Reactivity of Ti-B, Cr-S, and Mn-S powder systems during explosively-driven collapse

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Abstract. Metal-metal and metal-sulfur reactive powder mixtures have been previously tested for initiation of reaction via planar, normal-shock loading. In addition to reacting under shock, such powder mixtures may undergo exothermic reaction from other types of mechanical loading. The thick-walled cylinder technique was performed on samples of Ti-B (1:2 molar ratio), Cr-S (1.15:1 molar ratio), and Mn-S (1:1 molar ratio). These experiments were aimed to determine the effect of large shear strains exerted on reactive metal powder mixtures and to establish the relative effectiveness of shear loading in comparison to shock loading for initiating reaction. Recovered samples were analyzed via SEM and XRD to determine the degree of reaction.

1. Introduction
The mechanism of reaction in reactive powders under high dynamic loading has been extensively investigated, but the relative significance of shear loading versus shock compression in initiating reaction has not been unambiguously identified. Recently, the initiation of reaction via shock loading of metal-metal oxides, metal-sulfur, and metal-metal powder mixtures capable of exhibiting exothermic reaction was undertaken by Jetté et al. [1, 2]. His work determined criticality conditions for the explosively-driven shock loading of reactive powder mixtures in terms of the transmitted shock pressure, all done while varying powder density. Additionally, two geometries were used to test for reaction — one where the powder sample was contained in a steel capsule of larger diameter than that of the explosive charge, and the other, where the capsule was smaller than the explosive charge. The shock transmitted into the wider capsule containing the reactive sample had a naturally greater radius of curvature, thereby giving rise to both normal and radial (shear) stresses within the sample. The smaller capsule resulted in complex shock interactions with the sample, greatly increasing the local pressure in comparison with the wider capsule. In the case of low-density Mn-S powder systems, it was noted that with the large-diameter geometry with greater shock curvature, the powder was initiated by a lower amplitude shock than in the narrow-diameter geometry [1], suggesting a dominate role of shear, rather than transmitted pressure, for initiation.

The thick-walled cylinder (TWC) technique was developed by Nesterenko et al. to create a state of plane strain in materials (pure shear) with shear stresses driving deformation and, subsequently, forcing shear localization at some critical value of global strain, itself depending on the test material and strain rate [3 - 5]. This technique has been previously used to
examine reactive powder mixtures (Ti-Si, Nb-Si) to determine what parameters influence their initiation. The powders were first densified, then subjected to a standardized set of final strains while keeping shock loading low [4, 5]. It was found that shear localization, with its concomitant large plastic deformation, imparted sufficient energy to the powders to initiate their reaction. Furthermore, a critical global strain for their test geometry was found such that these compositions would reproducibly initiate at the specified strain. Given that the aforementioned study indicates the definite role of shear in reaction initiation, the TWC method was chosen to test mixtures previously studied by Jetté et al. within its shearing geometry.

2. Methodology

The TWC technique is used for high strain, high strain rate testing of both solid and porous materials. In short, a cylindrical sample is placed between an outer copper driver cylinder and an inner copper stopper tube, held axially between two steel spacers. The wall thickness of the inner copper stopper tube determines the final strain felt by the sample; in the case of a solid rod, a minimum amount of strain will be experienced. Either end of the copper driver is machined to house two steel plugs and then the entire assembly is placed into a plastic housing filled with a specified explosive. By selecting a thick-walled geometry for the driver tube made of a material resistive to shear localizations at a specified global strain (e.g., copper), a state of pure shear is experienced by the sample until the onset of material instability, itself in turn causing shear localization with very large shear strains [3 - 5]. The samples are sealed by the swaging action on the steel caps caused by the explosive loading, allowing for easy sample recovery and measurement of the final strain state. A schematic of the assembly is shown as figure 1.

