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K. S. Vandersall, N. N. Thadhani

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

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INVESTIGATION OF SHOCK-INDUCED CHEMICAL REACTIONS IN Mo-Si POWDER MIXTURES USING INSTRUMENTED EXPERIMENTS WITH PVDF STRESS GAUGES

Kevin S. Vandersall¹ and Naresh N. Thadhani²

¹*Lawrence Livermore National Laboratory, 7000 East Avenue, L-282, Livermore, CA 94550*

²*School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245*

Abstract. Shock-induced chemical reactions in ~58% dense Mo+2Si powder mixtures were investigated using time-resolved instrumented experiments, employing PVDF-piezoelectric stress gauges placed at the front and rear surfaces of the powders to measure the input and propagated stresses, and wave speed through the powder mixture. Experiments performed on the powders at input stresses less than 4 GPa, showed characteristics of powder densification and dispersed propagated wave stress profiles with rise time > ~40 nanoseconds. At input stress between 4-6 GPa, the powder mixtures showed a sharp rise time (<~10 ns) of propagated wave profile and an expanded state of products revealing evidence of shock-induced chemical reaction. At input stresses greater than 6 GPa, the powder mixtures showed a slower propagated-stress-wave rise time and transition to a low-compressibility (melt) state indicating lack of shock-induced reaction. The results illustrate that premature melting of Si, at input stresses less than the crush-strength of the powder mixtures, restricts mixing between reactants and inhibits "shock-induced" reaction initiation.

INTRODUCTION

The Mo-Si intermetallic-forming system contains constituents having large differences in properties (e.g., density, sound speed, yield strength, and melt temperature), and a high heat of reaction. Prior shock synthesis studies on Mo-Si have been performed by Meyers et. al. [1,2], Marquis and Batsanov [3], Montilla [4], Aizawa et. al. [5], and Vandersall and Thadhani [6], in which reaction products having a variety of microstructures have been observed. While, the microstructures observed via post-mortem analysis provide possible evidence of how the product phase may have been formed, it is difficult to ascertain whether the phases formed due to "shock-induced" reactions in time scales of pressure equilibrium, or subsequent to the shock event in time scales of temperature equilibrium via "shock-assisted" processes [7]. Inference of "shock-induced" chemical reactions can only be obtained via in-situ measurements of shock-properties using time-resolved experiments [8]. In the present work instrumented experiments employing PVDF stress gauges were used to study the reaction behavior during shock compression of Mo+2Si powder mixtures.

EXPERIMENTAL PROCEDURE

Mo (Cerac No. M2000) and Si (Cerac No. S1053) powders (-325 mesh, <44 μm) were mixed in a stoichiometric ratio corresponding to MoSi₂ (using a mechanical V-blender) and pressed into fixtures at a density of ~58% TMD. The setup for instrumented experiments is similar to that used in prior work [8]. PVDF piezoelectric stress gauges were placed in intimate contact with front and back powder-capsule planar surfaces to monitor both "input-shock" and "propagated-wave" characteristics. The propagation of shock wave sensed by the "input" gauge and "propagated" gauge at their respective locations, also provided the precise transit time through the ~3 mm thick (50.8 mm diameter) powder-mixture samples based on travel time through the powder layer. OFHC-copper flyer plates were used for experiments #9806, #9818, and #9902 and a tungsten alloy (MIL-T-21014) flyer plate was used in all other experiments for generating higher pressures. The projectile velocity was measured using shorting pins, spaced 12.7 mm apart and the digital oscilloscopes were triggered from standoff pins placed 6.35 mm from the impact surface.

Table I. Summary of experimental results.

