Shock compression response of Ti+B reactive powder mixtures

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Abstract. The shock compression response of Ti+2B (1:2 Ti:B stoichiometric ratio) reactive powder mixtures at ~50% theoretical material density (TMD) is investigated for shock pressures up to 5 GPa to investigate the possible shock-induced chemical reactivity of this highly exothermic mixture. The shock adiabat is produced from instrumented parallel-plate gas-gun impact experiments on encapsulated powders using poly-vinylidene fluoride (PVDF) stress gauges to measure the input and propagated stresses and wave speed in the powder. The shock compression regime is probed from crush-up to full density and onward to assess the potential onset of a shock-induced chemical reaction event in the powder mixture. A series of two-dimensional continuum meso-scale simulations on validated simulated microstructures are performed to predict the shock compression response and identify the meso-scale mechanics that are essential for reaction. The suitability of the synthetic microstructural representations is evaluated by comparing the experimental and predicted pressure traces.

1. Introduction
Energetic materials systems such as the Ni/Al, Ti/B, and Ti/Si intermetallic-forming systems show great promise as multifunctional energetic structural materials (MESMs) for dynamic loading applications due to their structural strength and reactive stability under normal handling conditions. The heterogeneous nature of these mixtures and the many reaction pathways provide tailoring opportunities at the meso-scale, allowing for control over the reactive behavior under shock loading. The Ti/B system is of particular interest because of the extraordinarily high enthalpy of reaction ($\Delta H_{\text{rxn}}^0 = -320 \text{ kJ/mol}$) when forming the stable TiB$_2$ product phase. This unconventional energetic mixture has many key ingredients that can enable shock-induced reactivity due to meso-scale transport processes [1, 2].

Ultrafast reactions occurring within the mechanical equilibration phase of shock compression were explored by Thadhani [3] and identified through post-mortem characterization from the original works of Horie and co-workers [4]. Subsequent work by Bennett et al. [5] and Iyer et al. [6] identified excess pressures at the back surface of the powder indicative of a chemical event causing an expanded state beyond that predicted from inert mixture theory. These reactions are differentiated from those occurring primarily through thermochemical processes at time scales greater than the rise and quiescent peak of the shock. Numerous configurations of isostatically compressed green powder compacts have been studied under dynamic loading [1, 7, 8]; the studies concluded that the extrinsic properties and microstructural configuration play a strong
role in shock initiation of these systems. The study by Thadhani et al. [1] in particular showed that the Ti/Si system was highly reactive and depended on mechanochemical events predicated by viscoplastic deformation, dissipative fracture, and agglomeration processes occurring at the meso-scale.

This work serves as a preliminary study of the shock compression response of 1:2 molar mixtures of Ti+B for shock pressures up to 5 GPa. PVDF stress gauges measure the shock speed and equilibrated stress at the gauge/powder interface and the Velocity Interferometer System for Any Reflector (VISAR) is employed for later experiments to compare the interface velocity at the powder/backer interface with the PVDF stress signal. The measured stress traces are compared with meso-scale simulations of a highly resolved uniform-random mixture of Ti+2B also at 50% TMD. The simulations are found to generally over-predict the recorded stress at the backer, though capture the salient features of the rise-time effects.

2. Experimental and computational details

2.1. Experimental configuration and sample preparation
Titanium (Atlantic Equipment Engineers ~625 mesh sponge powder) and boron (Alfa-Aesar Amorphous 94-96%, Mg nominal 1% < 5 microns. Irregular/flake powder) powders were first dried in a 110°C furnace and then pre-mixed in a 1:2 molar ratio in an inert atmosphere. The powders were sealed and transferred to a v-blender for further mixing (24 h) to ensure a uniform-random mixing of Ti and B. Further details of the powders used in this study can be found elsewhere [9].

Instrumented parallel-plate impact experiments on the Ti+2B powders were conducted using the 80 mm helium-driven gas gun facilities at Georgia Tech. A set of copper capsule fixtures were manufactured to contain the powder during the shock compression experiments. These capsules consisted of an outer copper containment ring, copper driver plate, and transparent fused silica backer plate sandwiching the powder to the driver. The powder was pressed into a dummy driver at 50% ± 2% TMD due to the high crush strength of this powder. The dummy driver was later removed and replaced with one containing a gauge package. Aluminum sabots carried the flyer plate (either copper, tungsten, or tungsten heavy alloy depending on the desired impact stress) and impact velocity was monitored by sequential shorting pins.

