

High-pressure shock activation and mixing of nickel–aluminium powder mixtures

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The adiabatic chemical reaction behaviour of shock-compressed Ni–Al powder mixtures of varying morphology and different volumetric distributions has been investigated by microstructural and differential thermal analysis (DTA) to understand the mechanistic changes responsible for chemical reactions occurring during shock treatment. Mechanically mixed Ni–Al powders undergo exothermic chemical reactions at temperatures close to the melt-temperature of Al. In contrast, shock-treated Ni–Al powder mixtures exhibit a “pre-initiation” exothermic event, before the main exothermic reaction. Different forms (reaction start and peak temperatures) of the preinitiation exotherm are observed depending on the degree of macroscopic mixing, contact intimacy and activation, accomplished during shock compression of the powder mixtures of different morphology and volumetric distribution, all shock-treated under the same conditions. Mixtures containing equimolar volumetric distribution of powders of more irregular (flaky) morphologies undergo a significant extent of configuration change during shock-compression, resulting in the formation of an activated, intimately mixed and close-packed state. In such a state, chemical reaction is readily initiated by external thermal stimulation, such as heating during DTA. In fact, a greater degree of configuration change, activation and more intense mixing occurring during shock-compression can even lead to reaction initiation and completion in the shock duration itself.

1. Introduction

Synthesis of materials by self-sustaining combustion reaction (also called self-propagating high-temperature synthesis or SHS) [1, 2] in a powder mixture is a novel processing concept that has been used to synthesize a number of materials. The use of shock-wave loading to initiate such self-sustaining chemical reactions in powder mixtures has also been explored and is known as shock-induced reaction synthesis (SRS) [3–6]. The SRS process utilizes the simultaneous application of high pressures and moderate temperatures generated during the passage of shock waves through a powder mixture to initiate the reaction. The fundamental processes that control shock-induced chemical reactions are not understood.

Based upon an extensive study of shock-modified and shock-synthesized materials, Graham [7] has proposed a conceptual model which establishes a basic framework describing processes occurring during the passage of the stress wave through the powder mixture causing the reactions to occur. Graham's model, based on CONMAH (*configuration change, mixing, activation, and heating*), though qualitative in nature, provides for all or most of the very complex processes occurring during shock-compression of powders and mechanisms responsible for reaction

initiation. There have been several other models that have tried to oversimplify the process by not taking all the mechanisms into account. These models have tried to identify only the aspects of localized energy deposition and localized temperature increase as being responsible for causing the reactions to take place. These models may also only concern themselves with equilibrium thermodynamics, which cannot be applied to a shock wave travelling through a porous material.

Because of the exothermic nature of the shock-induced chemical reactions, the reaction product exhibits a microstructure typical of melting and rapid solidification, and not that of the high-pressure shock state. Thus, the detailed reaction mechanisms can best be understood by investigating the state of the shock-compressed material just prior to reaction initiation. Microstructural and differential thermal analysis (DTA) can then be used as important probes to compare the configuration and the reaction behaviour of shock-treated (but unreacted) powder mixtures with that of simply mechanically mixed powders.

The objective of the present work, which builds upon the earlier Ni–Al shock synthesis work of Hammett *et al.* [5] and Thadhani *et al.* [6], is to obtain experimental evidence of the mechanisms of shock-

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induced chemical reactions and correlate them with the CONMAH model [4]. Thus, two aspects were studied: (a) the microstructural configuration of the shock-compressed pre-reaction initiation state, and (b) the chemical reaction behaviour of shock-compressed material during subsequent heating in the DTA.

To accomplish this, Ni–Al powder mixtures of different morphologies and different volumetric ratios of starting material were shock-compressed under identical conditions at intensities below the threshold for reaction initiation. DTA was then performed to correlate the reaction behaviour of shock-treated but unreacted Ni–Al powder mixtures of different volumetric ratios and powder particle morphologies.

In the following section, we will provide a brief review of prior shock-induced reaction synthesis studies, followed by a description of the experimental procedure and starting material characteristics used in this work. Finally, the experimental results will be provided and the observed reaction behaviour discussed.

