Shock-induced reaction behavior of Ti-Si and Ti-B powder mixtures

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Mechanistic processes controlling the shock-induced chemical reaction behavior of highly reactive Ti-Si and Ti-B powder mixtures were investigated. Recovery experiments were performed, using Sandia Bear fixtures, to determine the reaction initiation thresholds for the respective systems, and to produce compacts of unreacted states to characterize the shock-compressed configuration of reactants at conditions below the reaction threshold. X-ray diffraction line broadening and scanning electron microscopy analysis were used to determine the response of individual reactants during shock-compression. It was observed that the deformation and/or fracture response of reactants during shock-compression influences the threshold conditions for reaction initiation and the overall reaction propensity.

1. INTRODUCTION

An unusual combination of structural defects and powder packing characteristics are produced during high-pressure, high-strain-rate loading of powders. Such conditions can cause enhancement of chemical reactivity and accelerated mass transport, leading to chemical reactions in powder mixtures [1]. Controversies exist about the actual mechanistic processes that lead to reaction initiation in the microsecond time scales of the shock state before unloading of pressure to ambient conditions [2]. The postulated mechanisms have included both solid-state [1,2] and liquid-state processes [3]. A clear understanding of the reaction mechanisms has been complicated by the fact that chemical reactions can also occur subsequent to unloading, in an essentially shock-modified material, due to bulk (residual) shock-temperature increases in time scales of thermal equilibration (several tens of microseconds). On this basis, chemical reactions occurring in shock-compressed powder mixtures have been distinguished into "shock-induced" and "shock-assisted" chemical reactions [4]. Correlations with observed reaction products in samples obtained from shock-recovery experiments is further complicated by the exothermic nature of intermetallic or ceramic forming reactants. In such powder mixtures, the reaction results in melting of the products which masks the effects generated during shock-compression alone. Thus, except for time-resolved experiments in which the observed phenomena can be detected in real-time, it is difficult to infer if the reactions occur during the high-pressure shock state or after unloading. Shock-recovery experiments can, however, be used to make compacts of powder mixtures in the unreacted state, at conditions below the reaction threshold, to characterize the shock-compressed configuration of reactants that ultimately leads to "shock-induced" chemical reactions or provides the state for subsequent "shock-assisted" reactions.

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The objective of the present work was to study the mechanistic processes occurring during shock-compression of powder mixtures and leading to chemical reactions. The approach adopted was to explore the effect of properties of reactant materials by performing shock-recovery experiments on Ti-Si and Ti-B powder mixtures which represent systems with similar density differential between reactants, but different physical and mechanical property differentials, including: melt temperature (Ti-Si = 1670°C - 1410°C and Ti - B = 1670°C - 2079°C); sound velocity (Ti-Si = 4970 - 8500 m/s and Ti - B = 4970 - 13900 m/s); and elastic modulus (Ti - Si = 70 - 112 GPa and Ti - B = 70 and 440 GPa). Both of these systems also have distinct differences in their heats of formation (Ti₂Si₃ = -72.5 J/g, at and TiB₂ = -108 J/g, at). Detailed microstructural analysis was performed on both systems, prior to and after shock-compression, to compare the response of powder mixtures with constituents that have different deformation and/or fracture characteristics and chemical reactivities.

2. EXPERIMENTAL PROCEDURE

The Ti-Si powder mixtures of two different morphologies, medium (~15 μm) and coarse (105-149 μm) and Ti-B powder mixtures of the medium (~15 μm) morphology were used. The Ti powders used were the same in both Ti-Si and Ti-B mixtures. Shock-loading experiments were performed using the Sandia Bear series shock-recovery fixtures [5]. The powder mixtures were pressed directly into the copper capsule at a packing density of nominally 53% TMD. The shock-conditions achieved in the Bear fixtures have been computed by two-dimensional numerical simulation for 50% dense rutile powder [6]. For porous materials (powders), radial loading due to the lower impedance of powders with respect to the solid containment, dominates the shock-loading process. The final conditions generated are thus a function of wave focussing effects, and independent of the materials equation-of-state properties. The numerically computed peak pressures and mean bulk temperatures for the different Bear fixtures are [6-8]: Poppa Bear-Baratol (PB-B) - [bulk = 5GPa, 105°C, focus = 4.5GPa, edge = 75°C]; Momma Bear-Baratol (MB-B) [bulk = 7.5GPa, 225°C, focus = 27GPa, edge = 250°C]; and Momma Bear A-Comp B (MBA-CB) [bulk = 22GPa, 400°C, focus = 46GPa, edge = 650°C]. The recovered compacts were cross-sectioned into two halves. Optical and scanning electron microscopy was performed on unetched samples of polished cross-sectional surface (on one of the halves), to observe the grain structure of products in reacted compacts, and the deformation characteristics of constituents in unreacted compacts. X-ray diffraction analysis (XRD) was performed on the rear face of the other half-section after polishing off and chemically etching an ~500 μm thick layer. Line broadening analysis, based on the Williamson-Hall analysis method [9], was used to quantify the microstrain (resulting from deformation of powders) and crystallite size (due to fracture of powders) in unreacted shocked compacts. The instrumental broadening was subtracted from the full-width at half maximum (FWHM) values to obtain the integral breadth, βₐₙₓ. The (βₐₙₓ*costh) value was plotted versus sinθ, from which the crystallite size (t) and microstrain (ε) for each sample were calculated intercept and slope values:

