THE SHOCK-COMPRESSION OF REACTIVE POWDER MIXTURES

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Abstract

The shock-compression of reactive powder mixtures can yield varied chemical behaviour with occurrence of mechanochemical reactions in the time-scale of the high-pressure state, or thermochemical reactions in the time-scale of temperature equilibration, or simply the creation of dense-packed highly reactive state of material. The principal challenge has been to understand the processes that distinguish between mechanochemical (shock-induced) and thermochemical (shock-assisted) reactions, which has broad implications for the synthesis of novel metastable or non-equilibrium materials, or the design of highly configurable next-generation energetic materials. In this paper, the process of shock-compression in reactive powder mixtures and the associated role of various intrinsic and extrinsic characteristics of reactants in the triggering of ultra-fast "shock-induced" chemical reactions are discussed. Experimental techniques employing time-resolved diagnostics, and results, that identify the occurrence of shock-induced reactions are reviewed. Conceptual and numerical models used to describe the heterogeneous nature of such reactions through mesoscopic details of shock-compression are presented. Finally, a discussion of the application of recent results for the design of reactive material systems with controlled reaction initiation and energy release characteristics is provided.

1. Introduction

The application of pressure on a solid material can compress the lattice and bring atoms closer together in ordered or disordered configurations. As noted by Bridgman¹ in 1956, pressure can "break-down" the electronic structure of atoms, and as a result totally alter the properties of materials. Pressure has since been considered to play a revealing role in obtaining a fundamental understanding of condensed matter and for creation of new phases.^{2, 3} Dynamic application of pressure, or more appropriately shock-compression of condensed matter, generates even more unique and non-homogeneous states, and allows studies of materials in thermodynamic regimes not accessible by any other method. The response of materials to shock compression is dominated by effects of the deviatoric (shear) component of stress, manifested by the creation of crystalline defects (or disordered states) and significantly accelerated kinetics of chemical and physical changes, which can form radically modified structures, metastable phases, and even novel compounds or alloys, that may otherwise not be possible.⁴

Shock-compression of materials has been used to study structural phase changes since 1956, with the first notable scientific achievement being the discovery of the 13 GPa bcc-to-hcp martensitic transformation in iron.⁷ The shock-induced graphite-to-diamond transformation is an example of a standard commercial method, employing explosively generated shock waves, for the production of industrial diamond powder abrasives.^{8,9} The most notable recent achievement of shock-generated phase transformations has been the purported synthesis of metallic hydrogen.¹⁰ These phase transformations represent examples of structural changes from an initial low-density phase to a final high-density state. Shock-induced phase changes from high- to low-density structures, e.g., martensitic transformations and crystal-to-amorphous phase transitions have also been studied.¹¹⁻²¹ Solid-state structural phase transformations from low-to-high or from high-to-low density states have been considered to occur via *reconstructive* or *displacive* mechanisms.²² Such *displacive* phase transformations involve coordinated shifts of atoms comprising of homogeneous strain and shuffle, and hence, are favoured under high pressure, while *reconstructive* transformations are less likely to occur at high pressures due to the reduced mobility of atoms. According to Al'tshuler,⁴ shock-induced phase formation due to displacive phase changes occur via creation of nucleation centres at defects formed in the shock front, and a cooperative motion of many atoms to small distances.

Chemical changes involving “shock-induced” decomposition of compounds, oxidation-reduction (displacement) reactions, as well as reactions between two or more highly exothermic ($\Delta H_R \ll 0$) components, have also been extensively investigated for applications in materials synthesis, and more recently for applications in high-density energetic materials.²³⁻²⁷ Studies of such shock-induced chemical reactions have drawn significant interest in recent years for several reasons: (i) initiating reactions at the high-pressure state may lead to the synthesis of novel phases, not obtainable through conventional ambient-pressure techniques, (ii) the formation of high-pressure phases and their possible reversion upon unloading will result in unique reaction pathways and associated enthalpies, effectively altering the energetics of next-generation materials, and (iii) understanding the reaction initiation behaviour gives potential control of energy release characteristics over a wide range of spatial and temporal scales. While the mechanisms of “shock-induced” *physical* changes involving phase transformations from low-to-high (or high-to-low) density states are well understood, the mechanisms responsible for “shock-induced” *chemical* changes (or reactions) and their associated kinetics, remain to be fully established. It has been proposed that “shock-induced” chemical reactions occur as a consequence of mechanochemical effects, via processes involving solid-state structural re-arrangements of atomic constituents forming compounds via displacive-type processes.^{6, 28-30} Thermochemical mechanisms including liquid-phase

reactions, founded on the observation of localised melts (or “hot-spots”) at interparticle regions in powder mixtures have also been proposed.³¹⁻³⁴ However, the lack of availability of time-resolved spectroscopic measurements has inhibited direct observation and thus, not provided conclusive evidence of the mechanism(s) and kinetics of shock-induced chemical reactions. It has been difficult to characterise the physical processes associated with high-rate deformation leading to initiation of reactions, particularly at the different length and time scales that affect the micro-, meso-, and macroscopic response of reactants. Additionally, the present state-of-the-art in experimental diagnostics is not yet able to provide a reliable probe of the above mentioned processes that may encompass spatial resolution across atomic-to-macroscopic length scales and the temporal regime ranging from a few picoseconds to several milliseconds.

It is the intent of this article to review the current state of the understanding of the mechanisms and kinetics of “shock-induced” chemical reactions in highly exothermic intermetallic-forming powder mixture systems and their associated effects. The review will seek to describe the chemical response of reactive powder mixtures subjected to shock-compression, with particular focus on reactions initiated at very short timescales, i.e., tens to hundreds of nanoseconds corresponding to the shock-rise time and immediately following it. Post-shock chemical reactions in powder mixtures occurring after unloading from the high-pressure state, due to temperature increases in the time-scale of thermal equilibrium (tens of microseconds to milliseconds), will only be briefly discussed. In the sections to follow, we will first describe the fundamental challenges associated with description of chemical reactions under dynamic high pressure. Next, we will review the main features of the mechanics of shock-compression (dynamic densification) of powders. In section 4, a description of the time-resolved diagnostics used in shock-compression experimentation to deduce the occurrence of ultra-fast chemical reactions will be provided, with emphasis on supporting evidence of the occurrence (or lack) of shock-induced chemical reactions. This will be followed by descriptions of thermodynamic arguments employed for occurrence of reaction and its influence on the equilibrium shocked-state of reaction products. The proposed mechanisms for reaction initiation and efforts to model these mechanisms, or the powder compression process itself, will also be presented. Finally, based on the recent experimental and meso-scale numerical analysis work, an analysis of the design and control of shock-induced chemical reaction initiation is offered in the form of a map that combines the effects of the intrinsic (material inherent) and extrinsic (process-dependent) properties of constituents, influencing the configurational changes occurring during shock-compression and leading to reaction initiation and product formation. The review ends with a summary and concluding remarks, which also includes challenges that lay ahead and suggestions for future research.

2. Challenges Associated with the Shock-compression of Reactive Mixtures

2.1. Varied Reaction Response

Reactions in powder systems due to shock-loading can be separated into two categories: (1) *fast* reactions that occur while the material is still compressed at high pressure (few ns to tens of μ s), and (2) *slow* reactions that occur at much later times following unloading from the high pressure state. These *fast* reactions have been termed “shock-induced” reactions, and are initiated within the shock pulse due to the processes occurring during crush-up of the powders to their full density. The formation of reaction products immediately or shortly behind the shock front influences the equilibrium shock state, the changes of which can only be verified through time-resolved measurements.³⁵⁻⁴⁰ The category of *slow* reactions are known as “shock-assisted” reactions, which result as a consequence of the disturbed microstructure and elevated shock-generated residual temperatures. Reactions of this type are driven by atomic diffusion in the time scale of bulk temperature equilibration (tens of microseconds to milliseconds), and typically occur after the material has relaxed and the high-pressure has abated.

A schematic illustrating the differences between shock-assisted and shock-induced reactions is shown in Fig. 1. Consider Fig. 1(a-b), which depicts a shock pulse travelling from right to left through a close-packed bed of spherical particles. The pulse, represented by the pressure profile “*P*”, rapidly eliminates the void space between the particles, consolidating the powder to full density. Also shown is a profile of the bulk temperature, “*T_{bulk}*”, which rises to a peak value long after the material has unloaded. Regions indicating reaction for the shock-assisted and shock-induced cases are shown, with initiation dependent upon temperature for the former, and upon the mechanical state and its associated thermal effects for the latter. If time-resolved metallography could be performed, the evolution of microstructures that one might observe is shown in Fig. 1(c-d). The onset of phase formation for shock-assisted reactions coincides with the build-up of temperature, yielding an equilibrium microstructure. For shock-induced reactions, the critical thermal/mechanical states developed at the high-pressure state result in phase formation at pressure. Since these phases or stoichiometries may not be energetically favourable at ambient pressure, unloading may trigger the formation of the very same equilibrium microstructure shown in Fig. 1c.

Fig. 1 Schematic illustrating the spatial proximity of reactions proceeding through (a) shock-assisted and (b) shock-induced mechanisms. The black line represents the applied stress profile, while the red is the bulk temperature profile. The use of colour within the idealised microstructure is symbolic of reaction. Shock-assisted reactions occur due to thermal mechanisms, once bulk temperatures and diffusion-controlled transport are significant. Reaction occurs on the order of microseconds to milliseconds, long after the shock-front has passed. Shock-induced reactions, however, occur shortly behind the shock-front, while the material is at the high-pressure state. Also shown are examples of microstructures throughout the complete shock-loading event for the (c) shock-assisted and (d) shock-induced cases. Note that due to temperature increases at later times, both reaction types can yield an equilibrium microstructure, complicating the interpretation from observations of recovered post-shock specimens.

2.2. Mechanisms of Reaction

Understanding the mechanisms that govern shock-assisted and shock-induced reactions is an important step to gaining control over these types of chemical behaviour. If it is assumed that the propensity for reaction is fundamentally linked to the availability of activated, reactive complements, it follows that it is the processes bringing unbound atoms into contact that inevitably lead to reaction. For shock-assisted reactions, this is accomplished through thermal energy, and the resulting increased atomic mobility and diffusivities. For shock-induced reactions, however, the mechanism(s) responsible for bond-breakage and atomic intermixing is less clear. The influence of diffusion at these ultra-short times is negligible, the mobility imparted on the order of tens of angstroms. On the other hand, the timescales for shock-induced reaction and the crush-up to full density are commensurate. It is therefore assumed that the mechanisms responsible for the initiation of shock-induced reactions are related to the crush-up process. Determining the critical micromechanical processes for the onset of initiation has been the focus of many investigations dealing with solid-state reactions. While the specifics of micro-scale mechanochemical processes are quite vague, it has been suggested by Matteazzi et al.⁴¹ for ball-milling of powders, that the generation of free radicals, deformed bonds, and ions and free electrons at newly formed, nascent surfaces, during inter-particle collisions can give rise to a so-called “tribo-plasma”,

which can make it possible for inter-particle bonding and/or mechanical alloying to occur in the solid-state.⁴²

2.3. Identifying Reaction Products

In addition to determining the type and mechanism of reaction, investigations of reactive powder mixtures are also challenged with the task of identifying the products formed and their extent. Since powders and their mixtures are a class of heterogeneous material, the local component make-up and thermal/mechanical landscapes all vary greatly throughout the shock-compression and thermal equilibration events. This heterogeneous nature may lead to the formation of multiple phases that do not necessarily share the stoichiometry of the starting bulk mixture. Furthermore, at extended timescales the most stable phases are dictated through equilibrium thermodynamics and kinetics. Thus, the phases present in the microstructure may also vary with time (Fig. 1). Depending upon the operating timescale of diagnostics or characterization, very different interpretations of the phases present and their amounts in the microstructure may be deduced.

The primary concern when characterizing shock-assisted reactions (occurring following unloading from the high-pressure state) is this possibility of an evolution of multiple phases. The study of shock-induced reactions must contend with the additional complexity of phase synthesis under high-pressure. Such non-equilibrium phases are particularly difficult to identify, as they may become unstable and revert to ambient pressure phases upon unloading.⁴³ For example, extreme conditions have been known to alter the equilibrium physical structure of single-component materials, resulting in pressure-induced phase transformations in metals (α - ϵ transition in iron), ceramics (α -quartz to coesite/stishovite transition in silica), and molecular liquids (crystallization of water).^{1, 7, 44, 45} This task becomes markedly more difficult for multi-component mixtures, the constituents of which may be susceptible to formation of high-pressure allotropic phases (e.g., Si in silicide forming intermetallic systems).

2.4. Solid-state Detonation

As will become clear in the following sections, there is direct evidence that ultra-fast shock-induced reactions exact a change in the equilibrium high-pressure state. In many works, this change is signalled by a measured increase in shock velocity for a given pressure. Such an increase has led several investigators to question whether or not shock-induced reactions share similar characteristics with detonation reactions.^{46, 47} Detonation is a phenomenon observed in high explosives, such as TNT (trinitrotoluene), RDX (cyclo trimethylene trinitramine), and ANFO (ammonium nitrate/fuel oil), where

the reaction front propagates in a self-sustaining manner. Determining the propagation behaviour of reaction fronts in powder mixtures is a key step to understanding the kinetics of phase synthesis and exothermic heat release in shock-induced reactions, which will in turn lead to control over the incubation time, exothermicity, and transformation extent of chemical reactions. It should be noted that revealing the mechanisms of reaction, phase transformation pathways, and subsequent reaction front propagation behaviour does not immediately accord this control. Only after these behaviours are correlated to configurable parameters, such as particle size/shape, distributions, and mixture density, may one begin to regard shock-induced reactions as a designable phenomenon. Extending this understanding throughout the gamut of heterogeneity can ultimately provide the ability to synthesise new materials with predefined behaviour, or allow control of reaction and associated energy release for energetic material applications.

