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ATTEMPTS TO INITIATE DETONATIONS IN METAL-SULPHUR MIXTURES

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Abstract. The possibility of self-sustained solid-solid detonations (SSD) in Mn+S mixtures has been investigated. Charges 50 mm in diameter under different degrees of confinement were used. The initiation charges used include nitromethane, tetryl, and C-4. No self-sustained SSD were observed in the present study. Neither did the degree of confinement nor the type or weight of the initiation charge appear to make a significant difference in the results obtained. The shock and reaction front are initially coupled but decay rapidly. Decoupling occurs after about 25 mm of propagation when the shock has decayed to about 2.5 km/sec which corresponds to the estimated sound speed of the reactant. The lack of significant feedback of the chemical energy released to the shock via work done by the expansion of the solid products is probably the cause for failure to obtain SSD in Mn+S.

INTRODUCTION

Solid-solid reactions (i.e. solid phase reactants to solid phase products) of a compacted mixture of inorganic compounds have been shown to be extremely energetic[1]. Adiabatic flame temperatures are found to exceed those of conventional high explosives (e.g. Ca + S gives $T_a \cong 5000°K$ compared to $T_a \cong 3000°K$ for TNT). Self-sustained slow deflagrations (with propagation speeds of the order of centimeters per second) have been observed in many of these compacted powder mixtures, and form the basis for material synthesis (self-propagating high-temperature synthesis or "SHS"). Numerous shock compression experiments have also demonstrated that very rapid chemical reactions can be initiated by a shock wave in these compacted powder mixtures[2,3]. The combination of high energetics and fast shock-induced reactions led to speculation of the possibility of solid-solid detonation (SSD), i.e. a supersonic combustion wave with propagation speed of the order of thousands of meters per second. Theoretical analysis has been carried out by Bennett and Horie[4] and Merzhanov et al[5]. However, there are too many assumptions in these analyses to permit definitive conclusions about the possibility of SSD. We have carried out preliminary experiments on 25-mm diameter Mn+S charges confined by a steel casing of 4 mm wall thickness[6]. The shock and the reaction front are observed to decouple rapidly from each other after propagating over a distance of the order of a charge diameter. In some experiments, the reaction front was found to re-accelerate slightly after its initial decay. Merzhanov et al[5] have also reported a slight re-acceleration of the shock after an initial decay in mixtures of titanium-carbon-aluminum and paraffin. Failure to observe self-sustained SSD in these experiments may be due to (i) insufficient strength of the initiation shock wave and (ii) the charge diameter used is too small and is below the critical charge diameter. We have carried out further experiments with the Mn+S mixtures, and the present paper reports some of the recent results obtained.

EXPERIMENTS

It should be noted that the choice of the Mn+S mixture is based on (i) its high energetics ($T_a \approx 3332°K$) (ii) the combustion products are in the solid phase at the adiabatic flame temperature and (iii) the sulphur can be melted and resolidified to give a "voidless" reactant mixture at almost the theoretical density. In the present series of experiments, the charge diameter has been increased from 25 mm to 50 mm. Three types of

containment have been used – steel casings with 6 mm wall thickness, PVC pipes and paper tubes. The PVC and paper tubes used in the later experiments are based on the fact that the stronger steel confinement was found to have little influence on the phenomenon. Thus, weak outer confinement (e.g. PVC and paper tubes) with lower sound speed is subsequently used to encase the SSD charge to prevent any precursor wave from disturbing the medium ahead of the SSD.

Stronger initiation shocks are also used in the present study. In our previous experiments[6], nitromethane sensitized by 15% diethylenetriamine (DETA) was used as the initiation charge. The detonation pressure for nitromethane + 15% DETA is 10.2 GPa (Cheetah). In the present experiments, tetryl and C-4 with detonation pressures of 22.6 GPa and 25.7 GPa, respectively, were used. Hence, the initiation shock pressure is double that of the nitromethane used previously. The tetryl charges used are in the form of 50-mm-diameter × 50-mm-length pellets. One or more pellets can be stacked to increase the total weight of the initiation charge. The C-4 is packed into 50-mm-diameter paper tubes of different lengths to provide charges of different weights. In a few experiments, sheet explosive is wrapped around the top 10 cm of the SSD charge to provide a strong Mach disc for the initiation. Whereas in most of the earlier experiments, a single centrally-located blasting cap is used for initiation, a planar wave generator was used in some of the present trials to provide a more uniform initiation shock over the surface of the SSD charge. Piezoelectric shock pins, contact gauges, ionization probes as well as optical fibers were used to monitor the shock and reaction front time of arrival. Schematics of the various charge arrangements are illustrated in Fig. 1.

