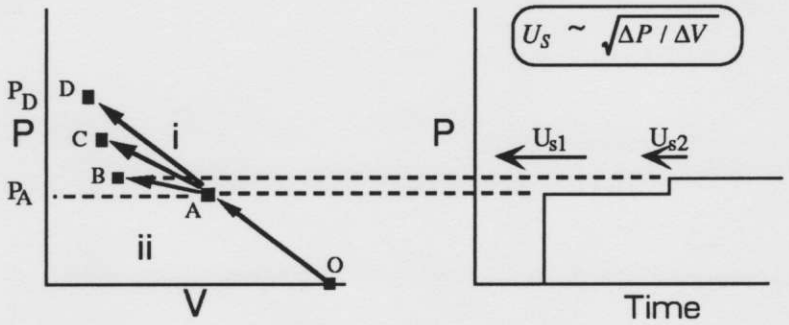


FIG. 1. Illustration of how a system undergoing a phase transition under shock produces a two-step wave-profile. Untransformed (i) and transformed (ii) graphite Hugoniots. The shock OAB produces a stepped wave profile in pressure vs time, and a corresponding one in mass velocity vs. time.

For pressures between P_A and P_D the shock occurs in two steps. The first step represents graphite shocked to a state incipient to the transition at a pressure P_A along the untransformed Hugoniot **i**. The second step is a compression into the phase-transformed state represented by Hugoniot **ii**. The shock speed of the steps (U_{S1}, U_{S2}) depends on the slope $\Delta P/\Delta V$ of the jumps in pressure-volume space. As the net shock pressure increases the speed of the second wave approaches the first until there is a single step, when the slope OD exceeds OA (the overdriven condition).

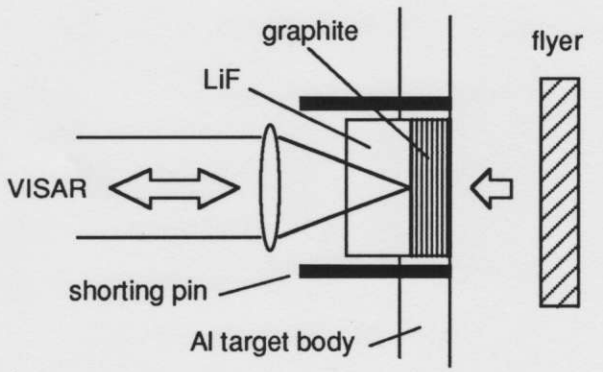


FIG. 2 Target Schematic. The VISAR laser beam is Doppler shifted by the movement of the LiF/graphite interface. An interferometer produces a fringe shift proportional to the interface velocity.

The speed of the phase transition is manifested in the risetime of the second step. If a set of simple displacements exists between two crystal structures the transformation is martensitic and will produce a fast risetime. Thus by measuring the temporal wave-profile we can determine the martensitic nature of the transition and through simple shock relations we can determine the location of the Hugoniot.

Shock-waves were generated by impact of a Cu disk accelerated by a two-stage light-gas gun to velocities of several km/s striking a graphite specimen normal to the basal plane. A schematic of the target is shown in Fig. 2. The specimen was backed by a LiF window through which a laser beam was reflected off the

graphite/LiF interface. Since LiF has a shock impedance similar to graphite, the perturbation of the first shock by the interface is relatively small. The laser is the illuminating beam of our VISAR interferometer[21], which measures mass velocities (U_p) via the doppler shift of the reflected light with a time response time of ~2 ns. Electrical shorting pins flush with the front surface of the sample provide a time zero for the start of the shock. Observation of shock arrival at the sample rear allows shock speed determination to 0.5%.

The majority of our samples were highly oriented monochromator grade (ZYB) graphite from Union Carbide measuring 3.5-4 mm thick and 15 mm square. Their densities were 2.254-2.259 g/cm^3, very near the handbook value[22] for crystalline graphite of 2.265 g/cm^3. Several shots were also fired with a lower grade graphite (ZYH) from Union Carbide, having a density 2.262 gm/cm^3. This grade is distinguished from the former by beta, the angular of the (002) x-ray diffraction peak, which measures the spread of misalignment of the crystallite c-axes. For the high- and low-grade samples beta is 0.8° and 3.5°, respectively.

FIG. 3. Wave-profiles of ZYB pyrolytic graphite. The curves have been staggered horizontally on the graph for clarity. The two-wave structure is direct evidence for a phase transition.