3. Compression of powders/distended solids

Any discussion of the shock-compression response of materials begins with an introduction of the Hugoniot.^{48, 49} The Hugoniot is a surface in pressure, volume, and energy space that prescribes the equilibrium states reached through shock-compression. When a material is subjected to shock-loading, delivered by the impact of a high-velocity projectile or upon explosive detonation, a discrete shock-wave front is produced separating the undisturbed state from material at pressure. As this shock wave propagates, material entering the front is brought instantaneously to some elevated state found on the Hugoniot. An example of the Hugoniot in P - V space is shown in Fig. 2a. The P - V Hugoniot gives an indication of the shock-compressibility of a material, and also reveals the velocity with which a shock wave of particular amplitude will propagate. This shock velocity (U_s) is proportional to the slope of the segment joining the initial and final states (Rayleigh line) on the P - V Hugoniot. Alternatively, it can be said that in the absence of physical and/or chemical changes, shock waves (of specific amplitude) in a given material will propagate at a characteristic velocity (U_s). This is an important statement, as it is the underlying basis used to infer the physical or chemical changes occurring in the time-scale of the high-pressure "shock" state.

Fig. 2 Hugoniots in pressure-volume space, illustrating (a) the relationship between shock amplitude (P_1 , P_2) and shock velocity (U_{s1} , U_{s2}) in a given material, and (b) the increase in energy due to shock-loading for a porous and solid material.

The Hugoniot of a powder differs from that of its corresponding, fully dense solid. In the first case, the initial state of a powder does not lie on the Hugoniot, but is instead displaced to some expanded volume, V_{00} , due to the interparticle void space. Upon shock-compression, the powder is rapidly consolidated to full-density, achieving a large net reduction in volume. The densification and collapse of voids during this consolidation process (absent in the compression of fully-dense solids) raises the internal energy of the material, yielding a powder Hugoniot shifted from the solid Hugoniot toward higher volumes.⁵⁰ There are two general approaches usually employed to construct the Hugoniot of a powder. The *isochoric* method locates the powder Hugoniot by performing a constant-volume shift from the Hugoniot of the solid material. In Fig. 2b, it corresponds to the shift from P_1 to P_2 at a constant V_1 . This shift is typically performed using the well-known Mie-Grüneisen equation-of-state, which relates the change in internal energy associated with a pressure change at a constant volume,⁵¹

$$P - P_0 = \frac{\gamma}{V} (E - E_0) \quad (1)$$

where, P , E , and the Grüneisen parameter γ are dependent upon the specific volume, V , and P_0 , E_0 refer to the pressure and internal energy at ambient conditions. This was the approach used by Herrmann,⁵² McQueen,⁵³ and Dijken,⁵⁴ to arrive at relations of the form,

$$P = \frac{[2V - \gamma(V_0 - V)]C^2(V_0 - V)}{[2V - \gamma(V_{00} - V)][V_0 - S(V_0 - V)]^2} \quad (2)$$

where, V_{00} is the starting density of the powder, C is the bulk sound speed, and S is the 1st-order coefficient to the U_s - U_p equation-of-state. For cases where the Grüneisen parameter is unknown, the Grüneisen ratio is usually approximated by,⁵⁰

$$\frac{\gamma}{V} \approx \frac{\gamma_0}{V_0} \quad (3)$$

where the Grüneisen parameter at ambient conditions γ_0 , can be calculated in a straightforward manner from thermodynamic properties. Criticism of the accuracy of this approximation for large differences in internal energy has led to the alternate *isobaric* approach, which performs a constant-pressure adjustment from the solid reference Hugoniot. In Fig. 2b, it corresponds to the shift from V_2 to V_1 at a constant P_2 . The contributions by Oh-Persson,⁵⁵ Wu-Jing,⁵⁶ Jones,⁵⁷ Krueger,⁵⁸ and Boshoff-Mostert⁵⁹ follow this second scheme. In the case of highly porous solids both the isochoric and isobaric approaches show poor correlation with measured Hugoniot, with the isochoric approach typically failing with porosity >50 vol% and the isobaric approach limited typically to porosity less than 60 vol%. With nanometre-sized particles, correlation of both models with the measured Hugoniot is even more limited as the internal energy contribution associated with the large surface area of the nanopowders dominates the densification response.⁶⁰ Example Hugoniots for a solid and porous material are shown in Fig. 2b. The shaded areas below the Rayleigh lines are the respective energy increases due to shock-compression, as given by the conservation of energy,⁵⁰

$$E - E_0 = \frac{1}{2}(P + P_0)(V_{00} - V) \text{ powder} \quad (4)$$

$$E - E_0 = \frac{1}{2}(P + P_0)(V_0 - V) \text{ solid} \quad (5)$$

where, the subscripted terms refer to the initial, unshocked states. It should be quite apparent from the shaded areas in Fig. 2b that the energy increase due to shock-compression for the powder is greater than that for the solid.

From the powder Hugoniot shown in Fig. 2b, one might conclude that full-density is achieved with negligible load, i.e., above $P = 0$ there is an instantaneous jump from the initial state, V_{00} , to V_0 . In practice however, all powders exhibit a certain resistance to complete densification at low stresses. The stress required to reach full density is known as the “crush-strength”, and varies greatly depending upon powder properties such as yield strength, particle size and morphology, and initial packing density. Below the crush-strength, the applied load is insufficient to completely eliminate the void volume, often resulting in an expanded, off-Hugoniot P - V state. The path of off-Hugoniot states below the crush-strength is known collectively as the “crush-up” curve, illustrated in Fig. 3a. Several models have been

proposed to describe the densification response of powders within this range, such as the P - α and P - λ models.^{52, 61-63} The crush-up curve shown in Fig. 3a is an example of the P - α model, the lower stress linear portion representing the extent of elastic response. It should be recognised that the crush-up curve applies only to dynamic compression, and does not necessarily coincide with the densification curve obtained under quasi-static loading. To illustrate this point, the dynamic densification response of *WC* powder within the crush-up regime is shown along with quasi-static compression data in Fig. 3b.⁶⁴ Notice that *WC* is more readily densified under quasi-static loading for an equivalent applied stress. Similar observations have been made for elemental Fe nano-powders and mixtures of Ni and Al nano-particles.^{60, 65, 66} On the other hand, Ni and Al powder mixtures of *micrometre-scale* particles collapse to full-density more easily under shock-compression.⁶⁶ It has also been shown that the dynamic densification behaviour of powder mixtures can be strongly affected by mixture configuration. The varying crush-up responses of three distinct configurations of Ni+Al powders, shown in **Fig. 4**, are related to the amount of particle surface-area, and have been fit using a modified form of the Fischmeister-Arzt equation,^{66, 67}

$$P_y = 2.97 \left(\frac{\rho - \rho_0}{1 - \rho_0} \right) \sigma_y \left(\frac{n}{n_0} \right)^{0.473} \quad (6)$$

where, P_y is the crush-strength, σ_y is the yield strength of the mixture, ρ_0 is the initial relative density, ρ is the final relative density, and n_0 and n are configuration parameters for equiaxed and non-equiaxed powder mixtures, respectively. In short, the properties of powders and their mixtures, i.e., interatomic bonding, flow strength, particle morphology and particle size, have a strong influence over the crush-strength, and overall densification response.

Fig. 3 (a) Illustration showing the crush-up curve for a powder system, which is a path joining the initial state at V_{00} to the Hugoniot of a fully-densified powder. The crush-up curve intersects the Hugoniot at the crush-strength. The shape of the particular crush-up curve shown derives from the P - α model, the

low-pressure linear portion representing the extent of elastic response. (b) Comparison of Hugoniot and quasi-static compression data for a *WC* powder (adapted from Vogler et al.⁶⁴).

Fig. 4 Crush-up behaviour of three distinct configurations of Ni+Al powder mixtures, revealing the dramatic influence of both particle size and particle morphology on the stress required to reach full density. The crush-strength for these three mixtures has been fit using the Fischmeister-Arzt equation, modified to account for differences in surface area (from Eakins and Thadhani⁶⁶).

The processes of void collapse, viscous flow in and around the voids, and crushing of the powder particles in the process of void annihilation, give rise to wave propagation features, such as shock-wave speeds, that are different from those observed in the same solid in the fully dense state. Stress-wave measurements have revealed that crush-up of powders to solid density produces complex wave loading characteristics.³⁸ As illustrated in the schematic in Fig. 5, shock propagation through highly porous solids (powders) shows large changes in wave speed, while only modest increases are observed in solid-density materials at pressures of the order of ~ 10 GPa. The measured shock-wave rise times are also observed to vary from a few tens to several hundreds of nanoseconds, depending on the magnitude of the shock.³⁸ Various void collapse models have been developed, based on rate-independent and rate-dependent, as well as perfectly-plastic and elastic-viscoplastic material considerations.⁶⁸ While rapid-loading rates at high pressures make it necessary to incorporate rate-dependent considerations, long rise-times at low pressures alter the otherwise prompt thermal effects and hydrodynamic considerations assumed in theoretical treatment of the shock state. A realistic analysis of shock-compression effects, therefore, becomes extremely complex.

Fig. 5 Schematic of wave speed versus pressure plots illustrating differences in the response of solid density materials and powders (highly porous solids) to shock compression (from Thadhani et al.³⁸).

Experimental measurements also show that the crush-strength of powders is not only a function of the initial packing density, but also the powder particle size and shape.³⁸ In the case of mixtures of powders, e.g., Al+Fe₂O₃, a two-step crush-up behaviour is observed, with each step indicating a response dominated by the compression characteristics of the respective components.⁶⁹ Thus, the crush-up of the mixture is influenced initially by the compressibility of Al (at low pressure) and later by the compressibility of Fe₂O₃ (at higher pressure). Such characteristics of the deformation response of powders make it very difficult to formulate simple models that can explain the mechanisms or phenomena occurring during shock compression in a wide range of temporal, spatial, and pressure scales.

A number of interesting particle-level processes also occur during the crush-up of powders to full density. As the void volume is eliminated, powder particles may experience several stages/regions of deformation, as illustrated in Fig. 6. *Rearrangement* refers to initial densification accomplished by particle reorientation and interparticle sliding, likely at the expense of minor protuberances. *Localized flow* describes heterogeneous deformation through shear and normal stress into the void regions. Lastly, *bulk deformation* takes place following the collapse of the voids, in response to a state of pressure.^{25, 64} The particular micromechanical modes active within these regions will vary according to the strain-rate and powder configuration, once again defined by the particle size, morphology, orientation, distribution, and initial density. The recent review by Sethi et al.⁷⁰ provides an in-depth discussion of the dynamic consolidation of single-component powders. For multi-component powder mixtures, the added heterogeneity of dissimilar yield strengths, mass densities, and sound speeds will also play an important role in how shock energy dissipation is partitioned and localised. These factors result in spatially inhomogeneous states of stress, defect densities, and microkinetic response, ultimately controlling the extent of mixing (or dispersion) between reactive components during crush-up. The extensive deformation and flow at particle interfaces will generate adiabatic, plastic work-induced temperature,

and steep thermal gradients extending into the particle interior. Once the material reaches the Hugoniot (complete densification) or a state along the crush-up curve (incomplete densification), it is assumed to be in mechanical equilibrium, bringing athermal mass mixing to an end. Thermal equilibrium, however, is not achieved until much later in time (micro- to milliseconds), only after the irregular thermal landscape has been homogenised. Mixing at these extended timescales must be accomplished through atomic diffusion, accelerated by the enhanced temperatures and presence of defects or disorder. Thus, mass mixing may occur over a wide range of timescales, as facilitated by either mechanical or thermal processes. Under certain conditions, mixing may be sufficient to trigger a chemical reaction over a wide time-scale.

Fig. 6 Illustration showing distinct regions of deformation during the shock consolidation of equiaxed powders. These regions mark the transitions between consolidation accomplished by rigid-body translations/rotations (Region I), shear/normal stress-driven deformation into the voids (Region II), and bulk volume reduction under pressure (Region III) (from Linse⁷¹).

4. Review of diagnostic techniques

Shock-compression can be used to probe the response of materials to extreme conditions, and establish their compressibility, the thermodynamic equation-of-state, and the high-pressure stability. For example, melting and evaporation at high temperatures provide an understanding of atomic bonding. Likewise, plastic deformation and fracture during straining describe the generation and interaction of defects, and chemical and/or electrical changes at high pressure are signatures of bond stability. Investigation of each of these phenomena and their like requires the use of specific experimental approaches and diagnostics; the study of chemical reactions initiated by shock waves is no exception. The diagnostic techniques employed fall into the categories of either time-resolved measurements or post-shock microstructural analysis of recovered shock-compressed materials. In terms of probing

chemical reactions in shock-loaded powder mixtures, time-resolved and post-shock recovery analyses can provide very different information.

Time-resolved diagnostics are used to obtain measurements of material properties during the shock-loading event. In most impact- or explosively-driven shocks (several to hundreds of GPa), the entire shock-loading event (rise to peak pressure, equilibration, and release) occurs over a time span of no more than a few microseconds. The rise and equilibration of the high-pressure state occurs over an even shorter time, anywhere from a few nanoseconds to a couple hundred nanoseconds. Correspondingly, the study of the response of materials within this very narrow interval is limited to only a handful of diagnostics. Examples of time-resolved diagnostics include polyvinylidene fluoride (PVDF) and manganin stress gauges, resistivity measurements, optical pyrometry, velocity interferometry (VISAR), and optical spectroscopy, all of which operate and collect data during the shock-compression event.^{35, 72-}

⁸¹ What temporal resolution is gained through time-resolved measurements is often lost in spatial resolution. In many of the techniques mentioned, measurements are obtained from an averaged area, such as the PVDF gauge area, or a limited region, such as the spot size for optical methods. This presents a problem if the characteristic scale of the feature or process of interest is not well matched to the resolution limit or sampling field of the chosen diagnostic. In addition, most of the mentioned diagnostics act upon a fixed surface. Line VISAR, for example, gathers information from a rear surface, with an averaged response of shock wave propagation through the thickness of the specimen.⁸² One notable exception is ultrafast dynamic ellipsometry (UDE), which can deduce the time-resolved motion of the shock front in thin-films.⁸³ The utility of this method, however, is limited to samples transparent to the diagnostic wavelength. It remains a challenge to monitor the evolution of mechanical/thermal/chemical state ahead and behind the shock front within an opaque material at the mesoscopic level.