\[ t = \frac{0.9Sl}{βₐₙₓcosθ} \] (1)

and

\[ ε = \frac{βₐₙₓcosθ}{2sinθ} \] (2)

where, λ is the wavelength of radiation, and θ is the diffraction angle.
3. RESULTS

Table 1 lists the experimental conditions used for each material system along with a remark about the reaction behavior deduced from optical microscopy observation.

Table 1
Experimental Parameters for Recovery Experiments on Ti-Si and Ti-B Powder Mixtures

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Powder</th>
<th>Packing Density G/cm³</th>
<th>Configuration</th>
<th>Reaction Behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-Si NMG-9122</td>
<td>Medium</td>
<td>1.92</td>
<td>PB-B (5 GPa)</td>
<td>none</td>
</tr>
<tr>
<td>NMG-9121</td>
<td>Medium</td>
<td>1.93</td>
<td>MB-B (7.5 GPa)</td>
<td>complete</td>
</tr>
<tr>
<td>SNL-2506*</td>
<td>Medium</td>
<td>1.912</td>
<td>gun (≈ 5 GPa)</td>
<td>none</td>
</tr>
<tr>
<td>SNL-2572*</td>
<td>Coarse</td>
<td>1.901</td>
<td>gun (≈ 5 GPa)</td>
<td>none</td>
</tr>
<tr>
<td>Ti-B NMG-9302</td>
<td>Medium</td>
<td>2.008</td>
<td>PB-B (5 GPa)</td>
<td>none</td>
</tr>
<tr>
<td>NMG-9306</td>
<td>Medium</td>
<td>1.962</td>
<td>MB-B (7.5 GPa)</td>
<td>none</td>
</tr>
<tr>
<td>NMG-9307</td>
<td>Medium</td>
<td>1.953</td>
<td>MBA-CB (22 GPa)</td>
<td>complete</td>
</tr>
</tbody>
</table>

* Gun impact experiment at ≈380 m/s using capsule design similar to MB configuration.

Shock-recovery experiments performed on the Ti-Si system included PB-B, MB-B, and gun configurations. The medium morphology Ti-Si MB-B sample (NMG-9121), shock-compressed at 53% density, was fully reacted. The microstructure revealed Ti₃Si reaction product with an equiaxed grain structure (≈10 μm), along with the presence of voids, typical of a reacted, melted, and resolidified material. The medium morphology PB-B (NMG-9122) and gun (SNL-2506) samples, and the coarse morphology gun sample (SNL-2572), packed at ≈53% density, revealed no evidence of reaction. As shown in Fig. 1(a,b), the bright-contrast Ti particles of both medium and coarse morphology reveal extensive deformation. On the other hand, the Si powders of medium morphology compacts (Fig. 1 (a)) show plastic deformation and flow along with Ti, while Si particles of coarse morphology compact (Fig. 1(b)) exhibit considerable fracture and cracking. The fractured fragments of the coarse Si particles also appear to remain trapped surrounded by the plastically deforming Ti.

