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CARBON IN DETONATIONS

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MASTER

CARBON IN DETONATIONS

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We review three principal results from a five year study of carbon and its properties in detonations and discuss the implications of these results to the behavior of explosives. We first present a new determination of the carbon melt line from release wave velocity measurements in the shocked state. We then outline a colloidal theory of carbon clustering which from diffusion limited coagulation predicts a slow energy release rate for the carbon chemistry. Finally, we show the results from the examination of recovered soot. Here we see support for the colloid theory and find the diamond phase of carbon. The main theme of this paper is that the carbon in detonation products is in the form of a colloidal suspension of carbon clusters which grow through diffusion limited collisions. Even the final state is not bulk graphite or diamond, but is a collection of small, less than 100 Å, diamond and graphitic clusters.

INTRODUCTION

Other researchers[1,2,3,4] have noted certain problems in the modeling of the detonation process, in particular, in plate-push and interface velocity experiments with variable explosive thickness, and appealed to special properties in carbon chemistry to explain the difficulties. It is easy to convince oneself that indeed carbon is unique among detonation products since it is the only product that can form arbitrarily large molecules in the form of pure carbon, C_n, n=1,2, ..., or the whole field of organic chemistry. This is in contrast to the nitrogen, oxygen, and hydrogen which go mainly into N_2, CO_2 and H_2O. This picture points to carbon as a prime candidate for a slow energy release as compared to the other chemistry. It just takes time for the carbon clusters (molecules) to diffuse together and grow to a bulk solid. This prompted us to study both the thermodynamic and cluster dynamic properties of carbon in the high temperature, high pressure regime of detonation products.

It is helpful to have a picture that, while oversimplified in detail, contains the essence of the carbon behavior. We envision "blobs" of carbon executing Brownian motion in the hot, dense background fluid of the other detonation products with the carbon clusters building up through random collisions. We assume there are no back reactions and no barriers to reaction; that is, the particles always stick if they touch. This can be refined with a sticking probability. The background fluid keeps the clusters at equilibrium with respect to temperature, carrying off heat when clusters merge. We assume that newly formed clusters anneal. We consequently view the carbon clusters as fairly compact, essentially spherical objects, although a significant deviation from this shape affects our results but little. For simplicity, our initial state for the clusters at the von Neumann spike is taken to be monatomic. The annealing process may cease at some large time and cluster size, say 10^4-10^5 atoms, and leave the infinite time state as a collection of large diamond and/or graphite clusters. This scenario differs from past modeling of carbon in that we do not have bulk, thermodynamic graphite or diamond, even in the final state.

The remainder of this paper has four sections. The first presents the new melt line as determined from release wave velocities. As we developed the picture outlined in the preceeding paragraph, the importance of this work declined. However, we give the results here for general interest; it is a nice piece of work. Next we develop our theory of carbon coagulation and show the resulting slow energy release with some discussion of its influence on detonation behavior. We then give some experimental support for the colloidal picture from the soot recovery experiments. Here we have seen diamonds in the soot. Lastly, we very briefly discuss the slow rate in relation to hydrodynamic studies.

CARBON MELT LINE

For some time (decades) the standard phase diagram of carbon has been qualitatively of the form shown in Figure 1. Here we are interested in the location of the melt line since even bulk carbon in the detonation regime is somewhat close to melting. If we consider that small clusters can melt at half the bulk melting temperature,[5] the location of the melt line becomes of even more significance. The melt line from the diamond to liquid phase is perfectly acceptable with thermodynamic considerations although the negative slope is anomalous, implying either that the liquid is denser than the diamond or that the entropy of the liquid is less than that of diamond.

To find the melting point along the Hugoniot, standard shock velocity particle velocity measurements are not at all sensitive enough to determine the small structure in the Us-up curve. A much more obvious signature, a discontinuous jump as a function of shock strength, occurs in the velocity of the release wave overtaking a shock. In the solid phase this wave travels with the longitudinal elastic velocity, while it drops to a bulk velocity if the material is shocked above melting. The rarefaction velocity is determined from the dimensions of the sample, the velocity of the shockwave, and the timing of the overtake. This technique has already been used successfully for iron,[6] tantalum,[7] and aluminum.[8]

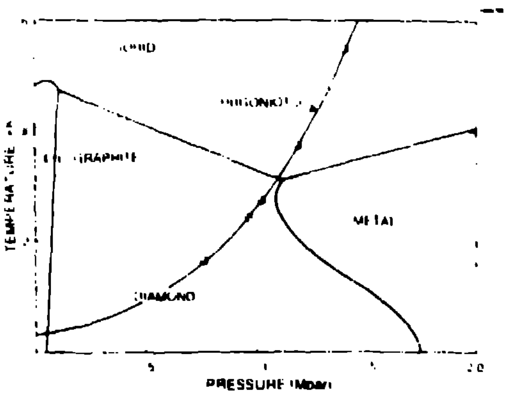

FIGURE 1
Phase of diagram of carbon. The principal Hugoniot is shown and longitudinal velocities are measured at the open circles.