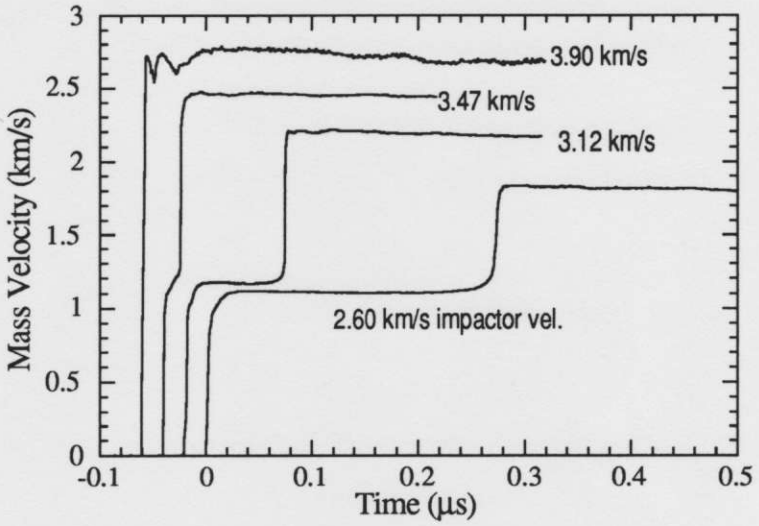
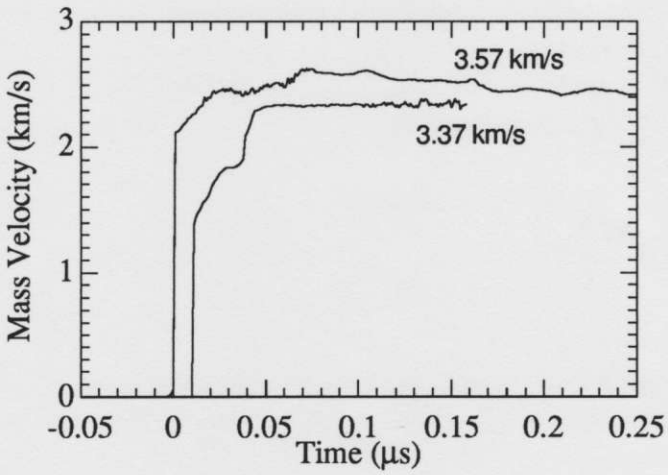


FIG. 4. Wave-profiles of ZYH pyrolytic graphite showing frustrated transitions due to insufficient orientational order. The curves have been staggered horizontally on the graph for clarity.



RESULTS

Measured wave-profiles on ZYB grade graphite are shown in Fig 3. The clean two-step structure demonstrates a martensitic transformation by the rapid (<10 ns) risetime of the second steps. As the impactor speed increases the delay between the steps decreases until a single shock is produced, analogous to the progression OAB, OAC, OAD in Fig. 1.

Measured wave-profiles on the lower grade, ZYH graphite are shown in Fig. 4. The lower orientational order causes frustrated transitions, characterized by higher and variable transition pressures (height of first step), and a significant bevel to the shoulder of the first step.

The ZYB grade graphite wave-profile data was analyzed using standard relations[23] conserving energy, mass and momentum across the shock front to find the description of the states of graphite during its compression and transformation. A

detailed description of the analysis is given in Reference [24]. The shots are plotted in the pressure–volume domain in Fig 5. Except for the two highest velocity shots which overdrive the transition, a two-step wave-profile exists and there are the following stages of compression: 1) initial shock to transition onset at pressure P_A. This is held until passage of the second wave whereupon there is 2) a rapid transition to the denser phase, and 3) reflection of the second wave off the LiF window.