PVDF stress gauge packages were built onto the driver and backer plates to monitor the stress state and wave arrival times at the front and back of the powder. These gauge packages consisted of alternating polytetrafluoroethylene (PTFE) layers to isolate the PVDF gauge, and a sputtered layer of Al (150 nm thick) at the end to mitigate the effects of pyroelectric interference [10] on the PVDF gauge. The transparent fused silica backer also permitted for simultaneous VISAR measurements (later experiments) through adequate preparation of the fused silica surface prior to attaching the gauge package. All mating surfaces were lapped to optical flatness (< 1 mrad tilt).

2.2. Microstructure-based simulations
Realistic simulated microstructures were generated by inserting Ti particles from a specially-crafted library created through montage serial sectioning [11], and simulating boron particles through a polar plot of a Fourier Sine series. Further details of the method are described in a prior work [9]. The particles are inserted into a simulation domain one at a time with a strict overlap control. The size distribution for each component replicated the vendor-supplied information and a uniform-random distribution of constituents is generated. A 50% TMD uniform-random distribution of particles is achieved and validated through two-point correlation functions when compared with real microstructures.
The impact simulations were performed using the Eulerian hydrocode CTH (Version 9.0, Sandia National Laboratories 2009) by placing the microstructure in a 2D simulation domain with simulated PVDF gauge packages, Cu driver, impactor (either Cu or W), and fused silica backer (figure 1). The simulation is a 1:4 scale model of the experimental fixture. The left and right boundaries were set as periodic symmetry boundaries and the top and bottom boundaries were set as sound speed absorbing (half-space). The Ti particles were modeled with the rate-independent Steinberg-Guinan-Lund constitutive model. The Cu plates were modeled with the Zerilli-Armstrong constitutive model and the gauge package was made hydrodynamic. The fused silica backer employed a Johnson-Cook model and the boron particles used a Von-Mises yield surface with thermal softening. All constituents except for boron were modeled with the SESAME equation of state as provided by the built-in SESAME tables; Boron was modeled with a Mie-Grüneisen equation of state. A set of ten tracer points were placed at each PVDF gauge center to track the velocity, stress, and temperature. A typical temperature profile is shown in figure 2 for a fully compacted structure.

3. Results and discussion
The shock compression experiments provide the shock speed and equilibrated stress at the powder/backer interface. The PVDF gauges at the driver/powder interface showed anomalous signals in several experiments possibly due to gauge failure before enough time passed for mechanical equilibration. Therefore, the shock stress in the powder was impedance-matched with the shock speed and impact velocity at the driver. The gauge package integrity is likely compromised within the first 50 ns of compression by the powders, leading to a large variation in recorded peak stresses. The shock speed through the powder was measured based on the transit time measured at the 10%, 50%, and 90% levels of the rise time to peak stress as shown in figure 3. Each level provides an independent measure of the shock speed and an average t-corrected
Table 1. Summary of shock compression tests showing flyer type, impact velocity $V_{imp}$, shock speed $U_s$, particle velocity $U_p$, impedance-matched powder stress $\sigma_I$, and relative volume change $V/V_00$ along with relative uncertainties.