2. Background

Substantial work has been conducted in the area of shock-induced chemical reactions and material synthesis [3–6, 8–16]. In early work, the effort was concentrated primarily on demonstrating that shock-induced chemical reactions can lead to synthesis of compounds. Simultaneous efforts were also focused on shock modification studies, particularly in ceramics, to enhance the sinterability, reactivity or catalytic properties by inducing large concentrations of defects in the microstructures. The review articles by Graham *et al.* [10] and Graham [11] provide a description of the area of shock modification of materials, as well as a listing of many of the systems on which shock modification and chemical synthesis experimental work has been carried out. Much of the preliminary modern work in understanding the reaction mechanisms in the Ni–Al system [5, 13, 14] and zinc oxide–iron oxide system [15, 16] has been carried out by researchers at Sandia National Laboratories.

One of the most revealing studies shedding light on the mechanisms of the shock-induced chemical reactions was conducted by Hammett *et al.* [5], who investigated the effect of shock loading on combustion (SHS) type chemical reactions initiated during heating during DTA. Elemental Ni and Al powder mixtures ($\text{Ni}_{80}\text{Al}_{20}$ by weight) and composite powders (80 wt % Ni deposited on a spherical core of Al) were studied after being shock-loaded using the Sandia Momma Bear recovery system. Fig. 1 shows the resulting DTA traces. While the unshocked powder mixtures yield a single exotherm at the normal initiation temperature of 650°C , the shocked mechanical powder mixture shows two exotherms, the main exotherm at 650°C and another “pre-initiation” exotherm at approximately 550°C . On the other hand, the shocked composite powder, unlike the shocked mechanical mixture, shows only the main exotherm at 650°C . X-ray diffraction studies showed that while the main exotherm (at 650°C) corresponds to Ni_3Al

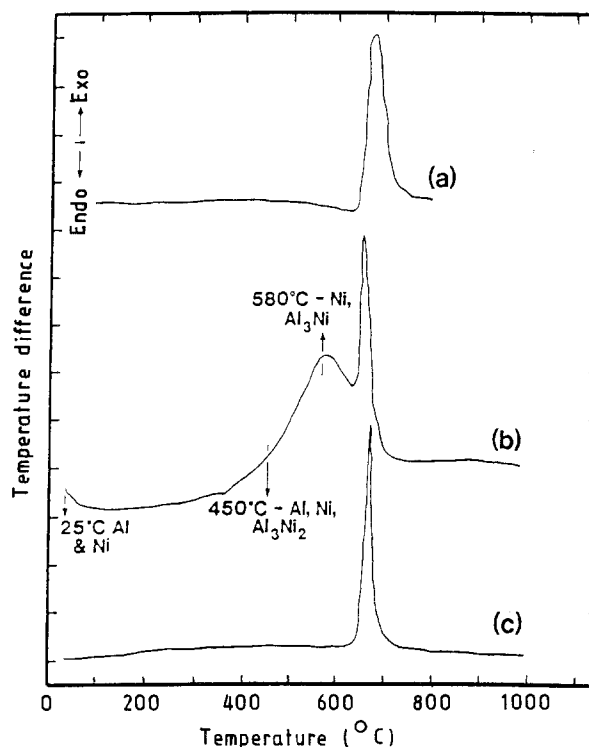


Figure 1 DTA traces showing the respective exotherms from (a) unshocked starting mixture, (b) shock-modified mechanically mixed powders and (c) shock-modified composite particles (from Hammett *et al.* [5]).

formation, the “pre-initiation” exotherm corresponds to the formation of NiAl_3 by solid-state diffusion at about 550°C .

Hammett *et al.* [5] attributed the pre-initiation event, observed in the shocked Ni + Al ($\text{Ni}_{80}\text{Al}_{20}$ by weight) mixture, to fine-scale mechanical mixing, generation of intimate contacts, and surface conditioning of the elemental powders attained during shock compression. Such a state then leads to enhanced chemical reactivity and solid-state diffusional reactions at lower than usual temperatures. The pre-initiation peak is not observed in the shocked composite powders due to the lack of similar mixing and conditioning of the elemental constituents. It was also observed that the area of the pre-initiation exotherm increases with increasing intensity of shock conditions in the mechanically blended powder mixture, while the composite powder mixture continued to yield only the main exotherm.