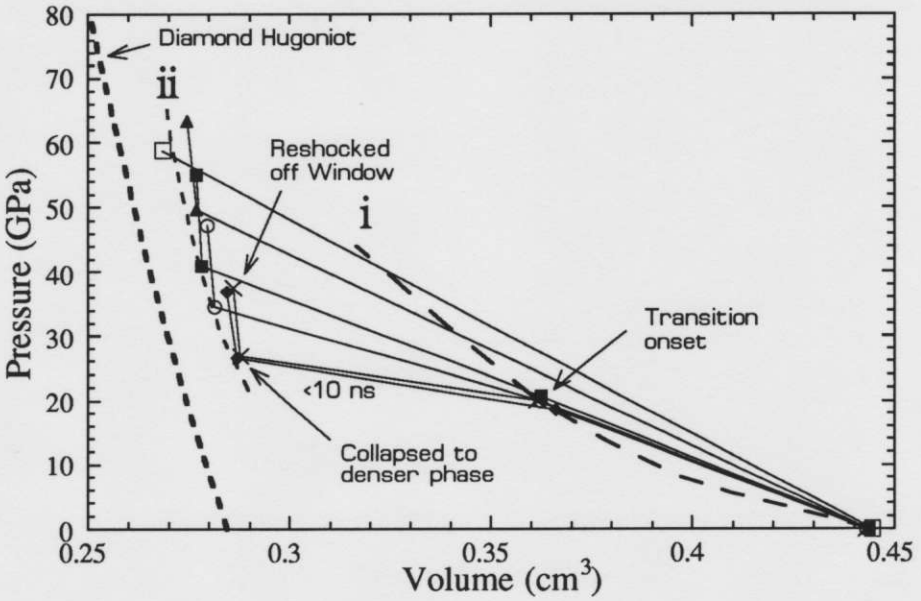


FIG. 5. Pressure - volume histories of high grade (ZYB) pyrolytic graphite. In the shots with the two highest impactor velocities (❑,▲) the transition is overdriven by a single shock which then reflects off the LiF window. In the other shots the shock splits into two waves and the pressure is held at the incipient value P_A until passage of the second wave. For comparison the measured Hugoniot of diamond[25], and of untransformed graphite[13,17,26] (i) is shown. Curve ii represents the Hugoniot of the transformed phase.

DISCUSSION

Figure 5 shows that a well-defined transition onset pressure of 19.6±0.7 GPa exits for ZYB graphite under shock compression. The endpoints of the shock trajectories in the figure fall along a Hugoniot curve (ii) which is distinct from, but parallel to the diamond Hugoniot[25], implying that the phase transformed graphite has a diamond-like compressibility. This is also indicated by the steep slope of the portion of the compression histories corresponding to the reflection of the second wave off the LiF window.

According to the separation between curve ii and the diamond Hugoniot, the density of the phase transformed state is ~5% less than that of diamond for an equivalent pressure. The density difference may be ascribed to thermal pressure and to disorder of hexagonal diamond. Poor crystallization was found in hexagonal diamond recovered from static compression experiments of Bundy[8]. In flash x-ray diffraction measurements during shock compression of pyrolytic graphite, Johnson & Mitchell found that above 20 GPa no well-defined diffraction peaks could be observed, whereas with the same apparatus shocking graphitic BN, well-defined peaks of the phased transformed BN structure were seen[27].

Another possibility is that Hugoniot ii represents a new form of carbon which is distinct from diamond but diamond-like in density and compressibility. A distorted

diamond form (n-diamond) has recently been recovered in shocked graphite by Hirai et al.[28]. The static compression studies[8-12] of graphite support that at least one new phase of carbon intermediate in density between graphite and diamond exists. Hemley[12] et al. indicate that this form has a diamond-like compressibility. That the shock compressed phase is electrically insulating has been determined by Shaner[29] et al. They observed in real time the electrical resistance of pyrolytic graphite shocked to 40 GPa to increase by three orders of magnitude.

The temperature of graphite shocked to the transition onset pressure was calculated[24] to be 500-550 K. This temperature is low compared to the melting point[30] of compressed graphite (~ 4000 K), and thus supports a martensitic transition rather than a diffusive reconstructive transformation to diamond, which occurs[31] at high shock pressures at 3000-4000 K.

CONCLUSIONS

Our results support a martensitic transformation for highly ordered pyrolytic graphite to a diamond-like state with a 19.6±.7 GPa transition onset pressure. This pressure represents the stability limit of the graphite lattice to shock loading, and is similar to the ~20 GPa transition onset pressures observed in static compression experiments[8-13]. Martensitic transformations are only observed with graphite having sufficient orientational order[18] (ZYB, not ZYH grade pyrolytic). The Hugoniot of the transformed state lies parallel to the diamond Hugoniot (implying diamond-like compressibility), but with ~5% less density. This suggests that the state is a disordered or distorted diamond-like form. The minimum overpressure needed to drive the transition has not been determined, but is as small as 6 GPa. The transition is overdriven above 40 GPa.

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