A series of five shots at pressures and temperatures given by the open circles in Figure 1 have been done.[9] All the release wave velocities are consistent with longitudinal velocities for diamond; no melt signature is seen. The higher pressure melt line must be moved significantly upward in temperature with the lower pressure region remaining essentially unchanged. The low pressure restriction comes from other, older experimental work.[10] We now have a positive slope with the melt line going to higher pressure above the highest data point. As an aside, the metal region, based on theoretical work of Yin and Cohen,[11] is pushed out beyond

10 Mbar or more.

Thus in modeling bulk, equilibrium carbon in detonation regimes, it is quite reasonable to consider only graphite and diamond. For finite clusters it is safer than with the old phase diagram to think of them as solid. Another benefit from the experiment is that one has from the sound velocities derivative information for equation of state determination.

COLLODIAL THEORY OF CARBON COAGULATION

We now turn to the picture of carbon coagulation given in the introduction. Here we will consider for ease of discussion a model system where at time zero we have only monatomic carbon in an inert background fluid. We assume that the background has no time dependence and has a temperature T. The carbon clusters are always spherical. Our coagulation theory comes from the classic work of Smoluchowski.[12]

If we denote the concentration of clusters with i atoms as ν_i, the basic growth equation is

$$\frac{1}{4\pi DR}\frac{d\nu_k}{dt} = \sum_{i+j=k} K_{ij}\nu_i\nu_j - 2\nu_k\sum_{j=1}^{\infty}\nu_j K_{jk}$$

$$k=1,2,\ldots \qquad (1)$$

The K_{ij} is a geometric factor that is a function only of the cluster radii. For our work a very accurate approximation is to set $K_{ij}=1$ independent of i and j. The combination D_iR_i, where D_i is the diffusion coefficient of an i cluster of radius R_i, is independent of i, thus we denote it as DR. The time is t. The interpretation of Equation (1) is that the first sum on the right represents the growth of a k cluster when i and j clusters with i+j=k collide to form a k. The second sum represents depletion of the k cluster population by collisions with any other cluster.

It is convenient to scale our variables to $n_i=\nu_i/f_0$ and $x=4\pi DRtf_0$, with $f_0=\nu_1(t=0)$. Then with $K_{ij}=1$ an exact analytic solution exists, namely,

$$n_i(x) = x^{i-1}/(1+x)^{i+1}, \quad i=1,2,\ldots \qquad (2)$$

We still require DR. We first appeal to the Stokes-Einstein relation[11] to relate DR to the viscosity η of the background fluid.

$$DR = k_B T/6\pi\eta \qquad (3)$$

We obtain η from the modified Enskog theory of dense fluids. Enskog is a reasonably accurate and easily applied transport theory for dense fluids. References 14 and 15 give nice overviews of modified Enskog. This completes our rather simple theory of carbon coagulation.

We now need to apply the above to calculate the quantity of interest to detonations. This is ΔE, the energy difference per mole of carbon between the total cluster energy at time t and the infinite time bulk carbon energy. ΔE is given by

$$\Delta E = \sum_i n_i(x)\Delta E_i \qquad (4)$$

where ΔE_i is the energy difference per mole between the i cluster energy and the bulk. This ΔE_i we approximate by a surface term, thus $\Delta E_i = a i^{-1/3}$. The a is obtained by fitting to data and theory on the energies of small carbon clusters (molecules). The result is [illegible] kcal per mole.

$$\Delta E = \frac{90}{(1+x)^2}\sum_{i=1}^{\infty} i^{2/3}\left(\frac{x}{1+x}\right)^{i-1} \qquad (5)$$

For large t (equivalently x) the sum in Equation (5) is well approximated by an integral and can be evaluated. Then

$$\Delta E - 80\ [illegible]\ x^{1/3} \qquad (6)$$

This shows directly that we have a slow energy release from carbon. The chemistry of the other detonation products should release energy at a much faster rate.

Our result, Equation (6), is not sensitive to the several simplifying assumptions, such as, spherical clusters, monatomic initial state, etc., that we made in our modeling; i.e., if we lift those simplifications, the answer will change little or none.