Microstructural analysis also showed evidence of more intense mixing occurring in the shocked mechanical powder mixtures and not in the shocked composite powders. Fig. 2 shows the micrographs and elemental dot maps of the compacts. These results (confirmed by electron microprobe analysis (EPMA)) revealed that Ni in some cases is present many tens of micrometres deep inside the Al in the case of mechanical mixtures, while mixing at such a scale is never evident in coated composite powders.

Thus, Hammett *et al.*'s [5] study revealed that shock-compression results in a complex array of characteristic events involving mechanical mixing, fracturing, and diffusion through highly defective solids. The mechanisms of mixing of Ni into the Al

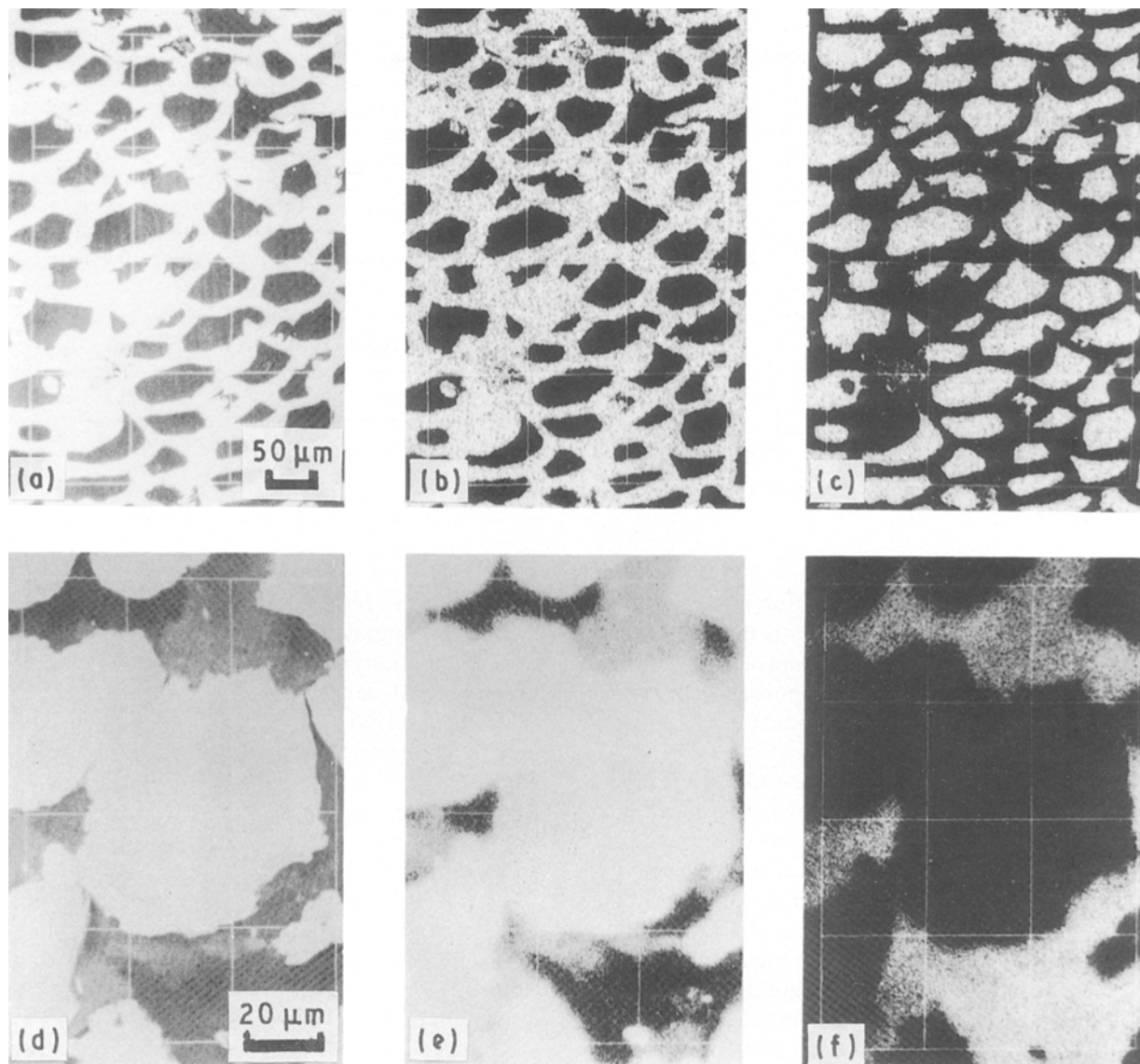


Figure 2 SEM images and elemental distribution maps of the different morphologies for shock-modified powder mixtures, showing the effect of morphology on mixing (from Hammett *et al.* [5]). Shocked Al-Ni composite: (a) SEM image, (b) Ni distribution, (c) Al distribution. Shocked Al-Ni powders: (d) SEM image, (e) Ni distribution, (f) Al distribution.

over such large distances possibly occur by the engulfing of fine Ni particles (by scuffing, fracturing, etc.) by the softer aluminium, relative mass motion forced by large acceleration forces, and large plastic deformation during void collapse at high rates of shock-loading.

The mechanistic model proposed by Graham [7] is based on the results of Hammett *et al.* [5] and other shock-synthesis and shock-modification studies in intermetallic and ceramic systems. [10, 12–16] The model concentrates on the basic issues of shock-induced chemistry [11] and suggests many different variables which have a noted effect on shock-induced chemical reaction, particularly prior to and during reaction