Expt. No.	Packing Density (g/cm ³ , %TMD)	Projectile Velocity (mm/μs)	Input Stress (GPa)	Input Risetime (ns) (10%-90%)	Equilibrium Propagated Stress (GPa)	Propagated Risetime (ns) (10%-90%)	Wave Speed (mm/μs) (toe-to-toe-10%, ½ max)	Relative Volume (toe-toe-10%, ½ max)
9806	2.59, 57	0.507	1.52	11.5	1.82	186	1.28, 1.23	1.58, 1.50
9818	2.50, 55	0.700	2.09	7.5	2.36	86	1.43, 1.41	1.43, 1.39
9902	2.69, 59	0.964	3.15	6.5	3.95	76.5	1.66, 1.61	1.13, 1.08
9910	2.70, 59	0.851	4.36	8.5	4.29	10, 14†	1.87, 1.87	1.46, 1.45
9908	2.71, 59	0.940	5.4	4.5	5.18	6	2.10, 2.10	1.55, 1.55
9907	2.71, 59	0.966	6.3*	‡	6.16	8,7†	1.99*	1.13*
9913	2.50, 55	0.967	6.3*	‡	5.07	22.5	2.07+	1.02
9919	2.51, 55	0.914	6.65	5	4.74	25.5	2.17, 2.15	1.10, 1.08

* indicates a calculated value, ‡ indicates no measurement obtained, † indicates a two slope wave structure, + indicates toe-to-toe at shock arrival instead of 10%

RESULTS AND DISCUSSION

A summary of the experimentally determined parameters obtained from the instrumented experiments is listed in Table 1. These include, the input stress and the input pulse rise-time (from 10% to 90% of peak) measured by the input shock gauge; the equilibrated propagated stress and propagated pulse rise-time recorded by the propagated stress gauge; wave speed determined using both the toe-to-toe and half-max values of input- and propagated-wave profiles; the relative volume calculated using the values of initial powder density, measured input stress, shock wave speed (both toe-to-toe and ½ max), and shock jump conditions for conservation of mass and momentum.

A plot displaying the measured input-stress profiles from all experiments is included in Fig. 1. The propagated stress traces for all three low velocity experiments are provided in Fig. 2 (a) and the remaining traces from the higher velocity experiments are shown Fig. 2 (b). The varying

amplitudes of the different input-stress profiles correspond to experiments performed at different impact velocities. The rise time of the input stress pulse is less than 10 ns, while the propagated stress

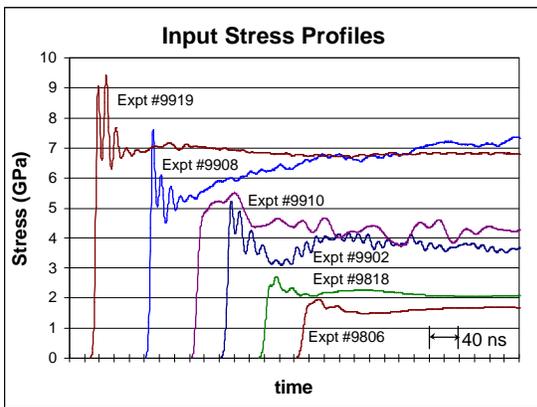


Figure 1. Combined plot of input stress traces.

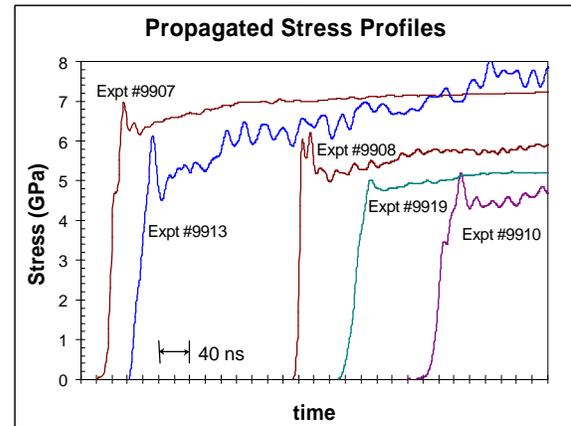
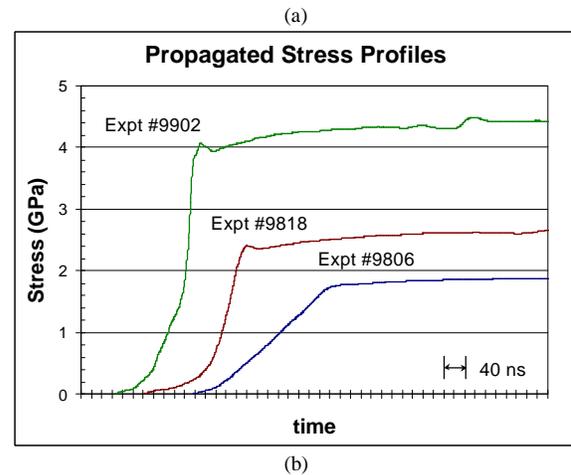