Still one wants to see how the numbers work out for real explosives. We have looked at both TNT and HMX; we will discuss HMX here. Putting conservative numbers into the just presented theory, that is, using estimates that always give the minimum ΔE, we find that ΔE at the end of the reaction zone is about 1% of the energy released. If, instead of conservative estimates, best guesses are made, for ΔE again at the end of the reaction zone we see that about 2-4% of the energy release is tied up in the slow rate.

This ΔE seems very small but there is an amplifier effect. We look to simple CJ thinking to obtain a feel for how the ΔE ~ 2-4% will affect experiments. From this approach we will get an *effective* shift in the pressure. This is very simplified thinking. We should really look at how the slow rate changes the reaction zone and from that go to the influence on, say, plate push and interface velocities. But we will get a handle this way. Bdzil[16,17] has demonstrated that a slow release of energy of O(δ²) produces changes O(δ) in the shock state. This effect comes from the fact that the Rayleigh line is tangent to the fully reacted Hugoniot at the CJ point. See Figure 2. The dotted curve is the partially reacted Hugoniot shifted O(δ²) ~ 2-4% by the slow energy release. (One might worry that, besides the ΔE from the slow rate, there is also a compensating ΔP due to the pressure from the motion of the clusters. However, the number of moles of clusters at the end of the reaction zone is small enough to neglect such.) The O(δ²) shift in the Hugoniot translates to a O(δ) ~ 10-20% shift in pressure in going from point CJ to A. For times comparable to the slow reaction zone (the slow rate) and longer, the detonation runs at the CJ velocity for the fully reacted Hugoniot. Until times larger than the slow reaction zone, the states from A to CJ along the Rayleigh line appear to be part of the Taylor wave. Thus we are looking at potential changes of 10%-20% in the shock state for time scales of microseconds and distance scales of centimeters. This is about the size of effects seen experimentally. See page 105 of Reference 3 and References 1 and 6.

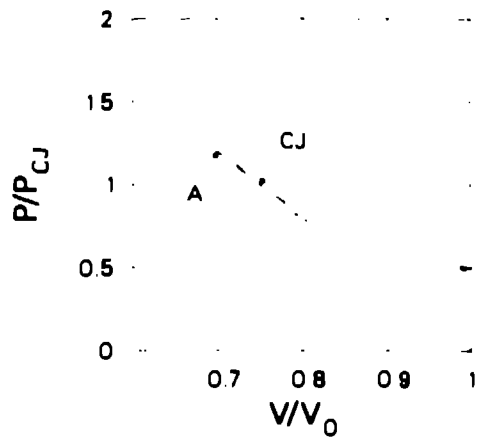

FIGURE 2
Influence on pressure of Hugoniot shift. The Rayleigh line is the solid line, the fully reacted Hugoniot is the solid curve, and the partially reacted Hugoniot is the dashed curve.

More details than are given in this section are presented in Reference 18.

SOOT RECOVERY

To give some experimental support to the assumptions in the coagulation model and just to understand better the soot from explosives, we have examined with several techniques the recovered soot from a variety of high explosives. We will discuss here only the early work on Comp B, a 50/50 mix of TNT/TATB, and a 50/50 mix of TNT/NQ. For more details than discussed here see Reference 19. The paper by Greiner and Hermes[20] discusses further investigations.

We looked to these recovery experiments fully realizing the difficulties with such; the character of the soot most certainly changes on release from the high-pressure, high temperature regime of interest to ambient. We mitigate this through the use of large containers, 1 cubic meter or larger, filled with argon. However, some observations at ambient can, with confidence, be related back to the explosive processes. For example, if we see diamond with specific characteristics, it is pretty certain these were not altered on release. But graphite can come from the release of diamond.

FIGURE [illegible]
Electron micrograph of Comp B sample. Scale 1 cm = [illegible] A graphitic ribbons, B diamond spheroids.

Our explosive charges range in size from 200 to 300 grams. After firing the soot is scraped off the tank walls and dried. A number of analyses are then performed; we will talk here only on the transmission electron microscopy (TEM), TEM electron diffraction, x-ray diffraction, and Auger/ESCA analysis.