| Shot # | Flyer | $V_{imp}$ (mm/μs) | $U_s$ (mm/μs) | $U_p$ (mm/μs) | $\sigma_I$ (GPa) | $V/V_00$ |
|--------|-------|-------------------|---------------|---------------|-----------------|-----------|
| 1225   | Cu    | 0.513 ± 0.35%     | 1.23 ± 4.14%  | 0.48 ± 7.08%  | 1.06 ± 4.06%    | 0.61      |
| 1227   | Cu    | 0.818 ± 1.61%     | 1.76 ± 1.95%  | 0.753 ± 4.54% | 2.24 ± 1.69%    | 0.57      |
| 1302   | Cu    | 1.044 ± 3.66%     | 2.16 ± 5.30%  | 0.944 ± 3.62% | 3.63 ± 1.49%    | 0.56      |
| 1307   | Cu    | 0.832 ± 0.28%     | 1.72 ± 2.02%  | 0.769 ± 4.45% | 2.36 ± 2.37%    | 0.55      |
| 1309   | WHA   | 0.921 ± 0.52%     | 1.79 ± 3.68%  | 1.01 ± 3.38%  | 3.83 ± 15.7%    | 0.43      |
| 1310   | W     | 0.933 ± 0.52%     | 2.13 ± 3.44%  | 1.12 ± 3.06%  | 4.1 ± 7.32%     | 0.48      |
| 1314   | W     | 0.890 ± 0.66%     | 1.81 ± 0.40%  | 1.08 ± 3.17%  | 3.84 ± 13.01%   | 0.42      |
| 1320   | Cu    | 1.06 ± 0.83%      | 1.86 ± 1.86%  | 0.966 ± 3.54% | 3.03 ± 0.71%    | 0.48      |

Figure 3. PVDF stress traces recorded at the driver (blue) gauge and backer (red) gauge for a Cu flyer impact velocity of 818 m/s. The shock speed is obtained from the recording times of the stress traces and the powder thickness. The recorded peak stresses were not used in the calculation of the Hugoniot.

Figure 4. Simulated (black) stress trace and PVDF (red) recorded trace at the backer interface. Both traces show a disturbance region during the rise-time of the wave caused by two separate equilibration events at the gauge during compaction.

The stress waves at the backer became dispersed at lower impact velocities, thereby increasing the transit time difference between rise time levels and thus the uncertainty in the single shock speed value. The results for each experiment are summarized in table 1. No clear trend is discernible, nor is there any clear evidence of a chemical event reckoned by a positive deviation from the linear trend in $U_s$-$U_p$ space. The simulations also underpredict the $U_s$-$U_p$ values from the experiments.

Simulations show a random distribution of hot spots exceeding 1400 K, but do not predict a large heat buildup in the bulk of the material as shown in figure 2. This can lead to quenching of...
any potential reaction. The size disparity between Ti and B causes the B particles to agglomerate and confine between the larger Ti particles. However, the high strength in B and the geometry of the Ti particles do not permit large hydrodynamic transport as previously observed [12].

A number of recorded stress traces at the backer gauge showed a dispersed “two-wave” structure, potentially due to differences in arrival times of the more loosely-bound particles near the surface of the PVDF gauge and the succeeding particle “avalanche.” The avalanching particles move at a group velocity impedance-matched with the Cu driver and move slower than the initial jagged front. This initial front creates an initial shock compression of the gauge which rings up to pressure for about 10-20 ns, subsequently equilibrating with the more sluggish particles that follow. This is confirmed by simulations which reproduce the same behaviors (see figure 4). The simulations also capture reshock events such as in figure 5 due to the continual compression of the backer by a fully compacted powder. The simulations also correlate extremely well with VISAR traces as shown in figure 6, capturing the peak velocity and even release-wave events, providing an initial validation for the simulation scheme and physical models employed.

![Simulation/PVDF comparison - $V_{\text{imp}} = 513$ m/s](image1)

**Figure 5.** Simulated (black, scaled by 4 in time) stress trace compared with the PVDF (red) backer gauge record for a low velocity shot. The gauge and simulation both captured a reshock event emanating from the fully compacted (higher impedance) powder.

![Particle velocity in backer $V_{\text{impact}} = 890$ m/s](image2)

**Figure 6.** Simulated (black) average velocity at the powder/backer interface compared with VISAR record (red). The simulated trace was scaled by 4 in time to match the VISAR trace. There is excellent agreement in both peak, rise time effect, and release wave record.

4. Conclusions
The Ti/B shock compression behavior was probed through impact experiments and meso-scale simulations. No clear evidence for reaction was observed. Further experiments are needed before an equation of state is firmly established for this mixture. Interesting rise-time effects recorded by the backer PVDF gauges were reproduced in simulations and reveal a two-stage compression process caused by initial compression of loosely-packed surface particles and a trailing wave from the fully compacted powder. The meso-scale simulations using highly-resolved simulated microstructures successfully capture the rise-time effects and peak velocities at the backer recorded through VISAR, though do not match the stresses recorded by the PVDF gauges.
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