Figure 2. Propagated stress traces for (a) three low velocity experiments and (b) higher velocity experiments.

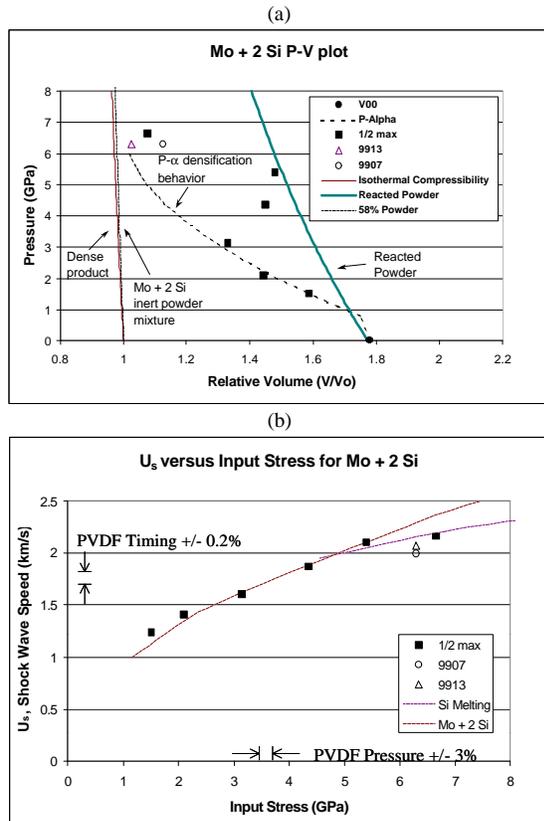


Figure 3. Plots of (a) measured input stress versus calculated relative volume (based on half-max values) plotted with the isothermal compressibility curves of dense MoSi₂ alloy, Mo+2Si inert mixture with zero crush strength, P- α densification densification behavior, and reacted product Hugoniot (data for Experiment #9907 based on calculated values of wave speed and input stress, and that for Experiment #9913 based on calculated value of input stress and measured wave speed) and (b) measured input stress as a function of powder wave speed, for Mo + 2 Si powder mixture with silicon behavior.

wave is dispersed (rise time varying between 6 to 186 ns). Lower amplitude stress waves show the longest rise time, due to the behavior being dominated by powder densification.

Densification of the powder mixture from an initial to final solid density was considered using the P- α pore collapse model [9]. A thermodynamic consideration was also used to generate the pressure-volume (Hugoniot) curve of a fully reacted MoSi₂ product, based on the model recently developed by Bennett and Horie [10], constant pressure adjustment of the reference state. The important concept of this analysis is that it actually determines a calculated Hugoniot of the *products* formed via “shock-

induced” reaction in a powder mixture. Details of both the P- α and thermodynamic curves as applied to this plot are described elsewhere [11].

Fig. 3 (a) shows the pressure-volume space with the calculated curves representing the P- α densification behavior and the pressure-volume data points obtained from the PVDF gauge experiments, and the calculated compressibility curve of the fully reacted MoSi₂ product formed from Mo + 2Si reactants at ~58% density. The calculated mixture Hugoniot is also displayed and considers densification of the Mo + 2 Si powder from V/V₀=1.78 to V/V₀=1, occurring at practically zero stress.