Efforts to understand the mesoscopic response of reactive materials to shock-loading have led to post-shock analyses of the recovered specimen microstructure. Compared to time-resolved diagnostics, recovery analyses are far more numerous, and comprise the vast collection of materials characterization techniques, which can be used to probe over a wide range of spatial scales. For example, precise measures of phase composition, configuration, and distribution can be obtained through combined metallography, X-ray diffraction (XRD), and scanning and transmission electron microscopy (SEM, TEM) analyses.^{30, 84-87} Measures of the degree of shock-activation (change in reactivity) can be determined through differential thermal analysis (DTA) and/or differential scanning calorimetry (DSC).^{30, 88} The only limitation to recovery is that measurements only apply to the final, as-shocked

state, with very little information concerning the critical particle configurations leading to reaction, or the product-phase transformation pathways. As shown in Fig. 7, which illustrates an (a) optical micrograph and (b) XRD trace of Ti_5Si_3 reaction product formed from a Ti and Si powder mixture of same stoichiometry, the complete formation of the equilibrium reaction product at extended timescales can mask evidence of ultra-fast chemical reactions that may have occurred at early times.³⁸ Thus, while recovery techniques permit very detailed, spatially-resolved analysis of reaction products (e.g., Ti_5Si_3 grains of $\sim 10\ \mu\text{m}$ average size, as shown in Fig. 7), they are hard-pressed to locate the onset time of reaction, and distinguish between products formed due to shock-induced and shock-assisted reactions.

It should be quite clear by now, that the occurrence of ultra-fast shock-induced reactions can only be verified through time-resolved measurements, as positive proof locates the onset of reaction within the several hundred nanoseconds of shock equilibration. Subsequent recovery analysis can supply potentially important information, in the cases where reaction does not go to completion, and the relative configurational changes in reactants and products is not obscured. Shock-assisted reactions however, require more rigorous validation. In addition to showing evidence of reaction products in the final, recovered specimen, complementary time-resolved measurements are required to show that the specimen remained inert during the initial shock-compression event, but reacted subsequently following unloading to ambient pressure, and in the time scale of thermal equilibration.

The next section will summarise prior investigations of reactive powder mixtures and the results of time-resolved and recovery techniques used to infer the occurrence of chemical reactions initiated by shock waves.

Fig. 7 (a) Microstructure of a shock-compressed and recovered Ti+Si mixture, revealing a homogeneous structure of reaction product grains and voids, typical of melting and solidification. (b) An accompanying XRD spectrum shows the product to be Ti_5Si_3 . Any evidence of ultra-fast, mechanochemical reactions is obfuscated by thermal equilibrium processes at later times (from Thadhani et al.³⁸).

5. Experimental Evidence of Chemical Reactions under Shock-Loading

5.1. Shock-Recovery Experiments and Analyses

The reactive system that has perhaps been most thoroughly studied throughout the history of shock-synthesis has been that of Ni+Al. In 1985, Horie and coworkers⁸⁹ were the first to report the synthesis of nickel-aluminum intermetallics following shock-compression, using the well-calibrated Sandia Laboratories' Bear series shock recovery fixtures.⁹⁰ Micrometre-scale powders were combined at a 7:3 Ni:Al volumetric ratio (corresponding to Ni_3Al product formation), and statically pressed to 60% TMD (theoretical maximum density) within Sandia's Momma Bear (A) recovery fixture. The powders were subjected to explosively-driven plane wave shocks in the range of calculated shock pressures of 14-22 GPa, and peak bulk (residual) temperatures nearing 600°C. Recovery microstructure characterization and electron beam microanalysis revealed the formation of reaction products in select regions. A combination of the Ni_3Al phase and residual Ni was found at the compact periphery, where the shock-generated temperatures reached their peak due to two-dimensional radial wave-focusing effects caused by the impedance difference between the low-density powders contained in high-density (copper) fixtures. Additionally, amounts of NiAl and Ni_2Al_3 were discovered bordering a largely unreacted central zone (Fig. 8a). Earlier simulations of the compaction event in Momma Bear-type recovery capsules showed this central zone to coincide with the region of highest pressure (Fig. 8b).⁹¹ The lack of reaction within this zone, coupled with a clear link between temperature and product formation, strongly suggests a thermally-initiated reaction due to shock-assisted mechanisms. This work also clearly illustrates the possibility of forming multiple phases, and the resulting complexity introduced in the study of reactions occurring at various time-scales in heterogeneous mixtures.

Fig. 8 (a) Illustration showing the configuration of phases through the cross-section of a recovered Ni+Al compact; the shock wave entered the powder from the top. Regions of predominant phase

formation coincide with the greatest shock-generated temperatures, as shown by the calculated contours (from Horie et al.⁸⁹). (b) For comparison, the region of highest pressure produced in Momma Bear-type recovery capsules lies along the sample axis, as shown from 2D numerical simulation (adapted from Davison et al.⁹¹).

Nearly identical experiments were performed on mixtures of Ti+Al (micrometre-scale powders, 7:3 volumetric ratio, 60% TMD), with shock pressures and bulk temperatures ranging from 5-27 GPa, and 150-800° C, respectively.⁹² Once again, reaction products were localised at the periphery of the recovered compact, identified by microanalysis to be a mixture of Ti_3Al , Ti_2Al , and $TiAl$ (Fig. 9). Extensive reaction was observed in only those compacts for which the shock-generated temperature within the reacted zone exceeded 450°C. The authors also observed unique deformation and mixing features in otherwise unreacted regions which were absent in the Ni+Al compacts, and attributed these to the relative differences in the hardness and melt temperature of the transition metal constituents (Ni, Ti).

Fig. 9 Micrograph showing the periphery of a recovered Ti+Al powder compact containing multiple reaction products: (A) Ti_3Al , (B) Ti_2Al , (C) $TiAl$, (D) Ti (from Horie et al.⁹²).

Similar recovery experiments on the Ti+Al system were conducted by Royal et al.⁹³ on micrometre-scale (-325 mesh) powders, mixed at a 3:2 volumetric ratio, and pressed to approximately 53% TMD. By varying the explosive used with Sandia's Momma Bear recovery assembly, maximum shock pressures of 5, 7.5, and 22 GPa were delivered. Only the specimen shocked to 22 GPa underwent

reaction, though products were localised at the edge and axial regions due to the 2-dimensional wave focusing effect similar to that observed in Horie's earlier experiments. The presence of shrinkage pores within these regions suggests that the products solidified from a liquid state (Fig. 10a). As shown in Fig. 10b, the unreacted material contained mostly undeformed Ti particles embedded within an Al matrix. This apparent preferential deformation of the Al phase showcases the influence of relative component yield strength in dictating the micromechanical response of heterogeneous powder mixtures during shock-compression.

Under more extreme conditions with the use of the 12-capsule Sawaoka type shock recovery fixture (shown in Fig. 11), shock-induced reaction synthesis in Ni and Al powders ($\sim 20\ \mu\text{m}$ particle size) mixed at a 3:1 atomic ratio, has been observed with the formation of the $L1_2$ -phase (Ni_3Al) at the calculated (initial) shock pressure of $\sim 12\ \text{GPa}$.^{94, 95} The same powder mixture, upon shock loading at a higher initial pressure of $\sim 17\ \text{GPa}$ showed formation of the BCC B2-phase (NiAl) but with Ni-rich ($3\text{Ni}+\text{Al}$) stoichiometry (deduced from XRD lattice parameter measurements). It was argued that under the extreme conditions, the solubility of B2- NiAl was significantly increased, to even encompass the Ni_3Al stoichiometry. Increased solubility due to extreme shock loading conditions has also been observed in the immiscible Cu+Nb system, with the formation of isomorphous Cu+Nb alloys and compounds.⁹⁶ Solubility of as much as 10 wt% solute in each phase and submicrometre-scale mechanical mixing of Cu and Nb into each phase has been observed (Fig. 12).

Fig. 10 Backscattered electron micrographs from a recovered Ti+Al mixture taken from the (a) edge, showing a reacted microstructure and shrinkage pores, and from the (b) unreacted bulk (adapted from Royal et al.⁹³).

Fig. 11 Schematic detailing the 12-capsule Sawaoka fixture used in shock recovery experiments. Powder samples are loaded into each of the 12 steel capsules, and held within a steel capsule holder plate. The uniform detonation of a main charge launches a thin metal flyer plate, which subsequently impacts the holder plate, driving a shock through capsules and compressing the powders. The rugged design permits recovery of the powder compacts for post-shock characterization (from Song et al.⁹⁷).

Fig. 12 TEM bright-field image showing submicrometre-scale mixing in a Cu+Nb powder mixture produced by shock loading. Energy dispersive spectroscopy obtained from the as-labelled Cu and Nb regions revealed increased solubilities in each phase of up to 10 wt% (adapted from Advani and Thadhani⁹⁶).

Shorokhov and coworkers⁴³ reported on the synthesis of intermetallics in the Ti+Al system under the action of spherical, converging shock waves. Micrometre-scale ($< 63 \mu\text{m}$) powders were mixed at Ti:Al atomic ratios of 3:1 (48% TMD) and 1:1 (59% TMD), and loaded into a thin-walled spherical steel

capsule, 18 mm in diameter, itself encased within a thick (~3 mm) brass shell. An explosive charge delivered peak shock pressures in the capsule wall of approximately 50 GPa (calculated). Recovery analysis of the 3:1 stoichiometric mixture revealed a mixture of β -Ti and a disordered Ti_3Al intermetallic. An equiaxed grain structure supports the conclusion that these phases solidified from a melt. The 1:1 stoichiometry contained a mixture of weakly ordered Ti_3Al and $TiAl$. Light microscopy revealed a dendritic microstructure, evidence of melting and solidification.

A great deal of work has also been conducted on the silicides, specifically Ti+Si, Nb+Si, Ni+Si, and Mo+Si mixtures. These mixtures differ from the work on aluminides, in that silicon is a metalloid, and will not necessarily deform through the same mechanisms as a metal. Furthermore, silicon exhibits reverse Clausius-Clapeyron behaviour, its melting temperature decreasing with increasing pressure.

An explanation for reaction initiation based upon thermal energy was developed by Krueger et al.,^{33, 98} following their work on Ni+Si powder. Micrometre-scale powders (Ni: 20-45 μ m, Si: -325 mesh) were mixed at a 1:1 atomic ratio and pressed to 60% TMD within a steel containment fixture. The powder was impacted directly by a stainless steel flyer launched from a 35 mm diameter gas gun. By avoiding initial contact with the fixture, their carefully designed experiments allowed a highly unidirectional shock-wave to be applied to the Ni+Si mixture, significantly reducing the 2-dimensional wave focusing effects inherent of the Momma Bear or Sawaoka recovery fixtures.^{90, 97, 99} By performing experiments at several impact velocities and starting densities, the shock energy from P - V work, E , deposited into the powder was varied (Table 1). Also listed are the thermal energy thresholds for reaction, E_T , determined through DTA. The presence of reaction products in the recovered specimens as related to calculated shock energy indicated a clear energy threshold (between 384-396 Jg⁻¹), below which reaction did not occur. Recovery analyses of unreacted systems showed deformation of nickel, cracking and fracture of silicon, and presence of resolidified regions from possible “melt pools” concentrated at the interfaces between the two parent phases (Fig. 13). Quantitative energy dispersive spectroscopy (EDS) suggested the reacted phase to be that of $NiSi_4$. From these results, Krueger et al. concluded that a critical “threshold” shock energy for reaction initiation is more appropriate than the previous notion of a critical shock pressure, since reaction could be confirmed at lower stress amplitudes in mixtures containing higher porosity. This is consistent with results shown in Fig. 8, which revealed a closer correlation with shock temperature than shock pressure. Vecchio et al.¹⁰⁰ and Meyers et al.³¹ obtained similar results using the Sawaoka capsules.

Fig. 13 Electron micrograph of a recovered Ni+Si specimen showing the presence of a product phase concentrated at the interface between Ni and Si (from Krueger et al.³³).

Table 1 Details of the recovery experiments performed by Krueger et al.⁹⁸ on Ni+Si powder mixtures. Results suggest a critical shock energy of $\sim 400 \text{ Jg}^{-1}$, above which reaction is observed in the recovered specimen.

Porosity (%)	Velocity (ms^{-1})	P (GPa)	E (Jg^{-1})	E_T (Jg^{-1})	React (Y/N)
37.5	1020	5.6	380	367	N
41.2	1060	5.38	421	410	Y
37.5	1050	5.86	398	384	N
39.9	1050	5.46	407	396	Y

It should be pointed out that the only direct measurement in the experiments by Krueger et al. were of the impact velocity; the shock pressure and energy values listed in Table 1 were calculated values obtained from this measured velocity and a calculated shock Hugoniot of the powder mixture. The analysis and conclusions relied solely upon observations of post-mortem microstructural analysis to identify reaction product phases, and their correlation with the calculated values of shock pressure and energy. Consequently, the conditions observed contain the effects of both the high-pressure shock state and the post-shock bulk (equilibrated) temperature, which makes it difficult to deduce if any or what part of the reaction was shock-induced or shock-assisted.