Shock-recovery experiments on medium morphology Ti-B powder mixtures were performed using the PB-B, MB-B and MBA-CB configurations. Optical microscopy of the MBA-CB sample (NMG-9307) showed complete reaction forming TiB₂ equiaxed grains (≈5μm) with TiB phase at grain boundaries. The PB-B (NMG-9302) and MB-B (NMG-9306) experiments showed no signs of reaction. SEM micrographs of these unreacted PB-B (NMG-9302) and MB-B (NMG-9306) compacts are shown in Figure 2 (a,b). Both samples show plastic deformation of Ti, and extensive fracture of B particles with continued dispersion of the fragments increasing from PB-B to MB-B configuration.
XRD line broadening analysis was performed on initial unshocked, as well as all of the shock-compressed unreacted compacts of Ti-Si and Ti-B powder mixtures, to determine residual strain and crystallite size reduction caused by shock compression effects. The Williamson-Hall plots generated separately for the Ti and Si medium morphology powders and the two shocked compacts are shown in Figure 3 (a,b). In the case of Ti (Fig. 3(a)), the initial powder mixture showed an almost flat line indicating little or no strain effects, while the data for both the gun recovery (SNL-2506) and PB-B (NMG-9122) configuration showed Ti lying along similar sloped lines, indicating the same level of microstrain in both shocked samples. The Ti data for the two shocked samples and the unshocked mixture cross the y-intercept at roughly the same value, indicating no change in crystallite size. The Si peak broadening data in Fig. 3 (b), shows similar strain values in the two shock-compressed samples and somewhat lower strain in the starting powder. Strain in the starting Si powder may have been introduced during powder fabrication. The effect of morphology of Si powders on shock-induced strain and crystallite size reduction is shown in the Hall-Williamson plot in Fig. 4 (a), which compares the behavior of coarse and medium powder.
Fig. 3. Williamson-Hall plots for (a) Ti and (b) Si in medium morphology Ti-Si system.

Fig. 4. Williamson-Hall plots of (a) Ti-Si comparing medium and coarse powder morphology gun experiment compacts, and (b) Ti-B compacts of PB-B and MB-B experiments.

morphologies in the gun experiments (SNL-2506 and SNL-2572). The slope of the curve for the shock-compressed coarse Ti is slightly greater than the corresponding slope of medium Ti, indicating that the microstrain in coarse Ti is greater than medium Ti powder at similar shock conditions. However, the data on Si show an interesting trend, with greater microstrain in the medium morphology powder compacts compared to the coarse compacts, as indicated by the larger slope for medium morphology Si and nearly zero slope for coarse Si. However, the intercept of the curve for the coarse Si compact is raised and is found to be higher than that of the coarse unshocked powder. This implies that while medium morphology Si powders undergo extensive plastic deformation, the coarse morphology Si powders show negligible microstrain but significant particle size reduction.
The Williamson-Hall plot obtained for Ti in PB-B (NMG-9302) and MB-B (NMG-9306) compacts of the unreacted Ti-B system is shown in Figure 4 (b). Line-broadening analysis was not performed on the B constituent because intensities for the B peaks were too low and could not be completely separated from the background radiation. As shown in Fig. 4(b), while the Ti in the initial powder mixture revealed essentially no strain effects, the data for Ti in the PB-B experiment sample (NMG-9302) follows a sloped linear relationship indicating the presence of microstrain. The higher pressure MB-B sample (NMG-9306) reveals a somewhat greater microstrain than the PB-B sample.

4. DISCUSSION

The Ti-Si and Ti-B powder mixtures show different reaction pressure thresholds as observed from results of microstructural characterization of shock recovery experiments. The medium Ti-Si powder mixture showed no reaction in the PB-B configuration but reacted completely in the MB-B configuration (7.5 GPa pressure threshold). Shock-recovery experiments on the Ti-B system indicated no reaction with MB-B, but complete reaction for the MBA-CB sample (22 GPa pressure threshold). Thus, the Ti-Si system has a greater propensity for chemical reaction (lower threshold) compared to the Ti-B system. It should be noted that under the shock loading conditions used for experiments with Ti-Si and Ti-B mixtures, the maximum bulk equilibrium temperatures generated are of the order of 250°C with the MB-B conditions and 650°C with the MBA-CB conditions. Thus, the occurrence of reaction in Ti-Si system with MB-B and Ti-B system the MBA-CB configuration cannot be attributed to post-shock temperature increases (resulting in melting of reactants), but rather to mechanochemical processes generating the configuration of intimately mixed, highly activated dense-packed constituents.

In Ti-Si powder mixtures, the unreacted Ti particles underwent extensive plastic deformation, while unreacted Si particles exhibited both plastic deformation and cracking (fracture) depending on the powder morphology. The dependence of particle size on the shock-compression response of powders and the reaction behavior has also been investigated using time-resolved measurements [10], at one-dimensional pressures of ~1 GPa. The results of these time-resolved experiments provide evidence of shock-induced chemical reactions in powders of medium morphology and no reaction in coarse Ti-Si powders.