In this experimental series, the TWC technique was significantly modified to use a uniform gelled explosive (96% nitromethane, 4% cast optically-clear polymethylmethacrylate by mass) made “tunable” via the addition of a sensitizer in the form of 3M K1 glass microballoons (GMBs). The sensitized explosive can be made less dense via the addition of more GMBs, which in turn lowers detonation velocity (VoD) and Chapman-Jouguet (CJ) pressure [6]. The strain rate in TWC testing correlates to CJ pressure (the impulse strength) and the thickness of the explosive layer (the duration of the applied impulse). To further reduce transmitted pressure below the point of shock initiation of reactive powders, an attenuating sleeve of polyvinyl chloride (PVC) between the exterior of the copper driver and the explosive was added to some tests. These modifications to the method allow for a large parameter space within which reactive compositions may be tested in the shearing geometry inherent to the TWC method.

Reactive compositions of interest included Cr-S (1.15:1 molar ratio — this composition was used as a preliminary test), Ti-B (1:2 molar ratio), and Mn-S (1:1 molar ratio) made with the specific powders listed in table 1. Each mixture was roller-milled for 30 minutes to ensure uniformity, and then loaded into the sample region as in figure 1. The TWC proper was first sealed and the entire assembly was filled with explosive, which was then detonated. Given the modifications to the TWC method, experimental variables for testing these reactive compositions included strain rate (governed by detonation pressure and amount of explosive) and shock attenuation (the presence of a PVC sleeve), along with the method’s classical variables of total final strain (the presence of a solid rod or tube) and theoretical maximum density (% TMD).

3. Results

Each swaged capsule was recovered post-experiment and the sample was carefully extracted so as not to initiate any reaction. Evidence of bulk reaction in the samples containing sulfur could be determined immediately upon sample recovery by heating the sample to a temperature greater than the melting point of sulfur (115 °C). Evidence of melting of the sample indicated no bulk reaction, while a sample remaining solid indicated conversion to sulfide product. This test was
not possible for the Ti-B compositions; X-ray crystallography (XRD) was used to determine reaction for Ti-B.

Cross-sections of the samples were cut for the purposes of viewing microstructure and superficial elemental composition via scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). Bulk powder samples were removed from each capsule for XRD to determine phase and, therefore, to confirm if a given sample had reacted. No ambiguity was found in the XRD results: bulk mixtures either reacted to completion or did not react at all. The XRD results were consistent with the melt-test described above.

The results of this study are summarized in table 2. Molar ratios are expressed as the fraction of the first element to the second. The detonation pressure in the GMB-sensitized gelled nitromethane was estimated following the method of Cooper [7]. The abbreviations SWT, ELT, and AT in the headings refer to stopper wall thickness ("rod" refers to the use of a solid 12 mm diameter copper rod to minimize strain), explosive layer thickness, and attenuator thickness (if
Figure 2. Implosion diamond illustrating a pure-shear deformation with effective strain expression.

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\varepsilon_{\text{eff}} = \frac{2}{\sqrt{3}} \varepsilon_{\text{rr}} = \frac{2}{\sqrt{3}} \ln \left( \frac{r_i}{r_f} \right)
\]

Table 2. Summary of results.

| No. | Species | % TMD | Molar Ratio | % GMBs | VoD [mm/µs] | \(p\) [GPa] | \(\varepsilon_{\text{eff}}\) | SWT [mm] | ELT [mm] | AT [mm] | Rxn ? |
|-----|---------|-------|-------------|--------|-------------|-------------|----------------|-----------|----------|---------|-------|
| 8   | Cr,S    | 65    | 1.15        | 5      | 4.82        | 4.71        | 0.346          | 1.0       | 12.0     | —       | Yes   |
| 10  | Ti,B    | 43    | 0.50        | 5      | 4.79        | 4.64        | 0.567          | 1.0       | 12.0     | —       | Yes   |
| 11  | Ti,B    | 43    | 0.50        | 5      | 4.76        | 4.58        | 0.085          | rod 12.0  | —        | Yes     |
| 13  | Mn,S    | 85    | 1.00        | 5      | 4.76        | 4.58        | 0.289          | 1.0       | 12.0     | —       | Yes   |
| 14  | Mn,S    | 84    | 1.00        | 5      | 4.83        | 4.73        | 0.012          | rod 12.0  | —        | Yes     |
| 15  | Mn,S    | 88    | 1.00        | 10     | 3.89        | 2.38        | 0.032          | rod 12.0  | —        | Yes     |
| 16  | Mn,S    | 50    | 1.00        | 10     | 3.86        | 2.34        | 0.096          | rod 12.0  | —        | Yes     |
| 17  | Mn,S    | 60    | 1.00        | 10     | 3.99        | 2.51        | 0.072          | rod 18.0  | 5.0      | Yes     |
| 18  | Mn,S    | 63    | 1.00        | 10     | 3.70        | 2.15        | 0.059          | rod 7.0   | 5.0      | No      |
| 19  | Mn,S    | 60    | 1.00        | 10     | 3.64        | 2.08        | 0.389          | 1.0       | 7.0      | 5.0     | No    |
| 20  | Mn,S    | 60    | 1.00        | 5      | 4.61        | 4.30        | 0.058          | rod 7.0   | 5.0      | Yes     |