One of the first explanations for the effect of ultra-fast chemical reaction on the high-pressure state was offered by Yu and Meyers,⁸⁷ following their recovery work on micrometre-scale (~ 325 mesh) Nb+2Si powder mixtures. The Nb and Si powders, mixed at an atomic ratio of 1:2, were pressed to 60% TMD within a Sawaoka recovery fixture, and impacted by a flyer plate at 2 kms^{-1} . The recovered Nb+Si specimen contained the NbSi_2 product phase throughout most of the compact, with unreacted regions at

the impact-side corners. Numerous pores were observed in the reacted zone, along with needle- and dendritic-shaped structures, which are characteristic of a microstructure evolving following melting and resolidification processes. The influence of shock-induced chemical reaction on the equilibrium shocked state of the mixture was estimated following a thermodynamic analysis in which the heat of reaction was assumed to affect the energy of the shock process through an increase in pressure, similar to the analysis applied to detonation reactions in explosives and used previously by Boslough¹⁰¹ for heat detonation type reactions in thermite mixtures,⁵⁰

$$E_2 - E_{00} = \frac{1}{2} P_2 (V_{00} - V) = \frac{1}{2} P_1 (V_{00} - V) + E_R \quad (7)$$

where, P_1 is the pressure of the inert powder, E_2 and P_2 are the energy and pressure of the reacted product, E_R is the heat of reaction, and E_{00} and V_{00} refer to the energy and volume of the porous mixture. The result, shown in Fig. 14, reveals a difference in the slope of Rayleigh lines joining the starting porous state to points on the inert and reacted Hugoniots. Evaluating Eq. 6 for the 2 kms⁻¹ flyer impact, Yu and Meyers⁸⁷ estimated an increase in pressure and shock velocity on the order of 33%. Though recovery techniques were employed, the analysis from this work was the first to reveal the metrics required to infer the occurrence of shock-induced chemical reactions on the basis of shock velocity increases.

Fig. 14 Proposed P - V Hugoniots of the solid, powder, and reacted powder for a Nb+2Si powder mixture. The slope of the Rayleigh line for (2) reacted behaviour is greater than for inert behaviour (1), indicating an increase in shock velocity (adapted from Yu and Meyers⁸⁷).

Mechanisms of shock-induced reaction have been proposed by Vecchio et al.¹⁰⁰ and Meyers et al.³¹ through observations of the morphology and configuration of reaction products in Nb+Si and Mo+Si

powder mixtures. Following shock-compression delivered by explosive detonation using the 12-capsule Sawaoka fixtures, the recovered compacts were examined for evidence of chemical reaction. In both mixtures, regions of partial reaction contained nodules of silicon-rich intermetallics ($NbSi_2$, $MoSi_2$). As shown in Fig. 15 for a Nb+Si mixture, nodules of $NbSi_2$ are observed bordering the Nb particles, and dispersed throughout the silicon matrix. From the morphology and sheer number of the nodules, the authors concluded that the formation of the nodules was associated with the melting of silicon. Dissolution of Nb into molten Si at the particle interface resulted in the formation of molten $NbSi_2$. During solidification, the disilicide was ejected into the Si melt, exposing fresh Nb to continue the reaction.

While this mechanism of reaction based on melting, dissolution, and precipitation is highly plausible, Vecchio et al.¹⁰⁰ and Meyers et al.³¹ supply no evidence for the time over which reaction is initiated and completed. In fact, had the nodules formed within the shock front at short time-scales, it stands to reason that there would be evidence of heterogeneous transport of nodules within the silicon melt, which is absent in Fig. 15. Reactions based on melting, dissolution, and reprecipitation are governed by thermally-activated processes similar to those observed during self-propagating or combustion-type chemical reactions, which are more consistent with shock-assisted reactions occurring in the time-scales of temperature equilibration.¹⁰²

Fig. 15 SEM micrographs of recovered Nb+Si compacts revealing (a) an unreacted portion, (b) the transition zone between unreacted and partially-reacted material, (c) a partially-reacted region, and (d) the transition zone between partially-reacted and fully-reacted material. The reaction product consists of $NbSi_2$ nodules, which are concentrated near the Nb particle interfaces (from Vecchio et al.¹⁰⁰).

As mentioned previously, both time-resolved and recovery analyses are needed to establish the timescale of initiation for shock-assisted reactions. Of the large amount of recovery work conducted on powder mixtures, only a few have included both of these techniques.

One of the first sets of dual time-resolved/recovery experiments was performed by Vandersall and Thadhani^{85, 103} on Mo + 2Si powder mixtures. Powder mixtures of micrometre-scale molybdenum and silicon were combined at 1:2 stoichiometry, and shock-loaded in cylindrical implosion and planar-pressure geometry experiments. The maximum peak pressure and mean bulk temperature at various locations in each configuration were estimated through two-dimensional simulations, while correlations to intermetallic phase formation were provided through post-experimental microstructural analysis. Results suggest the extent of reaction to be closely linked to pressure-induced melting and bulk temperature equilibration. In specimens subjected to pressures and temperatures exceeding the melt

conditions of silicon, partial reaction resulted from molybdenum dissolution in the silicon melt and precipitation of $MoSi_2$. Complete reaction was observed in regions experiencing melting of both silicon and molybdenum, yielding a solidification microstructure. The time scale of temperature initiated reactions of this type is on the order of milliseconds, and occurs long after the initial shock front has passed. Supporting these conclusions, time-resolved Hugoniot state measurements conducted on identical mixtures indicated inert compressibility behaviour within the duration of the shock pulse.¹⁰³

Similar evidence of shock-assisted reactions was observed in the Ni+Al system. Eakins and Thadhani⁸⁶ combined micrometre-scale, spherical Ni and Al powders at 1:1 volumetric ratio, pre-pressed to 60% TMD, and subjected them to input shock stresses of up to 6 GPa. Rather than performing Hugoniot and recovery analyses on separate experiments, a soft-catch recovery technique permitted time-resolved measurements and post-shock microstructure characterization from the same specimen. Above 5 GPa, the microstructure of the recovered sample contained the $NiAl_3$ intermetallic phase at the boundaries between the Ni particles and a molten and resolidified Al matrix. Reaction was believed to proceed following dissolution of Ni into the molten aluminum. As in the case of the Mo + 2Si work, time-resolved measurements revealed no evidence of reaction behaviour at the high-pressure state in this Ni+Al powder of spherical morphology.

5.2. Time-Resolved Instrumented Experiments

The investigations just described utilised post-shock recovery analyses to determine the reaction product characteristics and the calculated conditions (pressure, temperature, shock energy) under which chemical reactions are initiated. Most, however, did not couple time-resolved measurements, and therefore cannot unequivocally establish the timescale of the formation of the observed reaction product(s).

Evidence of shock-induced reactions was first demonstrated by Batsanov et al.³⁵ in their work on Sn+S mixtures. Starting tin and sulphur powders ranging in size from 5-10 μm were mixed at an equiatomic ratio, and statically pressed to ~92% TMD. The powder compacts were then subjected to explosively generated shock pulses up to 40 GPa, which travelled first through a polytetrafluoroethylene (PTFE) driver before reaching the specimen. The incident and reflected shock pressures were recorded using a piezoresistive manganin stress gauge located within the driver, several millimetres from the specimen. Evidence of reaction was provided through differences observed between the experimentally measured and calculated reflected stress amplitudes (Fig. 16). By assuming that reaction at high-pressure manifests as a constant-volume increase in pressure (consistent with detonation theory), the

change in specific internal energy of the inert powder and reacted mixture were written from the Rankine-Hugoniot relationship,

$$E_1 - E_{00} = \frac{1}{2}(P_1 + P_0)(V_{00} - V) \quad (8)$$

$$E_2 - E_{00} = \frac{1}{2}(P_2 + P_0)(V_{00} - V) \quad (9)$$

where E_{00} and V_{00} refer to the initial energy and specific volume of the starting powder, and the subscripts 1 and 2 are for the inert powder and reacted mixture, respectively. Solving for the heat of complete reaction, Q_v ,

$$Q_v = E_2 - E_1 = \frac{1}{2}(P_2 - P_1)(V_{00} - V) \quad (10)$$

Fig. 16 Shock compressibility of Sn+S mixtures measured by reflected shock measurements. Curve 1 is for the tin sulphide dense product. Curve 2 is the results of experiment conducted on stoichiometric mixtures of tin and sulphur. Curve 3 is the expected compressibility behaviour of an inert Sn + S mixture. At pressures below 15 GPa, the mixture exhibits inert behaviour. Above 15 GPa, the mixture deviates to the right (adapted from Batsanov et al.³⁵).

and then relating Q_v calculated in this manner to the enthalpy of formation of SnS , the extent of reaction was estimated. This early model has been criticised for ignoring the effect of specific volume and equation of state changes between reactants and products. Additionally, the standard enthalpy of formation was used when in fact, the enthalpy at high pressure would have been more appropriate. Finally, it fails to consider the influence of multiple (or intermediate) phase formation on wave propagation.

During the mid-90's, a reaction scheme based upon the detection of an “excess pressure” was promoted following a series of thoughtful experiments performed on Ni+Al powder mixtures. In the first work, Bennett et al.¹⁰⁴ considered micrometre-scale powders of Ni (3-7 μm) and Al (20 μm), combined at a Ni:Al atomic ratio of 2.604, and pressed to ~55% TMD. The pressed powder was contained within a 304 stainless steel target assembly, and impacted by a steel flyer. The response of the powder mixture was measured indirectly by a manganin gauge embedded within the steel backer opposite the impact face. The recorded pressure profile of the transmitted shock pulse was compared with pressures estimated from the P - U_p diagram constructed for inert behaviour. Experiments conducted at impact velocities ranging from 900-1450 ms^{-1} indicated a critical velocity of 1075 ms^{-1} , above which an “excess pressure” was detected (Fig. 17). The increase in pressure was attributed to the dual effects of exothermic heat release and volume change from reactants to products. Post-shocked specimens exhibited complete reaction of the aluminum to form NiAl_3 and residual Ni. A similar experiment utilizing a lower impedance backer material to inhibit compressive wave reflection was performed at an impact velocity well above the supposed threshold for reaction initiation. However, lack of reaction signatures in the gauge record or post-experimental microstructure supported the conclusion that the observed reactions were initiated by the reflected shock propagating through the already shock-compressed mixture.

Fig. 17 Time-resolved stress traces recorded in a Ni+Al mixture at two impact velocities, v . Pressures in excess of those expected for an inert material were observed in both experiments shown. The expected inert pressure was ~21 GPa for the closed and open data set, as shown by the dashed line (adapted from Bennett et al.¹⁰⁴).

Continuing Bennett's work on Ni+Al powder mixtures, Iyer et al.³⁷ investigated the effect of particle size on the reaction threshold. The nickel particle size was reduced to less than 3 μm (yet not nanoscale),

while the aluminum particles were kept at 20 μm . Once again, Ni+Al mixtures were prepared to an atomic ratio of 2.604 and initial density of 55% TMD, and tested in the same experimental and diagnostic configuration as before. It was found that the threshold impact velocity for reaction was increased to nearly 1400 ms^{-1} . This increase could not be explained through thermochemical considerations, as the shock energy was not altered. Rather, the dependence of critical velocity on particle size was attributed to mechanochemical effects, specifically the cleansing, exposing, and intimate mixing of fresh reactants through inter-particle shear, of which particle size plays a significant role.

In an effort to provide conclusive evidence for either the mechanochemical or thermochemical models, two series of nearly identical impact experiments were performed by Yang et al.¹⁰⁵ on the Ni+Al powder configurations considered previously by Bennett.¹⁰⁴ The experiments were designed to vary the reflected wave profile to exact changes in the rate of mechanical deformation, while at the same time depositing the same total energy into the mixture. This was accomplished by introducing a 0.254 mm aluminum layer on the rear surface of the powder compact. The multiple wave reflections at the powder/layer and layer/backer interfaces had the effect of producing steps in the reflected stress profile. Alternatively, experimental configurations without the layer were performed to reproduce a steep rise to peak pressure. Once again, the mixture theory was employed to calculate the shock-compressibility of the powder mixture for an inert reference. In agreement with the work by Bennett¹⁰⁴ and Iyer,³⁷ the initiation of reaction within 100 ns of the shock front resulted in a measurable “excess pressure”. On the basis of this measure, Yang et al.¹⁰⁵ were able to confirm reaction in only those specimens without the aluminum layer. Powders subjected to a multi-step reflected shock remained unreacted, even though the total input energy exceeded the supposed threshold energy (483 kJkg^{-1}) determined by the reacted series (Fig. 18). This result serves to refute the earlier theory of an “energy threshold” for reaction proposed by Krueger and Vreeland.³³ Furthermore, the apparent link between the rise-time of the reflected shock and chemical reactivity appears to strengthen the hypothesis that, at least for the experimental configuration considered, reaction was initiated in the pre-compressed, shock-modified reactants upon reflection at the sample/backer interface.

Fig. 18 Peak transmitted pressures as a function of shock energy for experiments with a sharp (open circles) and multi-step (closed circles) reflected shock front. The solid line corresponds to the calculated inert behaviour. Excess pressures are only observed above 483 kJ kg^{-1} when the reflected shock front is narrow (from Yang et al.¹⁰⁵).

In each of the works mentioned thus far, sample configurations were chosen such that the reflected shock profiles were recorded by a single manganin gauge ($\sim 50 \text{ ns}$ resolution typical). Used in the manner described, the manganin gauges were insensitive to the details of shock-loading within the rise-time of the shock pulse. Therefore, the reflected shock setup does not provide for the determination of reaction immediately behind the incident shock front. These studies also include unknown shock quantities that are indirectly determined. Only through the explicit knowledge of the Hugoniot of all interacting materials could the powder shock state be calculated.