initiation. The basic issues considered important in leading to shock-induced chemical reactions and incorporated in Graham's CONMAH model include: (a) a large degree of fluid-like plastic flow and mixing attained due to the kinetic energy of the shock wave; (b) enhancement of reactivity due to the introduction of defects, and cleansing and opening

of fresh surfaces; and (c) the thermal environment of high temperature created during shock-compression of the porous system.

The chemical reaction sequence in the CONMAH model consists of three stages, as shown in Fig. 3. The initial stage is the starting configuration which describes where the powders are located and how they relate to one another spatially. The initial configuration (affected by powder morphology, volumetric distribution of starting materials and porosity) plays a significant role because of the control on energy localization and subsequent mass mixing. The transition stage is where the pressure rises to its peak value and, depending on the shock condition, may occur over a range of times from a few to hundreds of nanoseconds. There are large gradients in particle velocity and localization of kinetic energy in this transition zone. The compressed configuration sees nominally constant pressure, particle velocity and temperature. The kinetics of reactions control the changes in conditions more than the initial shock conditions in this region.

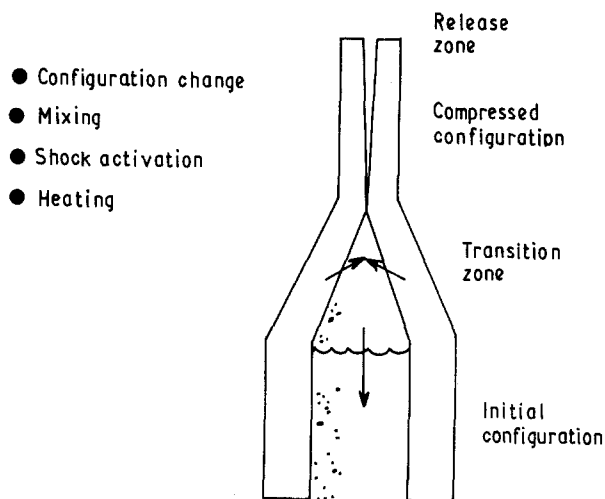


Figure 3 Schematic representing Graham's CONMAH model (from Graham [4]).

The release stage allows for reduction in pressure and temperature, and sees large gradients in particle velocity. The release, however, is from a solid, shock-modified state instead of from a porous state, which limits further mixing compared to that occurring during the initial porous state.