It can be seen that while the cluster of the three data points at pressures less than 3.1 GPa follow the trend representing the P- α densification behavior, the two data points at 4.3 and 5.3 GPa show significant expansion as they approach the fully reacted powder (forming MoSi₂ product) Hugoniot curve. Hence, it can be reasoned that the 5.3 GPa data point corresponds to almost 100% shock induced reaction occurring in the 58% dense powder mixture and the 4.3 GPa data point represents a shock pressure state in which the 58% dense Mo + 2 Si powder mixture undergoes an appreciable (but not complete) shock-induced reaction. From Fig. 4 (a), if the 5.3 and 4.3 GPa data points are respectively considered to represent evidence of complete and partial shock-induced chemical reaction in 58% dense Mo + 2 Si powder mixtures, then the cluster of data points corresponding to the three experiments at 6.2-6.6 GPa, which show minimal expansion and remain close to the inert Mo + 2 Si mixture Hugoniot can be considered to reveal very limited or practically no shock-induced reaction.

The experimentally obtained data points of wave speed versus input stress are plotted in Fig. 3 (b) along with the calculated curve corresponding to the 58% dense inert Mo + 2 Si powder mixture (illustrated as a dashed line). It can be seen that the experimental data points appear to follow the inert Hugoniot curve at stresses < 6 GPa. At higher stresses, the data points actually show lower wave speed corresponding to that of low- compressibility melt phase of Si (obtained from [12]). As shown in Fig. 6, it can be seen that the Hugoniot of melted silicon (dashed-dot line) intersects the Mo + 2 Si inert

Hugoniot curve at P_m (~5 GPa) which represents the stress at which Si in the ~58% dense Mo + 2 Si powder mixture undergoes melting. The data points corresponding to experiment numbers 9919, 9907, and 9913 are found to lie more closely on the silicon melt Hugoniot than on the Hugoniot of the Mo + 2 Si powder mixture or its product.

A similar result has also been observed in the prior work on ~55% dense Nb-Si powder mixtures [12], in which the authors in fact observed that in experiments performed at the same shock pressure (and thus particle velocity) the data points fell on either of two branches. Hence, premature melting of silicon (observed in some cases) was considered to inhibit shock-induced reaction, while in other cases under similar conditions, lack of melting of silicon led to shock-induced reaction in Nb + Si powder mixtures, at stresses in the vicinity of the crush strength. Also, in recent modeling work of Tamura and Horie [13] on reaction initiation in Nb + Si powder mixtures inside regions of an adiabatic shear band, they observed that a higher shear rate resulted in greater degree of deformation of reactants and consequently both mixing and increased propensity for shear-induced solid-state reaction initiation. In contrast, presence of a melt phase decreased the shear rate and resulted in inhibiting the reaction.

CONCLUSIONS

Time-resolved experiments performed on ~58% dense Mo + 2 Si powder mixtures at input stresses less than the crush strength (measured to be ~4 GPa), show characteristics of densification represented by the P- α behavior. The measured propagated wave stress profiles show characteristics of wave dispersion with rise time > ~40 nanoseconds. In experiments at input stress between 4-6 GPa, the powder mixtures show evidence of shock-induced reaction, based propagated wave profiles showing a sharp rise time (<~10 ns), and the data points of shock states revealing expansion and approaching the pressure-volume compressibility curve of thermodynamically determined Hugoniot of reacted powder. Experiments on Mo+2Si powder mixtures at input stresses greater than 6 GPa, showed lack of shock-induced reaction which is inferred based on the following: (a) propagated stress profiles showing a slower rise-time, (b) reduced wave speeds recorded in these experiments performed at even higher pressures, (c) data points falling on the pressure-

volume compressibility curve corresponding to unreacted (inert) Mo + 2 Si powder mixture in the P-V plane, as well as along the melted silicon Hugoniot curve in the wave speed versus input stress behavior.

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