A study conducted by Graham et al.³⁶ using Bauer piezoelectric polymer gauges demonstrated a new experimental setup allowing the direct measurement of shock pressure and shock velocity. The polyvinylidene fluoride (PVDF) gauges offered a resolution of 1 ns up to a maximum pressure of 100 GPa . Used in conjunction with a gigahertz frequency oscilloscope, information about pressure equilibration and shock wave reverberation could be captured. PVDF gauges placed at the impact and propagated specimen/fixture interfaces allowed the direct measurement of input stress and shock transit time through the specimen. Several series of experiments have been conducted to illustrate the capability of performing accurate shock-compressibility measurements on powder systems exhibiting inert and reactive behavior.³⁶ Stoichiometric mixtures of $3\text{Ni}+\text{Al}$ and $5\text{Ti}+\text{Si}$, as well as rutile (TiO_2) powder, were pressed to initial densities of 35, 53, and 60% TMD, respectively. Specimens were contained within a Cu fixture, and impacted by a Cu flyer launched by a compressed-gas gun, sending a shock wave through the powder and diagnostic gauges. For the $3\text{Ni}+\text{Al}$ mixture, the P - V states above 3.7 and

4.7 GPa seemed to follow the calculated mixture Hugoniot, indicating inert behaviour. On the other hand, the 5Ti+3Si powder mixture tested at 2.5 GPa revealed a measured shock state considerably displaced from the calculated mixture Hugoniot toward higher volumes (Fig. 19). Coupled with reports that the crush strength of such a mixture was in the vicinity of 800 MPa, this shift is not indicative of incomplete densification, as was the case for the TiO_2 powder, but suggestive of shock-induced reaction.

Fig. 19 Pressure-volume data obtained through PVDF measurements for 3Ni+Al, 5Ti+3Si, and TiO_2 powders. Reaction is only suspected in the 5Ti+3Si mixture, which exhibits an expansion to higher volumes above its supposed crush-strength of ~800 MPa (adapted from Graham et al.³⁶).

Time-resolved experiments on the 5Ti+3Si system were continued by Thadhani et al.,³⁸ to investigate the influence of particle size on shock-induced reaction sensitivity. Mixtures of coarse (Ti,Si: 105-149 μm), medium (Ti,Si: < 45 μm), and fine particles (Ti: 1-3 μm , Si: < 10 μm), were combined to the stoichiometry of Ti_5Si_3 and pressed to within 45-53% TMD. Using a similar experimental configuration as Graham et al.,³⁶ PVDF measurements of input stress and shock velocity were obtained from impact experiments conducted in the range of 0.2-2.9 GPa. Results for the coarse and fine powder mixtures revealed a regime of densification under ~1.25 GPa, above which both mixtures followed the calculated Hugoniot of the solid mixture (Fig. 20). On the other hand, the medium powder mixture exhibited a lower crush-strength (~1 GPa) and signatures of shock-induced reaction above 1.5 GPa, namely, deviations from the inert solid mixture Hugoniot to higher volumes. Since the shock energy deposited into each of the three mixtures at a particular pressure was very similar (especially so for the medium and coarse mixtures pressed to the same initial packing density), it follows that the cause of reaction cannot be solely attributed to thermochemical processes. Rather, this study shows that particle

deformation behaviour, such as the transition from plastic deformation to cracking in silicon with changing particle size, can strongly affect the intimacy of mixing and the propensity for shock-induced chemical reaction.³⁸

Fig. 20 Time-resolved results obtained from mixtures of coarse, medium, and fine 5Ti+3Si powders. All three mixtures show similar densification behaviour, reaching the solid Hugoniot at 1.0-1.25 GPa. Above 1.5 GPa, the medium mixture deviates from the solid Hugoniot to higher volumes, presumably from the effects of shock-induced chemical reactions (from Thadhani et al.³⁸).

The importance of extrinsic mixture properties on shock-induced reactions was further investigated by Xu and Thadhani,³⁹ in their study of the effect of powder pre-treatment on the chemical response of shock-compressed Ni+Ti powder mixtures. Spherical-shaped (rounded) Ni and Ti powders of -325 mesh ($<44\ \mu\text{m}$) were combined at a 1:1 atomic ratio, and statically pressed to 50% TMD. The powders were then ball-milled for 0, 4, 8, and 18 hours to introduce varying degrees of damage and defects. From preliminary XRD and DTA studies, the pre-treated powders exhibited increased alloying and reduced heat-of-reaction with longer ball-milling duration. For the shock-compression experiments, PVDF gauges were once again used to monitor the input and propagated stress profiles, from which the shock transit time through the powder mixture was also determined. Results from the as-pressed mixture (0hr ball-milling) showed a substantial deviation from the Hugoniot of the inert mixture at 3.22 GPa (Fig. 21a). With increased duration of ball-milling, this deviation was reduced until negligible for the specimen ball-milled for 18hrs (Fig. 21b). This result may be in large part due to the reduced amount of parent Ni and Ti phases available for reaction with longer ball-milling duration. Interesting to note are

the clear distinctions between the various data, which altogether suggests that such deviations in time-resolved data might be sensitive enough to infer the extent of shock-induced chemical reactions in powder mixtures.

Fig. 21 Pressure-volume data obtained for Ni+Ti powder mixtures (a) without pretreatment and (b) following 0 to 18 hours of ball-milling (BM). The reaction product states were calculated using the Ballotechnic model, considering varying reaction enthalpies as measured for the different BM conditions. Notice that the extent of deviation from the inert curve appears to decrease with increased duration of ball-milling (adapted from Xu and Thadhani³⁹).

Building upon the recovery work of Song and Thadhani⁹⁷ and Dunbar et al.,⁸⁸ Eakins and Thadhani⁴⁰ investigated the influence of particle morphology on shock-induced chemical reactivity in the Ni+Al system. In the first mixture, micrometre-scale (-325 mesh, $<44 \mu\text{m}$) Ni and Al particles of rounded morphology were combined at an equivolumetric ratio, and statically pressed to 60% TMD. For the second mixture, the rounded Ni particles were substituted with Ni flakes (-325 mesh diameter, 350 nm

thick), and the mixture prepared to the same equivolumetric ratio, and pressed to 45% TMD. Parallel-plate impact experiments, similar to those performed by Graham et al.³⁶ and Xu and Thadhani,³⁹ were conducted utilizing time-resolved PVDF diagnostics up to 6 GPa. As shown in Fig. 22a, the shock-response of the spherical Ni+Al powder mixture matched well with the response of an inert mixture estimated from McQueen's mixture theory.⁵³ On the other hand, the flake mixture exhibited increased shock-velocities above an input stress of 3.5 GPa (Fig. 22b).

Fig. 22 Shock velocity versus input stress for the (a) 60% TMD spherical Ni+Al and (b) 45% TMD flake Ni + spherical Al powder mixtures. While the spherical mixture remained inert up to 6 GPa, the flake mixture exhibited a deviation from inert behaviour above 3.5 GPa, suggesting the occurrence of shock-induced chemical reaction (from Eakins and Thadhani⁴⁰).

In the parallel-plate impact experiments performed by Graham et al.,^{36, 106} Thadhani et al.,³⁸ Vandersall and Thadhani,¹⁰³ Xu and Thadhani,³⁹ and Eakins and Thadhani,^{40, 66} there was a strong desire to avoid 2-dimensional radial-focusing effects in order to promote a 1-dimensional shock event. To accomplish this, very large aspect ratios (e.g., diameter to thickness ratio of 20:1 for a ~2.5 mm thick powder layer) were employed.⁴⁰ While more than sufficient to record increases in shock velocity associated with ultra-fast chemical reactions, this experimental setup (with only a single pair of PVDF gauges) did not allow for tracking the propagation behaviour of the reaction front. Such behaviour is required to distinguish between deflagration- and detonation-type reactions, and may be more noticeable in thicker powder layers.

To address the possibility that shock-induced reactions might propagate with detonation-like character, Gur'ev et al.¹⁰⁷ performed a series of shock velocity measurements through Zn+S powder

compacts of varying thickness. The mixtures were comprised of Zn and S powders 3-5 μm in size, mixed at a 1:1 atomic ratio, and statically pressed within a low sound-speed cylinder (I.D. = 16.5 mm) to 60-70% TMD. Shock-loading was delivered by an explosive charge, and the shock velocity through the specimen determined from arrival gauges located at both ends of the cylinder. The height of the cylinder (and thus the thickness of the powder) was varied from 40-200 mm between experiments, the lower limit chosen such that the shock wave in an inert Zn+S mixture would fully attenuate before reaching the transmitted gauge. Data from these experiments is presented in Table 2, where L is the sample thickness (propagation distance), U_s is the reaction front velocity with associated error δ , and ρ_{00} is the initial mixture density. In each experiment the transmitted gauge was triggered, which suggests that the energy released due to ultra-fast chemical reaction serves to support and extend the range of wave propagation, and thereby delay attenuation.

To more clearly describe the shock propagation behaviour in this set of experiments, the data in Table 2 is plotted in Fig. 23. From the combined density/shock velocity plot, it is reasonable to suggest that the large swings in shock velocity for $L = 40$ -75 mm are due to the varying sample densities. However, in the $L = 75$ -100 mm range an apparent jump in U_s is observed (1.39 to 2.55 $\text{mm } \mu\text{s}^{-1}$), with only minor difference in density (60.7 to 62.4 % TMD). Beyond $L = 150$ mm, any increase in shock velocity is less obvious, and may even indicate a steady state. These results seem to indicate a transition between an unsteady to steady solid-state detonation-like behaviour developed in the range of $L = 75$ -150 in Zn+S powder mixtures subjected to explosive shock loading.

Table 2 Reaction-front propagation results in a mixture of Zn+S.¹⁰⁷

L (mm)	U_s (mm μs^{-1})	δ (%)	ρ_{00} (% TMD)
40	2.27	0.6	68.1
60	1.3	0.2	63.0
75	1.64	0.2	71.6
90	1.39	0.2	60.7
100	2.55	0.2	62.4
150	2.195	0.1	63.5
150	1.915	0.1	62.4
200	2.169	0.1	59.4

Fig. 23 Experimentally measured shock velocities in Zn+S powder compacts of varying thickness. The initial decrease and subsequent increase in shock velocity suggests a transition to solid-state detonation in the realm of 75-100 mm. Also shown are the sample-to-sample variations in packing density, which appear to correlate with the scatter in data.

6. Thermodynamic Models for Shock-Induced Reactions

Despite uncertainties concerning the manner in which shock-induced reactions affect the high-pressure state, several analytical models have been proposed to predict the equilibrium shocked state of a reacted powder mixture, to further support the measured states as indicators of reaction. One of the first models accompanied the observation by Batsanov et al.³⁵ of shock-induced reaction in the Sn+S system. As discussed previously, the heat of reaction released due to the formation of a given product phase was assumed to manifest as a constant-volume increase in pressure (Equation 8). By assuming the product to be SnS , and from the measured shift in Hugoniot data, Batsanov et al.³⁵ estimated the degree of product formation to be ~27%. A similar analysis was performed later by Yu and Meyers,⁸⁷ as described in Fig. 14, albeit, based on results of shock recovery experiments performed on Nb+Si powder mixtures.

Based on their results in the 5Ti+3Si system, Graham et al.³⁶ suggested that phase transformations occurring within 100 ns of the shock front can be responsible for a constant-pressure deviation from the reference Hugoniot, in direct contrast to the constant-volume assumptions claimed prior.^{35, 87, 97} He proposed the change in volume from reactants to products to take the form,

$$\Delta V = (V_{00} - V) + \frac{\beta Q}{C_p} \quad (11)$$

where, V_{00} is the specific volume of the starting powder mixture, β is the coefficient of thermal expansion at pressure and temperature, Q is the heat influencing the wave propagation, and C_p is the specific heat at pressure and temperature. With increased shock pressure the deviation from inert behaviour is amplified. Graham et al.³⁶ described the locus of possible reaction product states as the “Ballotechnic” curve, shown in the schematic in Fig. 24. A physical explanation for the shape of the Ballotechnic curve lies in the nature of shocked powders and their mixtures.

Fig. 24 An illustration of the Ballotechnic curve defining the locus of reacted states leading to the reaction product Hugoniot. By comparing Rayleigh lines joining the starting and shocked states, it becomes clear that the formation of the reaction product during the time-scale of pressure equilibration results in an increased shock velocity. Also shown are shock front rise-times that might be observed at an input and propagated stress gauge as a function of pressure. Reaction will be limited when the front rise-time drops below the critical value for reaction, t^* , due to dispersive effects through the powder mixture.

When a shock wave propagates through a powder mixture, a portion of the shock energy is deposited into the densification process. Thus, as the wave propagates the front becomes dispersed, resulting in a decrease in loading rate.¹⁰⁸ Therefore, while the proper conditions for reaction may be realised early on, broadening of the shock front profile prevents the critical environment from being produced further in the specimen. Consequently, the heat of reaction influencing wave propagation, Q , will be related to the fraction of material undergoing reaction, and is reflected in the measured shock velocity. Hence, there is a range of pressures within which reaction is incomplete; the lower- and upper-bound of this range are

defined when the input and output profile, respectively, possess the critical rise-time for reaction (Fig. 24). Furthermore, at pressures between these hypothetical initiation and completion pressures, the reaction front propagates at a velocity that is an intermediate value, evidenced by the range of influenced shock velocity. Increased shock velocities in powders undergoing reaction can be explained by comparing Rayleigh lines joining the starting state to positions on the inert and Ballotechnic curves.