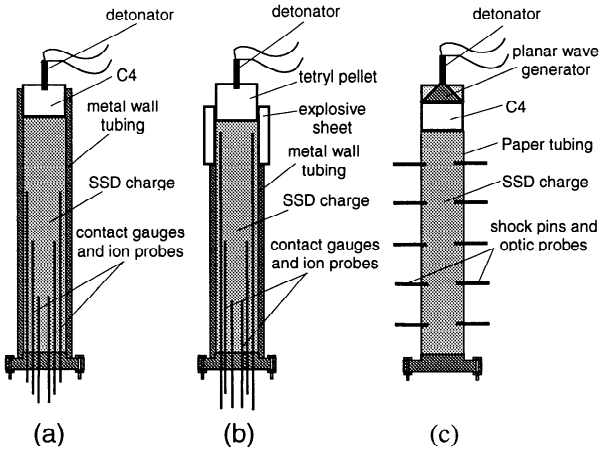

FIGURE 1. **Charge configurations studied**

RESULTS AND DISCUSSIONS

In the steel-confined 50 mm charges using C-4 as the initiation charge, it is observed that the shock decays rapidly from an initial velocity of about 3 km/sec to about 1.36 km/sec after a distance of the order of a charge diameter. Shock and reaction fronts are coupled initially and rapid decoupling occurs in less than half a charge diameter. Thus, in spite of a larger charge diameter and high initiation shock pressure, no self-sustained SSD is observed, and the results obtained are similar to those in the smaller 25 mm charges reported earlier[6].

Using a PVC tube (5 mm wall thickness) instead of a steel tube for confinement, similar results are also observed indicating that confinement appears to have little effect on the velocity-diameter dependence for SSD. In a few experiments, approximately 1% of glass microballoons is added to the Mn+S charge. The results indicate that the microballoons do not sensitize the Mn+S mixture by creating hot spots.

In an effort to further increase the initiation shock strength, the configuration shown in Fig. 1b is used. A 100 mm length of bare SSD charge is wrapped with a PETN-based sheet explosive (Detasheet). The detonation of the outer sheet explosive drives a Mach disc in the SSD charge at the velocity of the sheet explosive (~ 6 km/sec). The results indicated that in the driven section of the charge, the shock velocity in the SSD material is of the order of about 6 km/sec. However, the shock decays rapidly upon exiting the driven section and again decays to about 2.5 km/sec within about one charge diameter (i.e. 50 mm) followed by rapid decoupling of the reaction front from the shock. A slightly longer distance of coupling is obtained for this case.

In the final series of experiments, faster response piezoelectric shock pins are used instead of contact gauges for detecting the shock arrival. Furthermore, rather than using ionization probes, a shielded optical fibre is used to detect the arrival of the reaction front. In previous experiments, it was found that the ionization probes sometimes give spurious signals due to the semi-conducting nature of the shocked material. This led to ambiguous interpretation. In this series of experiments (configuration shown in Fig. 1c) the SSD material is enclosed in a paper tube to avoid any precursor wave within the casing. The C-4 donor charge was initiated (~ 182 g) by a planar wave generator to provide a more uniform shock loading across the surface of the SSD charge. The results all indicate that the shock decays rapidly (from an initial value of about 4 km/sec at 10 mm from the initiation

surface) and decoupling of the reaction zone from the shock occurs at about 25 mm (half the charge diameter) when the shock velocity is about 2.5 km/sec. A typical trajectory and velocity plot is shown in Fig. 2.