A significant variation of configurational change between the unreacted constituents is observed in the Ti-B powder mixtures. The Ti particles undergo plastic deformation, while the B particles fracture and fragment extensively. However, unlike the fracture and entrapment of Si, it appears that the B fragments flow and are dispersed within the deforming Ti. The size of the B particles (determined using stereological methods) also observed to decrease from 2.41 ± 0.55 µm in the PB-B sample to 2.20 ± 0.66 µm in the MB-B configuration. Although the difference in average particle sizes is small and within the standard deviation, it is interesting to note that the data from the higher pressure MB-B compact also show a larger standard deviation, indicating that B particles continue to fragment and exist over a wider particle size distribution at higher pressure.

The calculated residual microstrain values for each reactant in the shock-compressed samples of Ti-Si and Ti-B, were determined using equations (1) and (2) obtained from the Williamson Hall plots. The microstrain in the starting Ti powders was negligible (within the standard deviation of the linear fit), while the starting Si powders contained some microstrain.
The microstrain present in Ti and Si in the various compacts are listed below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti Configuration</th>
<th>Si Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-B sample (NMG-9122)</td>
<td>Medium Ti - 3.65 x 10(^{-3})</td>
<td>Medium Si - 3.14 x 10(^{-3})</td>
</tr>
<tr>
<td>Gun experiment (SNL-2506)</td>
<td>Medium Ti - 3.22 x 10(^{-3})</td>
<td>Medium Si - 3.12 x 10(^{-3})</td>
</tr>
<tr>
<td>Gun experiment (SNL-2572)</td>
<td>Coarse Ti - 3.98 x 10(^{-3})</td>
<td>Coarse Si - 5.76 x 10(^{-4})</td>
</tr>
<tr>
<td>PB-B sample (NMG-9302)</td>
<td>Medium Ti - 4.34 x 10(^{-3})</td>
<td>-----N/A-----</td>
</tr>
<tr>
<td>MB-B sample (NMG-9122)</td>
<td>Medium Ti - 5.10 x 10(^{-3})</td>
<td>-----N/A-----</td>
</tr>
</tbody>
</table>

Measurements of microstrain from XRD line broadening analysis have been extensively used by Morosin [11], even on shock-compressed ceramics. The calculations of microstrain were extended to estimate the dislocation densities using the Williamson and Smallman [12,13] method. Based on this, the dislocation densities in Ti in the various shocked compacts were determined to be of the order of 10\(^{11}\) cm\(^{-2}\). It is interesting to note that the strain values calculated for Ti in Ti-Si and Ti-B systems for PB-B samples are virtually the same, which indicates that the overall configurational change and ultimately the propensity for reaction is controlled by the deformation and/or fracture behavior of the secondary constituent, i.e., Si or B. Comparing the differential flow stress and modulus of reactants in Ti-Si and Ti-B, it can be seen that while Ti and Si powders deform at similar stress levels, the deformation of Ti and B powders occurs at different stresses. Simultaneous deformation of Ti and Si makes it possible for the two to be intimately mixed producing a configuration susceptible for reaction initiation. However, an exception is the behavior of coarse Si powders which do not deform but rather fracture and remain entrapped. A different response is observed with Ti-B, which has a larger differential in the flow stress of reactants. The extremely brittle B fractures at very low stress, however, with increasing stress approaching the flow strength of Ti, the fragmented B particles are dispersed and become engulfed in the deforming Ti. This combined flow and fracture response of Ti and B results in an optimally mixed configuration of reactants making it susceptible for reaction initiation.

The results of the present work provide characteristics of mechanistic processes that lead to chemical reactions during shock-compression. The information about residual strains in shock-compressed powder mixtures, can be used to compare with analysis of numerical simulation models developed for predictions of shock chemistry. The data obtained for strain measurements and dislocation density can also be used to predict optimal post-shock reaction sintering conditions for materials synthesis via "shock-assisted" chemical reactions [14].

5. CONCLUSIONS

The shock-induced reaction behavior of Ti-Si and Ti-B powder mixtures is influenced by the deformation response of constituents, which is affected by the differences in mechanical property differential between reactants. Ti-Si powder mixtures of medium morphology show simultaneous deformation of both reactants, and thus provide an optimal configuration for shock-induced chemical reaction initiation; however, with coarse morphology powders, the Si particles fragment and remain entrapped within the deforming Ti particles, limiting mixing and the occurrence of reaction. In Ti-B powder mixtures, B particles fracture, but unlike the coarse Si powders, the B fragments disperse within the deforming Ti, thus providing the configuration of intimately mixed constituents. Under similar conditions of shock-loading, particle morphology, and packing density, Ti-Si powder mixtures have a lower threshold for shock-induced reactions, compared to Ti-B, although the Ti-B system has a higher heat of reaction.
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REFERENCES

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