Continuing the work by Graham et al.,³⁶ Bennett and Horie¹⁰⁹ compared the methods of calculating the reaction product Hugoniot based upon the constant volume and constant pressure adjustment schemes. In both methods the dense product Hugoniot, referring to the compressibility curve of the compound, was used as the reference from which adjustments corresponding to the effects of deformation energy and heat of reaction were made. For the constant volume approach it was assumed that the reaction resulted in an increase in pressure, likened to the detonation response of explosives. Equations for energy conservation were written for the reference and hypothetical reaction product curves,

$$E_{RP} - E_{00} = \frac{1}{2}(P_{RP} + P_{00})(V_{00} - V_{RP}) \quad (12)$$

$$E_H - E_0^* = \frac{1}{2}(P_H)(V_0^* - V_H) \quad (13)$$

where, the subscripts *H* and *RP* correspond to the dense product Hugoniot and reaction product, respectively. Using the Mie-Grüneisen equation under the assumptions $V_H^* = V_{RP}$, $E_{00} = E_0$, and $P_0 = 0$, the following equation for the reaction product Hugoniot was derived,

$$P_{RP} = \frac{(E_0^* - E_0) + P_H^* \left[\frac{1}{2}(V_0^* - V_{RP}) - \left(\frac{V}{\gamma} \right)^* \right]}{\frac{1}{2}(V_{00} - V_{RP}) - \left(\frac{V}{\gamma} \right)^*} \quad (14)$$

For the constant pressure adjustment, Bennett and Horie derived an expression to replace the Mie-Grüneisen constant volume relation,

$$E_{RP} - E_S^* = (V_{RP} - V_S^*) \left[\left(\frac{V}{\gamma} \right)^* \left(\frac{\beta_S}{V_S} \right)^* - P_S^* \right] \quad (15)$$

where, β_s is the isentropic bulk modulus. Following the same procedure as before where instead of constant volume, the condition $P_S^* = P_{RP}$ is assumed,

$$V_{RP} = \frac{V_S^* \left[\left(\frac{V}{\gamma} \right)^* \left(\frac{\beta_S}{V_S} \right)^* - P_S^* \right] + \frac{1}{2} P_S^* V_{00} + \int_{V_0^*}^{V_S^*} P_S^* dV_S^* - (E_0^* - E_0)}{\left(\frac{V}{\gamma} \right)^* \left(\frac{\beta_S}{V_S} \right)^* - \frac{1}{2} P_S^*} \quad (16)$$

This relationship allows calculation of the reaction product Hugoniot through a constant pressure scheme referenced from the dense product isentropic compression curve. It has been argued that the constant pressure adjustment is more appropriate for intermetallic forming systems, since the degree of gas evolution is generally negligible.

The constant pressure model for Ballotechnic reactions has been employed in the recent study of shock-induced reactions in Ni+Ti powder mixtures by Xu and Thadhani.³⁹ Reaction product Hugoniot curves for the *NiTi* compound were calculated using the Ballotechnic model and the ambient pressure heats of reaction determined for each powder by DTA. The measured shock states were in good agreement with the calculated curves as illustrated in Fig. 21.

It should be reminded, however, that the interpretation of deviant Hugoniot data on the basis of a single product phase (most often aligned with the starting mixture composition) ignores heterogeneous mixing and nucleation mechanisms. The consideration of multiple possible phases and reaction extent greatly complicates such a thermodynamic analysis. This possibility was explored by Eakins and Thadhani⁴⁰ for the flake Ni + spherical Al system. Rather than assuming a fixed product stoichiometry, the possible formation of any mixture of the *NiAl*, *NiAl*₃, and *Ni*₃*Al* product phases was considered. Using the positions of the deviant data, inert reference, and limits for complete reaction calculated using the Ballotechnic model, a ternary reaction-composition diagram was constructed (Fig. 25), where each surface describes the possible phase make-up of a given deviant Hugoniot measurement. By assuming that the series of deviant data represented varying degrees of the same process, it was concluded that the product mixture be predominantly composed of the equiatomic *NiAl* phase. Additionally, the lack of intersection between the starting mixture composition (dotted) and the reaction-composition surface at 5.5 GPa suggests that not all material behind the shock-front was converted to product, and that reaction proceeded through heterogeneous mechanisms.

Fig. 25 (a) Ternary composition diagram derived from the displaced Hugoniot data shown in Fig. 22, assuming complete reaction. Also shown is the composition of the starting mixture (dotted). Solving across the complete range of reaction extent yields a reaction-composition diagram (b), which reveals the relative stoichiometry of the phases that may be formed due to shock-induced chemical reaction.

7. Proposed Shock-Induced Reaction Mechanisms

Through the investigation of shock-induced reactions, several models and concepts concerning the critical processes responsible for reaction initiation have been proposed.

A general conceptual scheme for the shock-induced reaction event has been described by Graham.¹⁰⁶ Shown in Fig. 26 are several stages in the overall shock-compression event. Material in the undisturbed, initial configuration is brought to the high-pressure, compressed configuration through a transition zone. The events in the transition zone are comprised of **C**ONfiguration change, **M**ixing, shock **A**ctivation, and **H**eating, and are collectively responsible for the initiation of chemical reactions. *Configuration change* refers to modifications in the size, morphology, and distribution of phases; *mixing* characterises the evolution of boundaries between reactant species; *shock activation* describes the enhanced interatomic mobility due to increased defect concentration and cleansing of surfaces; and *heating* corresponds to the thermal environment caused by bulk heating, energy localization near collapsed voids or defects, and transport across the thermal landscape.

Fig. 26 Fundamental framework for shock-induced reactions proposed by Graham.¹⁰⁶ The schematic illustrates the transport of material from an initial configuration to a final, compressed configuration. The transition zone is the time interval over which the effects of configuration change, mixing, shock activation, and heating are experienced. Little is known about the specific processes occurring within the transition zone.

CONMAH outlines the important processes that must occur during the transition zone, but does not specify the mechanisms of mixing responsible for the ultra-fast reactions similar to those observed in, e.g., Sn+S, Ti+Si, and Ni+Ti systems. It ascribes importance to the intermixing and activation of reactants, but is not intended to qualitatively or quantitatively describe how these events occur. Several other investigators have proposed mechanisms for mixing and reaction initiation. Dremin and Breusov²⁸ conceptualised a model to explain the synthesis of new phases during shock-compression. Fig. 27 is an illustration of the *ROLLER* model, which describes the formation of a compound A_xB_y at a sliding interface between A and B crystals. It is suggested that the relative movement of the component surfaces produces a nucleus, which “rolls” between the surfaces, and about which adjacent atoms may attach to form a new phase. Thus, formation and growth of the new phase is not governed by diffusion, but rather by mechanical transport of material to the numerous nuclei at particle interfaces.

Fig. 27 Illustration of the *ROLLER* model proposed by Dremin and Bruesov,²⁸ extended to a binary system, to explain the mechanism of ultra-fast reaction initiation under shock-loading. The sliding interface between A and B crystals produces a small *AB* nucleus, which accumulates material in the formation of a new phase.

Another mechanical explanation for mass mixing and reaction initiation was offered by Batsanov et al.³⁵ following their work on Sn+S, in which they observe that the intrinsic properties of tin and sulphur (density, moduli) result in differing particle velocities at pressure. Within the range of 10 to 40 GPa, the difference, ΔU_p , is in the range of 0.7-2.0 kms^{-1} . The differing relative high-velocity motions between particles results in the forced travel of one component into another. Iyer³⁷ expanded this mixing mechanism by attributing relative particle velocities to the development of interparticle shear. Yano and Horie¹¹⁰ performed a discrete element numerical simulation (DM2) to calculate particle velocity differences of 20-100 ms^{-1} in the Ni+Al system.

Nesterenko et al.⁸⁴ have also provided clues to the type of mixing that may be promoted during the shock-compression of reactive powder mixtures. A cylindrical converging shock was used to produce shear localization in reactive powder mixtures. Recovered specimens exhibited distinct shear bands (Fig. 28), within which evidence of particle comminution, vortex formation, and chemical reaction was observed. The vortexes were deemed responsible for increased temperatures and mass transfer, and were believed to form as a consequence of the variations in flow stress due to inherent mixture heterogeneity. Tamura and Horie¹¹¹ investigated the mechanism of mixing within shear bands through DM2 simulations, and demonstrated the influence of void content and component mechanical response on the effectiveness of mixing.

Fig. 28 Evidence of vortex flow in shear bands produced through thick-walled cylindrical implosion experiments performed on Nb+Si powder mixtures. The vortices are regions of increased temperature and mass transfer, originating from instabilities in flow stress (from Nesterenko et al.⁸⁴).

Each of these models seeks to explain the micromechanical conditions necessary for shock-induced reaction initiation. Batsanov's³⁵ particle velocity dispersion (PVD) model is based entirely upon the differences in intrinsic properties of reactants. No consideration is made of the *configuration* of reactants, such as the morphology and arrangement of particles, voids, or contacts. The experiments by Nesterenko et al.⁸⁴ were designed to probe the micromechanical details of particle fracture, vortex formation, and thermally-induced reaction in deliberately created zones of intense shear. They do not, however, explain reaction under mechanochemical mechanisms and under the initial consolidation event, during which intense shear at interparticle regions is a direct consequence as particles of dissimilar characteristics come together in the process of void collapse. Dremin and Breusov's²⁸ *ROLLER* model, in fact, also explores reaction through a mechanism grounded firmly in a particular, however general, configuration of reactants (sliding interface). The influence of intrinsic properties of the reactants is not incorporated.

In reality, the initiation and propagation of shock-induced reactions is intimately linked to both the intrinsic and extrinsic properties of the powder mixture. Indiscriminate shear at a phase boundary, or

arbitrary selection of components based upon relative impedances, is hardly enough to guarantee reaction. Furthermore, reactions proceeding through dissolution and growth rely on melting at extended time-scales. A study has yet to be completed that seeks to explain shock-induced reaction initiation mechanisms on the basis of both intrinsic properties and extrinsic powder configuration in a real, non-idealised system.

8. Computational and Meso-scale Modelling of Dynamic-Compression/Shock-Induced Chemical Reactions

Due to the immense restrictions on real-time diagnostics imposed by the ultra-short lifetime of the shock event, there is a limit to the type and amount of information that can be gathered experimentally. As illustrated in the preceding section, the information available has provided only indirect inference of shock initiation of chemical reactions, with no spectroscopic type information of the type of reaction product and its extent. Many of the questions that have been posed or conceptually described concerning shock-induced reactions have, therefore, been tackled through computational approaches.

One of the first computational studies of shock-induced reactions was accomplished by Horie and Kipp.¹¹² An illustration of their model is shown in Fig. 29, which conceptually describes the conversion of powder reactants (A,B) to products in a generalised system. It is assumed that the reaction pathway includes a transition phase before arriving at the equilibrium end-state product, i.e., for a 1:1 stoichiometry mixture,

where, r , m , and p are the molar amounts per unit volume of the reactants, transition phase, and products, respectively. Rate equations of an Arrhenius form are prescribed to govern the conversion, and the heat generated from reaction is included in the conservation of energy,

$$\rho \frac{dE}{dt} = - (P + q) \frac{\partial u}{\partial x} + \dot{Q} \quad (18)$$

where, E is the internal energy, ρ is mass density, u is the Lagrangian particle velocity, P is the pressure, q is the artificial viscosity, and $\dot{Q}$ is the rate of heat generated from reaction, given by,

$$\dot{Q} = \Delta H \frac{dp}{dt} \quad (19)$$

where, ΔH is the reaction enthalpy. Using the one-dimensional finite-difference wave propagation code WONDY-V, the influence of chemical reactions on pressure and temperature profiles in a 3Ni+Al system were investigated.¹¹³ Based upon prior work on SHS reactions in the Ni/Al system, and

considerations of typical liquid activation energies, energy barriers of 62.8 and 16.7 kJmol⁻¹ were considered, respectively. Results for a 3 cm thick specimen impacting a rigid boundary at 1.5 kms⁻¹ revealed a strong correlation between the activation energy, transformation timescale, and increases in pressure and temperature. Lowering the threshold for reaction resulted in increased reaction rates, and more pronounced changes in the shock profile (Fig. 30). For high activation energy, the shock pulse has constant amplitude. On the other hand, an increase in pressure of ~5 GPa is observed for the lower (16.7 kJmol⁻¹) case at 9 μs. Similarly, the shock temperature (bottom) reflects these differences.

Fig. 29 Illustration of the transition from reactants (A, B) to products generalised from Horie and Kipp's model for shock-induced chemical reactions. As a shock wave propagates from left to right, the void separating reactants is eliminated and mixing is accomplished. After a threshold energy barrier is exceeded, reaction takes place, forming initially a transition phase, which after time forms the final end-state product (adapted from Horie and Kipp¹¹²).

The authors conclude that for sufficiently quick reactions (those with low activation energy), changes in the structure or character of the shock wave can be used as signatures of reaction. It should be pointed out, however, that the increases in shock amplitude result from an assumed form of the P - α equation-of-state, which ensures that all contributions to internal energy from chemical reaction will directly influence the pressure,

$$P = f(V_s, E) \propto \Gamma \rho_s E \quad (20)$$

No experimental evidence has yet to be supplied that would imply that such inorganic, gasless reactions do indeed produce an increase in pressure of 4-5 GPa. On the other hand, substantial changes to the shock profile are predicted for very long timescales (5-9 μs), which is many times the shock-event and diagnostic lifetimes of most time-resolved experiments. For example, the powder thickness for many

experiments is kept to several mm (and diameter being an order of magnitude larger) to avoid 2-dimensional effects, resulting in shock-event lifetimes (before reflection) of approximately 1-3 μs for PVDF and optical pyrometry measurements.^{40, 76} In any event, this early model does not appear to reproduce appreciable changes in the shock state at very short timescales (or through thin powder layers), as shown in the experimental work on Ni+Ti, Ti+Si, and Ni+Al.³⁸⁻⁴⁰

Fig. 30 Spatial profiles of stress, transition phase concentration (m/r), and temperature at 2, 5, and 9 μs following shock compression at 1.5 km s^{-1} , with an activation energy of (a) 15, and (b) 4 kcal mol^{-1} . For the lower (16.7 kJ mol^{-1}) activation energy, the stress and temperature profiles show a significant increase in amplitude due to chemical reaction after 9 μs (from Horie and Kipp¹¹²).