Let us first dispose of the diamonds. Under the TEM we see for all three samples roughly spherical particles, typically 50 Å diameter but ranging in the extreme from 20 to 200 Å. See Figure 1. TEM electron diffraction on these particles identifies them as diamond clusters. See Figure [illegible]. The "spotty ring" pattern indicates that the microcrystals are fairly clean of defects. The other morphology, the ribbons, is identified as turbostratic graphite, carbon black. The cluster sizes are in the same range as the diamond. Upon treatment of the soot in nitric and perchloric acids to remove the graphitic form, we recover a brown powder, 25% of the soot. X-ray diffraction on this powder verifies the diamond identification and the diffraction ring width gives a microcrystal size of [illegible] Å. Contemporaneous with us, Titov and his coworkers have found diamond clusters with very similar characteristics in explosive soots[21].

We now look to what we can learn relative to our modeling. First and most important, we see from the TEM micrographs that the soot is not bulk graphite or diamond. Even at ultimate size we have clusters with 15-20% of their atoms residing in the surfaces. Also

FIGURE 4
Electron diffraction pattern showing diamond diffraction rings from (111), (220), (311), (400), and (400) weakly

the turbostratic graphite has curved layers and the interlayer spacing is 3.5 Å as compared to 3.35 Å for pure graphite. For early times where the carbon clusters are much smaller than our 50 Å, we cannot at all model the carbon with bulk thermodynamic thinking. For the infinite time final state it is a good approximation, if one knows the proportion of graphitic and diamond forms, to take bulk graphite and diamond thermodynamic and correct for surface curvature and expansion contributions.

We have lost the use of the equilibrium phase diagram to determine whether we have graphitic or diamond phases. The surfaces shift the relative stability of the two morphologies of clusters. In fact, if one thinks of all the dangling bonds a diamond cluster will have compared to a graphitic one, one wonders why diamond forms at all. The answer must lie in the bonds being capped off by C=N, or CO, or H. With Auger/ESCA analysis on the acid processed diamonds we do see O and N atoms which disappear upon surface sputtering. Van Thiel and Ree in Reference 22 also use shifts in the graphite/diamond phase line to explain the detonation velocities of high carbon-content explosive. The importance and difficulty of this surface chemistry, especially for the small clusters at early time, means that simple, semiempirical modeling is probably the best strategy.

The basic building blocks of the soot are the 50 Å "blobs". This supports our simplifying assumption of spherical clusters and the picture of annealing. We see that the larger soot structure consists of a loose collection of the "blobs" thus implying that the annealing process shuts down when the fraction of atoms in the cluster surfaces is 10-20%. This makes some sense if we appeal to any combination of the following mechanisms: (1) the heat from bond formation becomes too small a fraction of the total energy of a cluster; (2) the effective melting temperature for a finite cluster shifts with cluster size; (3) the kernal in the coagulation equations[14] changes character as a function of cluster size; (4) the thermal fluctuations in a finite cluster are smaller on a percentage basis in larger clusters; and (5) surface tension can no longer sphericalize the clusters. Our theory from the previous section is, of course, not valid with the approximation $K_{ij}=1$ once the annealing stops. However, this is not important for detonations because we have most of the energy out before this point.

Finally, we find that the soots contain large quantities of volatiles, say around 25 wt%.[20] This makes it difficult to relate the heat of formation as measured for the soot to the heat of formation of <u>pure</u> carbon as needed for standard modeling.

SLOW RATE AND HYDRODYNAMICS

In the theory section we discussed the influence a slow carbon rate has on explosive behavior through a simple CJ model. This is a somewhat crude approach since such modeling does not really have the necessary physics to deal with the carbon chemistry. As a result, the slow rate appeared as a change in the *effective* CJ pressure. It is more correct to make detailed modeling of the reaction zone and look to the influence of the carbon coagulation on the reaction zone and subsequent detonation behavior. Fickett with his mathematical analog has looked at some of these questions.[23]

Another approach to this is to implement a slow carbon rate into the equation of state and burn models of a numerical hydrodynamic study for detonations. In particular, one should look at plate-push and interface velocity experiments. This has been done by Tang[3] and Tarver et al[4], independently of each other and of us. By including a slow rate they found the agreement between experiments and calculations for TNT, HMX, and TATB nicely improved. The time scale that Tang chose for the slow reaction agrees with our estimates.

We are also looking into hydrodynamic calculations to see if details beyond the zeroth order approximations done by Fickett, Tang, and Tarver et al are important. In addition we are interested in a more physical functional form for the energy release rate.

This work of our colleagues does support our view of the place carbon occupies in detonation behavior. The philosophies of our approaches differ; we form a microscopic picture and derive the conclusion of a slow energy release from carbon while they add an extra piece to their macroscopic hydrodynamic code and observe the consequences. The two views are complementary and supportive.

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