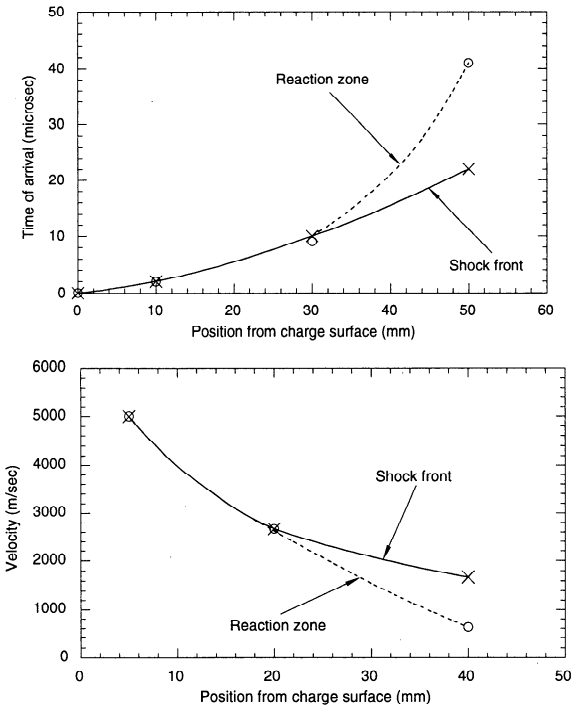

FIGURE 2. Trajectory and velocity plot in the Mn+S charge

DISCUSSIONS

Although self-sustained SSD was not observed in the present experiments, it was found that the shock and reaction zone are intimately coupled for shock velocities above about 2.5 km/sec. In order to interpret the results in more detail, the equation of state or the shock Hugoniot of the Mn+S mixture is required. Shock Hugoniot data for Mn+S is not available from the literature. However, an estimate for the shock Hugoniot of Mn+S mixture could be obtained using the additivity rule of Dremin and Karpukhin[7] if the Hugoniot for Mn and S are known. The Hugoniot for S is given as $U = 2.334 + 1.588\ u$ where "U" and "u" denote the shock and particle velocity respectively in Batsanov's book[3]. For Mn, the Hugoniot is not given, but one can estimate it from the values of the bulk modulus and the pressure derivative (also given by Batsanov[3]). The Hugoniot of Mn is found to be $U = 4.265 + 1.51\ u$. For the equimolar mixture of Mn+S, the weight fraction of Mn and S are 0.6314 and 0.3685 respectively. Using the formulas given in Batsanov's book, the Hugoniot for the mixture Mn+S is found to be $U = 2.58 + 1.54\ u$. Thus, the sonic velocity for the mixture is close to 2.6 km/sec. The present results therefore indicate that shock and reaction fronts can be coupled down to shock velocities of the order of the sonic speed. Using the shock relationship $p = \rho_o U u$ and the Hugoniot for Mn+S, the shock pressure near a sonic speed of about 2.7 km/s is found to be 1.11 GPa. The results suggest that rapid chemical reactions require that the material be under compressive and shear stresses (generated from the difference in density between the particles of the sulphur substrate).

When the medium is not compressed, the combustion wave propagation reverts back to one depending on heat diffusion as in SHS with a propagation velocity of the order of centimeters per second.

That chemical reactions can be of non-thermal mechanical nature had been advanced by a number of Russian researchers in recent years. For example, Benderskii et al.[8] advanced the hypothesis that the global activation energy of the reaction is given by the difference between the usual thermal activation energy and the elastic compression energy (i.e. $E = E_0 - \alpha\pi$ where α is of the order of unity and π is the elastic energy of compression). Thus, for sufficient high compression energy, the material will undergo spontaneous ignition even at room temperatures. Of particular relevance to SSD is the work of Enikolopyan[9] who reported "cold" detonations in thermite mixtures of Fe_2O_3 + Al and Fe_2O_3 + Mg under high compression and shear. Enikolopyan stated that the detonation is initiated and sustained "isothermally" at room temperature by mechanical processes. Enikolopyan also postulated that high compression reduced the interatomic distances and also strongly deformed the bond angle of the molecules. Such "deformed" molecules are equivalent to excited species and are highly reactive during their relaxation. Sudden removal of the stresses (breaking of chemical or Van der Waal bonds, shear deformation, etc.) can hence result in ultrafast chemical reactions between the species. For a heterogeneous system where mixing between the various components is required, Batsanov[10] postulated a superfast diffusion mechanism based on the difference in the mass velocities of the different species under shock acceleration. This leads to interparticle penetration and fragmentation, thus giving rise to the required mixing rate for the rapid chemical reactions observed. It should be noted that these rapid solid phase reaction mechanisms have not been studied

in detail. The fact that rapid shock-induced reactions in solids is observed does indicate that these (or other) "non-traditional Arrhenius rate reaction" mechanisms do exist.

Apart from high energetics and rapid shock-induced reactions, the existence of an SSD also depends on the feedback of the chemical energy released to sustain the propagation of the shock front. In conventional explosives, the expansion of the detonation products can do work on the reactant and drive the shock front. In a solid-solid reaction, the volume change is extremely small in general (and can even be negative). Thus it is difficult (at least within the hydrodynamic theory of detonation), to see how the shock can be maintained for self-sustained propagation. In a study by Knyazeva and Dynkarev[11], and more recently by Viljoen and Hlavacek[12], the propagation of a thermal plastic wave in a chemically-deformed solid is studied. An ignition mechanism where the activation energy can be reduced by mechanical loading is used. Apart from the slow deflagration wave solution associated with the SHS process, a steady state supersonic wave solution is also obtained. This stationary supersonic wave can be identified as an SSD. The implication of Knyazeva's result is that an SSD may not fall within the classical hydrodynamic theory of detonation. The nature of an SSD may be that of a thermal plastic reactive wave. As such, the material and transport properties may play a significant role rather than energetics and the reaction rate in a hydrodynamic detonation.

CONCLUSIONS

The present study failed to demonstrate the existence of self-sustained SSD in Mn+S mixtures in spite of the high energetics of this reaction. Neither confinement nor the strength of the initiating shock wave appears to influence the phenomenon significantly. Shock and reaction fronts decay rapidly within a couple of centimeters from the initiation surface. Decoupling of the shock and reaction front occurs at around the sonic velocity when the material is not sufficiently compressed. This indicates that the fast reaction observed initially depends on the strong mechanical compression of the medium, in accordance with the postulates of Russian researchers. In spite of the high energetics and fast shock-induced reactions, it appears that a means of sustaining the shock by the chemical energy release is required for a self-sustained SSD. In a solid-solid phase reaction, the volume change is too small to permit significant work done by the expansion of the solid products to maintain the shock. It is of interest to explore further the theoretical analysis of Kynazeva on the propagation of a thermal plastic wave in a reacting deformable medium to obtain some guidelines for further studies of the SSD phenomenon.

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