The likelihood of particle-velocity-dispersion (PVD) being the driving mechanism of component mixing and reaction was investigated numerically by Yano and Horie.¹¹⁰ Using the discrete element method (DEM), binary mixtures of Ni+Al and Ti+PTFE were randomly assembled according to mass fractions, $X_m = 0.3, 0.6$, and 0.9 of the heavier component (Ni, Ti), and an element size of $1\ \mu\text{m}$. Shock compression was simulated at particle velocities of $U_p = 150, 300, 450$, and $600\ \text{ms}^{-1}$, and the resulting particle velocity for each component determined through averaging within a $4\ \mu\text{m}$ window. The PVD was then calculated by considering the difference between these two measures. For both mixtures, the maximum PVD was observed within the shock front, shown in Fig. 31. The following expression was used to define s , the spatial scale of mixing:

$$s = \frac{36\gamma}{\rho(\Delta u_p)^2} \lambda_s \quad (21)$$

where, $\gamma = 1\ \text{Jm}^{-2}$ is a representative surface energy for metals, ρ is the mixture density, Δu_p is the measure of PVD, and λ_s is the fraction transformed. They were able to calculate the scale of mixing s of approximately $60\ \text{nm}$ for the Ni+Al system. Based upon this result, they conclude that PVD is a plausible mechanism for shock-induced reaction initiation.

Fig. 31 Spatial profiles of particle velocity taken $15.4\ \text{ns}$ after impact ($U_p = 0.6\ \text{ms}^{-1}$) for mixtures ($X_m = 0.3$) of (a) Ni+Al and (b) Ti+PTFE. The maximum difference in particle velocity occurs within the shock front (from Yano and Horie¹¹⁰).

Unfortunately, these simulations and their elegant analysis do not directly relate to the experiments they are based from. The model treats each binary system as a fully-dense mixture, and does not

consider the influence of porosity. Furthermore, the random arrangement of each component constructs element assemblages whose size depends upon the mass fraction. As a result, the spatial character and magnitude of PVD in granular mixtures, and the resulting mixing dimension, may be quite different from those reported.

In another study, Tamura and Horie¹¹¹ also applied the discrete-element method (DM2) to investigate interparticle mixing through shear band formation in the Nb+Si and Ni+Al systems, as observed in the experimental work by Nesterenko et al.⁸⁴ on Nb/Mo+Si mixtures. The creation of a shear band was simulated by considering an interface between two materials (e.g., Nb and Si) and prescribing a velocity boundary condition at the upper and lower domain edges, as shown in Fig. 32a. Through the thickness (between the boundaries), the particle velocity was varied linearly. The authors investigated the influence of internal void content, strain-rate, relative yield strength, and melting on the degree of mixing and chemical reaction within a shear-band. The result was an excellent parametric study providing great insight concerning the processes that govern mass mixing. For example, by systematically adjusting the flow stress of Si in the Nb+Si system, Tamura and Horie were able to show that there was an optimum strength ratio between components that resulted in the most effective mixing. Additionally, both the width of the shear-band and the overall extent of mixing increased with shear strain-rate, as shown by comparing Fig. 32(b,c). However, melting also occurred more rapidly at high strain-rates resulting in a loss of strength, increased strength ratio, and therefore a negative effect on mass mixing, which consequently hindered chemical reaction.

Fig. 32 DM2 model configuration (a) for the initial case, showing a simple interface between two particles of differing materials, and shear loading prescribed by upper and lower velocity boundaries, (b) following straining to shear strain of 16 at a strain-rate of $1.6 \times 10^8 \text{ s}^{-1}$, and (c) following straining to a shear strain of 16 at a strain-rate of $8.0 \times 10^7 \text{ s}^{-1}$. The unfilled regions in the starting and final configuration represent voids. Notice that the configuration in (b) shows a larger shear-band width and degree of mixing than in (c) (adapted from Tamura and Horie¹¹¹).

In considering chemical reactions, the threshold for initiation was set to the melt temperature of the lower melting point component (Si in Nb+Si mixtures, Al in Ni+Al mixtures), and heat released due to reaction was deposited in the mixture through Arrhenius kinetics. The onset of Si melting at the higher strain-rates in the Nb+Si mixture was shown to deleteriously affect the degree of reaction through poor mixing, as observed in the time-resolved experiments on Nb+Si and Mo+Si.^{103, 114} On the other hand, the much larger thermal conductivity in the Ni+Al mixture served to prevent melting at high strain-rates, allowing the solid constituents to participate in further mixing and chemical reaction (Fig. 33).

Fig. 33 Measure of the extent of reaction as a function of shear strain and strain-rate in the (a) Nb+Si and (b) Ni+Al systems. Reaction in the Nb+Si system at the higher strain-rate is arrested following melting of Si (from Tamura and Horie¹¹¹).

Throughout the experimental literature, there is no single accepted indicator or signature of shock-induced chemical reactions. As discussed above, measures of expanded states, excess pressure, energy thresholds, and increased shock-velocities have all been used to argue the occurrence of ultra-fast chemical reactions.^{33, 35-37, 40, 98, 107} The influence of these reactions on high-pressure state variables such as pressure, temperature, and particle/shock velocities were investigated numerically by Do and Benson^{115, 116} using the multi-material Eulerian hydrocode *Raven*. The shock-compression of a Nb+Si powder mixture was simulated in 2-dimensions. Simulated circular particles ranging in diameter from 30-50 μm were randomly distributed within a 500 x 1000 μm space (180 x 90 elements, ~ 5.6 μm /element edge), and packed to 60% TMD using a “pseudo-gravity” method.¹¹⁷ Both components were modelled with a Mie-Grüneisen equation-of-state; the Steinberg-Guinan and Johnson-Cook strength models were used for Nb and Si, respectively. The shock was delivered through a Nb plate moving at a constant velocity from the left boundary, while symmetric boundaries were prescribed at the top and bottom edges. For the given Nb+Si system, reaction was assumed to form the disilicide, NbSi_2 . The reaction rate of the k -th reaction for the i -th species was given by,

$$r_k = \left\{ k_{fk} \prod_{i=1}^I [x_i]^{v'_{ik}} \right\} - \left\{ k_{bk} \prod_{i=1}^I [x_i]^{v''_{ik}} \right\} \quad (22)$$

where, I is the number of components in the system, $[x_i]$ is the molar concentration of the i -th species, v'_{ik} and v''_{ik} are the stoichiometric coefficients for the forward (fk) and backward (bk) reactions, and the reaction rate coefficients k_{fk} and k_{bk} are defined as,

$$k_{f_k} = A_{f_k} T^{\beta_{f_k}} P^{\eta_{f_k}} \exp\left\{\frac{-E_{f_k}}{RT}\right\} \quad (23)$$

$$k_{b_k} = A_{b_k} T^{\beta_{b_k}} P^{\eta_{b_k}} \exp\left\{\frac{-E_{b_k}}{RT}\right\} \quad (24)$$

where, the coefficient A is the frequency, E is the activation energy, R is the gas constant, and T is the reacting temperature. Values of A and E were set to 10^{17} and 72 kJmol^{-1} based upon the requirement that reaction is completed within a single travel of the shock wave. The coefficients T and P in Equations 22,23 allow for a temperature and pressure dependence of the reaction rates, but were set to unity ($\beta, \eta = 0$). In addition, the backward reaction was ignored ($k_{b_k} = 0$). Transport of the reactants through the product phase was also considered in order to avoid arresting of the reaction once all reactant interfaces were consumed. Due to the lack of experimental evidence that would suggest otherwise, no limits on the transport rate were specified, i.e., it was assumed that transport through the product layer was not a rate-limiting process for further reaction.

The evolution of reactant and product material configuration following shock-compression at $U_p = 1 \text{ kms}^{-1}$ is shown in Fig. 34. Reaction appears to be initiated almost immediately behind the shock front, leaving a mixture of $NbSi_2$ and residual Nb. Fig. 35 shows the particle velocity in the x-direction averaged through the model height for both the inert and reacted case. In the reacted mixture, a nearly two-fold increase in particle velocity was observed within a zone approximately $100 \mu\text{m}$ in thickness behind the shock-front. Also obvious is an apparent increase in the shock velocity, evident when comparing the half-max positions at $t = 0.3 \mu\text{s}$. The U_s - U_p relationship determined through a range of initial particle-velocities is shown in Fig. 36, which shows a deviation from inert behaviour above $U_p = 0.5 \text{ kms}^{-1}$. The authors also examined the temperature, pressure, and micro-kinetic energy profiles at these same time intervals, noticing that each showed a marked increase near the shock-front. Such observations agree with the work of Boslough,⁷⁶ Iyer et al.,³⁷ Benson et al.¹¹⁸ and Nesterenko.¹¹⁹ Based upon the irregularity in simulated pressure profiles and the relative precision of shock velocity measurements, the authors suggest that the latter is a more precise indicator of shock-induced reactions.

Fig. 34 Time series of reactant and product material configuration in a mixture of Nb+Si during shock-compression at $U_p = 1 \text{ km s}^{-1}$. Note that the shock and reaction fronts are hardly distinguishable from each other. The residual unreacted material behind the fronts is excess Nb, due to the non-stoichiometric starting mixture (from Do and Benson¹¹⁵).

Fig. 35 Spatial particle- x -velocity profiles averaged through the model height as a function of time for simulations (a) with no chemistry, and (b) with chemistry. Those with reaction considered exhibit a nearly two-fold increase in the particle velocity at the shock-front. Notice also the increase in shock velocity, evidenced by the half-max positions of the front at $t = 0.30 \mu\text{s}$ (adapted from Do and Benson¹¹⁶).

Fig. 36 Simulated U_s - U_p data for the inert and reacted Nb+Si mixture. The reacted mixture shows a strong deviation from the inert response. The equation-of-state for the solid $NbSi_2$ compound is also shown for comparison (from Do and Benson¹¹⁶).

This work does well to approach an upper-limit on the influence of shock-induced reaction on material response. The assumed reaction-rate activation energy and frequency, infinite transport rate, and ignored backward reaction, ensures that reaction goes to completion immediately behind the shock-front, clearly influencing the degree of mixing (micro-kinetic energy), pressure, temperature, and particle/shock velocities. The general form of this model also provides flexibility to alter the chemistry (multiple product phases) and kinetics of reaction to reflect the results of additional sets of experimental data.

Most simulations of the shock-compression of powder mixtures employ idealised representations of the simulated material microstructure. Particles are typically represented as circles/squares (or spheres/polyhedra in 3-D), and their distributions are either close-packed or pseudo-random.¹²⁰⁻¹²⁴ Real microstructures, as used in the studies of static deformation, crack propagation, and the shock studies of Benson¹²⁵ and Eakins,^{126, 127} may contain highly irregularly-shaped particles and non-uniform orientation/spatial distributions.¹²⁸⁻¹³¹ It follows that the micromechanical behaviour of powders and their extent of mixing during shock-compression may depend heavily on these irregularities.

Simulation of the shock-compression of realistic Ni+Al powder mixtures was performed by Eakins and Thadhani^{126, 127} using imported experimentally-obtained SEM micrographs. Micrometre-scale mixtures of varying density (45 – 80% TMD) and particle morphology (spherical, flake) were imported into the *CTH* hydrocode as 1620 x 260 μm 2-dimensional fields. The responses of both Ni and Al were governed by a Mie-Grüneisen equation-of-state and Steinberg-Guinan constitutive strength model. Shock-compression was simulated by the movement of a Cu piston at several constant velocities ($U_p = 0.5, 0.75, \text{ and } 1 \text{ kms}^{-1}$), and the features of void-collapse, particle deformation, and mixing were noted.

Results showed that the simulations did well to match the experimental U_s - U_p data within the range of inert behaviour, and that such measures of macroscopic material response, while strongly influenced by mixture density, are quite insensitive to variations in particle morphology, orientation distribution, or constituent yield-strength difference. The construction of pressure surfaces and profiles for the 45% TMD spherical- and flake-shaped Ni + spherical Al mixtures, shown in Fig. 37, revealed the role of large, consolidated void space in the mechanical stability and structure of shock fronts through granular materials. The delayed collapse of particle-sized voids in the spherical mixture introduced release pockets within the rise to peak pressure, effectively dispersing the shock front ($\sim 74 \text{ ns}$ rise-time). On the other hand, the homogeneously distributed void space in the flake mixture ensured a highly planar, sharp rise ($\sim 15 \text{ ns}$ rise-time), leading to a stable high-pressure state. As shown in the work by Yang et al.,¹⁰⁵

shock-induced chemical reactions are critically dependent upon the front width, and do not occur if the shock front is too dispersed. The findings of these simulations are thus in agreement with the corresponding experimental work, which revealed shock-induced reaction in only the flake Ni containing mixture, evidenced by increases in the measured shock velocity and generation of expanded pressure-volume states.⁴⁰

Fig. 37 Simulated spatial pressure surfaces and temporal pressure profiles for a 45% TMD (a) spherical Ni + Al and (b) flake Ni + spherical Al mixtures (adapted from Eakins and Thadhani¹²⁷).

Scatter plots of pressure, strain, and “nearest reactive-neighbour distance” (NRND) were constructed to indicate the change in mixture configuration. As shown in Fig. 38, the minimum distance separating reactive partners, or NRND, is equivalent for Al and Ni in the spherical mixture (Fig. 38a), but is greatly reduced for Al in the flake mixture (Fig. 38b). Such change in NRND was shown to be due to a particular deformation event known as “flattening”, shown in Fig. 39. Flattening of Al particles served to rapidly increase the amount of intimate Ni/Al interface, and was attributed to the increased propensity of shock-induced reaction in the flake mixture. Though the equiaxed mixtures also underwent severe modes of deformation, such as focused flow and vortex formation, such events were highly localised and concentrated within the softer aluminum phase. While these conditions could very well have led to

short-range reactions, lack of widespread deformation and intermixing between the two phases prevented shock-induced reaction at the bulk scale.

The details of shock-wave propagation, particle deformation, and mass mixing uncovered in this work for the Ni+Al system were used to expound Graham's¹⁰⁶ CONMAH scheme, which again, attributes the initiation of shock-induced reactions to the processes of **CON**figuration change, **M**ixing, shock **A**ctivation, and **H**eating. As discussed previously, the acronym CONMAH is a general statement concerning the critical processes for reaction, and does not describe the mechanisms of mixing and mass transport particular to each system. The work on two distinct configurations of Ni+Al powder mixtures reveals that the transition zone is greatly affected by mixture configuration, leading to unique shock-wave structures, deformation modes, and mixing extent (Fig. 40). This suggests that there exists for every reactive powder mixture, a transition zone of critical character for shock-induced reaction, which is not only a function of the differences in the intrinsic properties of the reactants, but can be produced (or controlled) through manipulation of starting powder configuration.