present) respectively. Effective strain was calculated from recovered and cut cross-sections via the geometry in figure 2 [3 - 5]:

4. Discussion

The experimental progression as described by table 2 was chosen to see if a composition, for a fixed explosive loading, would undergo bulk reaction at a high strain \(\varepsilon_{\text{eff}} \approx 0.5\), but not at a low one \(\varepsilon_{\text{eff}} \approx 0.05\). Should this have occurred, one could state that deformation brought on
through shear, decoupled from shock loading, was the principle cause of the reaction. In the majority of tests, however, it was found that reaction occurred both in the case of high strain and low strain. This result suggests that the shock loading was sufficient to initiate reaction in these cases. In order to reduce the shock loading, the concentration of GMBs in the explosive driver was increased and an attenuator was used.

Much of the work was done within Mn-S systems, and the experiments numbered 17, 18, and 19 are highlighted for further discussion. All these involved the same lower-strength explosive (sensitized with 10% GMBs by mass), similar % TMD, and the same attenuator thickness. However, their explosive layer thicknesses (ELT) and stopper wall thickness (SWT) varied, which govern strain rate and total strain respectively. At an ELT of 18 mm (#17), reaction occurred, but at values of 7 mm, no reaction is observed (#18, 19). Experiment 18 featured minimal strain (due to the presence of a solid stopper rod), but 19 shows significant deformation, due to the presence of a collapsing stopper tube with wall thickness of 1 mm.

Experiment 19 at right in figure 3 demonstrates clear 45° cracks within the Mn-S mixture, whereas such features are absent within the minimally-deformed 18. These cracks represent the onset of shear localization [4, 5]. Shear localization is inherently coupled with large plastic deformations, which can produce sufficient energy to initiate reaction within such compositions [4, 5], in turn linking shear with reaction in Mn-S systems. This leads to the question, at what ELT (greater than 7 mm but less than 18 mm) would the strain rate be sufficient to further propagate these cracks, localize shear, and initiate reaction. Furthermore, once this ELT is identified, the parameter of SWT may be varied to control effective strain and determine its criticality condition for causing sufficient shear localization to initiate reaction in Mn-S.

5. Conclusion
This study has demonstrated the ability of the thick-walled cylinder method to determine critical conditions for the initiation of an exothermic reaction in solid-solid metal-metal or metal-sulfur powder mixtures. By parametrically varying the explosive loading, shock attenuation, and stopper tube wall thickness, the ability to initiate reactive compositions via shock loading (with comparatively little global shear strain) or equal shock loading followed by significant strain caused by shear has been demonstrated. By sufficiently lowering the shock loading by both lowering the density of explosive and attenuating the transmitted shock, non-initiation

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Figure 3. Experiments 18 (left with no signs of localized shear) & 19 (right with localized cracks and shear zones) — sulfur is light in the figure, manganese is dark.
of compositions has been demonstrated. Furthermore, within Mn-S systems, the onset of shear localization has been directly observed. This technique lays a potential foundation for determining the comparative role of shock and shear in the initiation of reactive powder compositions within a single test geometry.

Acknowledgments
The authors would like to thank the assistance of Jason Loiseau, Alexander Capozzi, Atefeh Nabavi, Samuel Goroshin, and Oren Petel in conducting the experimental investigation, along with Gary Savard and John Boisvert for their technical support.

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