Fig. 38 Nearest reactive-neighbour distance (NRND), pressure, and strain scatter plots obtained 100 ns after shock-compression within a $\sim 200 \mu\text{m}$ window for each component in 45% TMD mixtures of (a) spherical Ni + Al and (b) flake Ni + spherical Al. The change in Ni particle morphology greatly reduces the scatter in pressure, and the minimum distance separating Ni and Al (NRND) (from Eakins and Thadhani¹²⁷).

Fig. 39 Time sequence showing the flattening of aluminum particles in the 45% TMD flake Ni + spherical Al mixture. Total time is 45 ns, corresponding to a local particle strain-rate of $5 \times 10^9 \text{ s}^{-1}$ (from Eakins and Thadhani¹²⁷).

Fig. 40 Schematic illustrating Graham's¹⁰⁶ conceptual CONMAH model, which generalises the processes responsible for shock-induced chemical reactions. This model has been updated for the Ni+Al system with details of the transition zone obtained from numerical simulation (from Eakins and Thadhani¹²⁷).

9. Design and Control of Shock-Induced Reactions

The observations of the effects of intrinsic and extrinsic properties on reactive powder mixtures from the meso-scale computational investigations and experiments involving time-resolved measurements can be used to develop guidelines or criteria for promoting reaction in various intermetallic-forming systems. Such guidelines would be useful for the deliberate design of material systems based on desired mechanical, chemical, and energetic behaviour. The following section describes a proposed design schema, which maps the criteria for shock-induced reactions in binary intermetallic-forming systems. As mentioned previously, mixing and reaction in the micrometre-scale, spherical Ni+Al mixture is

suppressed due to the limited deformation of the harder, denser nickel phase.^{126, 127} This preferentialism is caused by the large differences in properties between the two components, such as density, sound speed, and yield strength. The results of experiments performed on the flake-Ni and equiaxed-Al mixture indicates that there is also an effect of particle morphology.⁴⁰ Qualifying these factors into a plausible schema requires consideration of work on other equiaxed mixtures, while also considering the reactivity of individual systems on the basis of the heats of reaction. As observed by Thadhani et al.,^{30, 38} systems in which the difference between intrinsic properties of reactants is small, tend to show a greater propensity (implying lower threshold stress) to react under shock-induced mechanisms, irrespective of the thermodynamic effects of the heat of reaction. Likewise, extrinsic properties can be used to facilitate reaction in otherwise difficult-to-react materials systems. Continuing this rationale, it is of particular interest to construct a diagram that graphically depicts these differences for several intermetallic-forming systems. Though the combination of properties is endless, an attempt was made to schematically represent the propensity for a system to react based upon the differences listed above, namely, the density, sound speed, and yield strength, i.e., resistance to plastic deformation. Shown in Fig. 41 is an intrinsic-extrinsic property difference space for equiaxed mixtures, where the vertical axis is a measure of the difference in mechanical impedance, which couples the effects of both density and sound speed, and the horizontal axis shows the difference in yield strength. A number of binary exothermic aluminide- and silicide-forming systems are shown, where the size of the datum is proportional to the maximum heat of formation for the given system.

Fig. 41 Schematic of an intrinsic-extrinsic difference space for several binary mixture systems of equiaxed particle morphology. The size of the data points is proportional to the maximum heat of formation for any of the system's stoichiometric compounds. Note that the data points for the W, Ta, Mo, and Nb-aluminides are indicated by closed circles due to their small size. The systems represented by centre-filled points have been reported to undergo shock-induced chemical reaction at modest pressures, while those represented by centre-crossed points remain inert. The proposed reaction zone corresponds to small differences in impedance and yield strength; systems that differ greatly in these properties are predicted to remain inert at modest pressures. Note that the Ni+Al system is well outside the reaction zone, and did not exhibit shock-induced reaction (in the spherical mixtures) up to 6 GPa.

Fig. 42 Intrinsic-extrinsic difference space for several binary systems of silicide- and aluminide-forming mixtures. Changing the particle morphology from uniformly equiaxed ($\Delta e = 0$) to a combination of equiaxed and flake-like ($\Delta e \rightarrow 1$) serves to shift the boundary separating reaction and inhibited zones from the origin. Such a mixture of spherical Al and flake-like Ni particles exhibited shock-induced chemical reaction above 3.5 GPa.

It is revealing to note that the systems reported to undergo shock-induced chemical reaction, e.g., Ni+Ti; Ti+Si; Nb+Si; and Ni+Si (shown centre-filled), are clustered near the origin, where the impedance and yield strength differences are least.^{33, 36, 38, 39, 87, 100} On the other hand, those systems that remain inert, Ni+Al; Mo+Si; Ti+Al (shown centre-crossed), are far removed from the origin, and are associated with large differences in intrinsic properties.^{85, 92, 103, 132} From the distribution of data, it appears that shock-induced reaction will be suppressed above impedance and strength differences of $\sim 175\%$ and $\sim 200\%$, respectively. Based on these limits, a reaction zone can be prescribed through the difference space, indicating where the differences in impedance and strength satisfy the proposed conditions for shock-induced reaction at modest pressures, in the regime of the crush strength of the powder mixture systems.

The intrinsic-extrinsic difference map is a useful design tool for selecting material systems based upon their ability to exhibit shock-induced chemical reactions at modest pressures. From the distribution of data, the V+Si and Zr+Si systems are both associated with large heats of reaction, and small combined differences in impedance and strength. It follows that these systems would be attractive

alternatives for energetic materials, benefiting from both high exothermicity and ease of reaction. On the other hand, the Co+Al system, which would ordinarily be attractive based upon its exothermicity, may not react as easily due to its nearly 600% difference between component yield strengths.

Thus far, the systems shown in Fig. 41 comprise the results of equiaxed, micrometre-scale particles. Accordingly, the Ni+Al system is not expected to undergo shock-induced chemical reaction at modest pressures. Work on the flake mixture however, indicates that reaction does indeed occur.⁴⁰ The question remains of how to incorporate the influence of the extrinsic properties such as particle morphology and initial density. It is suggested that a reflection of the influence of particle morphology can be captured by defining an additional measure, Δe , which is the difference in eccentricity between the particles of each component,

$$\Delta e = e_A - e_B \quad (25)$$

where, e_A and e_B are the meridional eccentricities of particles of component A and B, defined for each by,

$$e = \frac{\sqrt{a^2 - b^2}}{a} \quad (26)$$

where, a and b are necessarily the longest and shortest of the three semi-axes, respectively. For equivalently equiaxed particles, such as those in the systems represented in Fig. 41, $\Delta e = 0$. In the case of the recent results for the Ni+Al flake mixture, however, and assuming a semi-major and semi-minor axis for the Ni flakes of 12.5 μm and 0.175 μm , respectively, Δe approaches 1. It is proposed that an increase in Δe serves to shift the boundary of the reaction zone away from the origin (Fig. 42), allowing progressively greater differences in impedance and yield strength to be tolerated.

Such a shift is believed to have accompanied the change in nickel particle morphology from spherical to flake, moving the inhibited zone boundary to higher difference limits, and allowing reaction in the otherwise inert Ni+Al powder mixture system. The precise limits as a function of particle eccentricity require additional morphology-based studies on systems such as Ta+Si, Mo+Si, and Ti+Al. Similarly, the initial powder density also influences the boundary of the inhibited zone. As shown in the simulations, increases in starting density (from 45% to 80% TMD) result in decreased volume for particle deformation, mass flow, and mixing. Accordingly, increases in starting mixture density will result in a shift in the inhibited zone boundary toward the origin.

Based on these projections, one can also make predictions concerning the response of metal powder configurations not tested, e.g., a mixture of flake Ni + flake Al. Such a system is likely to enjoy a planar and stable front, due to the stacking of flakes and homogeneous distribution of particles and void space. The initiation of reaction, however, would suffer from the loss of the flattening process, as the softer

aluminum particles are pre-thinned. In the reaction criteria map, this would be reflected by the difference in eccentricity, which would be zero, similar to the mixtures of equiaxed particles. Thus, the extent of deformation for both components will be diminished, and the local shear-induced mixing processes will not occur.

All of these observations serve to illustrate the significant impact the reactant configuration can have on the mechanical and chemical behaviour of a shock-compressed powder mixture. Through seemingly subtle changes in the intrinsic properties and configuration of components (extrinsic effects), the behaviour of materials can be widely affected. It follows that control over the stability, and shape of the high-amplitude front can be gained through deliberate manipulation of the particle size, morphology, and initial density. This promises to be a particularly useful technique for intrinsic pulse-shaping. Such activities have been pursued for solid materials, in the form of density-graded flyers.¹³³ Furthermore, deliberate promotion of either shock-induced or shock-assisted mechanisms of reaction allows control over the time of reaction, from the tens of nanoseconds (10^{-8} s) time scale, to microsecond (10^{-6} s) or even millisecond (10^{-3} s) durations. This combined understanding of the influence of intrinsic and extrinsic properties, and effect of heterogeneity on front character, level of “shock-like” behaviour, and details of mixing, can ultimately be used to guide the selection of component properties in the design of new materials with predefined mechanical and chemical behaviour.

10. Summary and Concluding Remarks

Our understanding of chemical reactions in shock-compressed reactive powder mixtures has matured considerably since their discovery. Two classifications of chemical response have been recognised, according to their initiation mechanisms (and timescales), following years of shock-compression recovery and time-resolved experimental work. Reactions initiated on the microsecond to millisecond timescale due to thermally-assisted processes benefiting from the shock-activated state of the material have been termed “shock-assisted” reactions, and have been the subject of much of the recovery work. These reactions are controlled by the total internal energy increase due to the shock process, reacting only when a minimum energy threshold has been surpassed.⁹⁸ Ultra-fast chemical reactions, labelled “shock-induced” reactions, which register as increases in shock velocity (and perhaps pressure) in time-resolved traces, have instead been proven sensitive to powder configuration, which in turn is influenced by differences in intrinsic and extrinsic properties of the reactants.^{36-40, 87, 104} Time-resolved studies of the effect of particle size, particle morphology, and powder pretreatment have shown that extrinsic properties, specifically those that influence the local particle-scale mechanics of deformation, can

greatly alter the propensity of a powder mixture to undergo shock-induced chemical reaction, even in the case of systems with larger differences in intrinsic properties.^{38, 40, 66 39} Several thermodynamic models have been proposed over the years to explain the effect of ultra-fast chemical reactions on the high-pressure state, and aid in the interpretation of experimental data.^{35, 36, 97, 109} Due to the lack of appreciable gas evolution in intermetallic reactions, isobaric methods of constructing the reaction product Hugoniot have taken favor.³⁶ One such model (Ballotechnic) has been used with fair success to match experimental data in the work on Ni+Ti powder mixtures.^{39, 109} Additionally, a limited attempt has been made to apply the Ballotechnic model to infer the products formed and their extent from time-resolved data in the Ni+Al system, and has even been successful in characterizing the spatial distribution of reaction (heterogeneous).⁴⁰ Despite these developments, the micromechanical details of particle-scale deformation and mass mixing leading to shock-induced reaction are still beyond the reach of current experimental diagnostics. To fill this void, computational methods have been employed to investigate the shock-compression process at temporal and spatial scales unreachable through experiment. Discrete-element models by Yano¹¹⁰ and Tamura¹¹¹ have shown that mass mixing through particle velocity dispersion and shear bands are both plausible transport mechanisms.^{35, 84} Particle-scale continuum simulations by Do and Benson¹¹⁶ using assumed kinetics have demonstrated that ultra-fast chemical reactions can indeed cause increases in shock and particle velocities. Meso-scale simulations on imported microstructures have revealed the unique deformation modes contributing to reaction initiation in a particular morphology of Ni+Al powders.¹²⁷

Through the coupling of experimental, theoretical, and numerical work, it has become clear that the response of reactive powders to shock-compression is not easily generalised for all powder systems. There are as yet no global cut-offs or thresholds that can be applied to guarantee shock-induced reaction to a given product or extent. What has developed however, is a trend of behaviour, that when considered carefully suggests that there is an inextricable link between the propensity for a mixture to react and its intrinsic/extrinsic material properties. The more similar the starting components are in density, sound speed, and yield strength, the more effective the mixing process during crush-up to full density. Recent work has also shown that the configuration of reactants can be used to alter the threshold pressure for reaction, i.e., inhibiting reaction by changing the relative particle size in Ti+Si mixtures, or promoting reaction through changes in particle morphology in a Ni+Al mixture.^{38, 40} Continued investigation of the influence of component configuration on shock-induced reactivity is needed to further develop these trends, and establish the design methodology needed to control the timescale, extent, and exothermicity of chemical reactions in shock-loaded powder mixtures. This will require a forward path which focuses

future work aimed at addressing challenges involving: (1) multi-scale modelling incorporating molecular dynamics with particle-level simulations to clearly elucidate mechanisms of bond-breakage/formation in the highly turbulent transition zone whose states are defined by meso-level simulations accounting for effects of intrinsic and extrinsic properties of reactants; (2) innovative experimental methods in which the spatial and temporal scale of experiments and simulations is comparable, for example employing laser-generated shocks, combined with instrumentation/diagnostic techniques that provide more direct inference of the progression of reaction, such as ultra-fast XRD, Raman spectroscopy, or even electrical conductivity measurements; (3) coupling with first principles calculations for phase formation and preservation in the non-equilibrium state so as to allow the possibility of synthesizing novel phases/compounds or even providing predictions of what non-equilibrium structures can potentially be formed under extreme conditions; and (4) designing reactive systems that can potentially be employed as structural reactive materials with tuneable mechanical properties and energy release characteristics.

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