It should be emphasized that the CONMAH model considers the basic shock-compression issues in porous mixtures relating plastic flow, mixing and defect structure generation, to enhanced chemical reactivity. It also relates the shock-compression conditions to the configuration change in the compact prior to reaction initiation, leading to a subsequent chemical reaction. It is this shock-compressed configuration that is the subject of investigation in the present study. Thus, the approach for our overall research effort is to isolate the different aspects of the CONMAH model and systematically study their influence by varying starting powder mixture characteristics. The primary focus of this paper, however, is to simply investigate the aspect of configuration change and shock-induced mechanical mixing resulting during shock-compression and its role in enhancing reactivity of powder mixtures.

3. Experimental procedure

Mixtures of Ni and Al powders of different morphology and volumetric ratios were shock-loaded under identical conditions using the Sandia Momma Bear system [17, 18]. The characteristics of the different types of powders used are listed in Table I. Three notations were used to identify the different types of morphology. *Fine* indicates a spherical Ni powder size of 3–7 μm mixed with spherical Al powder of 10–20 μm . *Flaky* indicates a flaky-type Ni powder of size 44 μm (– 325 mesh) mixed with spherical Al of 10–20 μm . *Coarse* indicates spherical Ni powder of 45–70 μm mixed with spherical Al of 45–150 μm in size. Characteristic photomicrographs of each of these powder types are shown in Fig. 4. Powder mixtures of each of these morphology types were prepared in three different volumetric distributions of Ni and Al corres-

TABLE I. Powder mixture characteristics

Powder type	Shape	Size (μm)	Purity (%)	Source ^a
Ni (flaky)	Flaky	44	99.9	A/-13788A
Ni (fine)	Spherical	3–7	99.9	A/-10256
Ni (coarse)	Spherical	45–70	99.9	C/-N-1095
Al	Spherical	10–20	99.9	C/-A-1182
Al	Spherical	45–150	99.5	C/-A-1001

^a A/ implies Aesar powder and C/ implies Cerac powder.

TABLE II Volumetric and weight ratios of Ni–Al mixtures

Atomic composition	Weight ratio	Volume ratio
3Ni + 1Al	87:13	66:34
1Ni + 1Al	69:31	40:60
1Ni + 3Al	42:58	18:82

ponding to the Ni_3Al , NiAl and NiAl_3 atomic stoichiometry compounds. The actual volumetric and mass distributions of each of the atomic stoichiometry mixtures used in the present study are given in Table II. The 1Ni + 3Al case shows a major imbalance in volumetric distribution of the potential reactants.

The powder mixtures were packed at approximately 65% theoretical maximum density and shock-loaded in the Sandia Momma Bear A fixture (with Comp B as the explosive). The powder is contained in a copper capsule surrounded by a split square block of 4340 steel which provides containment support. The explosive is placed on a mild steel driver plate, and upon initiation of the explosive (with a plane-wave generator), a planar shock wave is transferred through the driver plate into the powder. The steel driver plate acts to shape the pressure pulse with the shock-induced 13 GPa structural phase transition. Two-dimensional numerical simulations, based on a 60% dense rutile powder compact, have been done for the fixture. The simulated maximum mean bulk temperatures and peak pressures in the compacts are 135–350 $^\circ\text{C}$ and 19–22 GPa, respectively. Rutile was used in the simulation due to its well-known shock-compression (porous) properties [19]. Furthermore, for porous materials, the crush strength and crush-up behaviour dominate the “two-dimensional” shock-loading process, and the equation-of-state properties of actual materials have minor effects (at least up to the stage of chemical reaction initiation in powder mixtures). This is particularly true because the incident shock conditions are too low (< 2 GPa) to initiate any chemical reaction. Thus, the numerically simulated shock conditions (pressure and temperature contours) obtained can be used as an accurate representation for most porous materials (including Ni–Al) encapsulated in a solid-density heavy containment.

DTA experiments were performed by sectioning sample regions into approximately 50 mg samples and heating them to 800 $^\circ\text{C}$ in a DuPont 9900 DTA under a 5% H_2 + Ar atmosphere at a heating rate of 10 $^\circ\text{C min}^{-1}$.

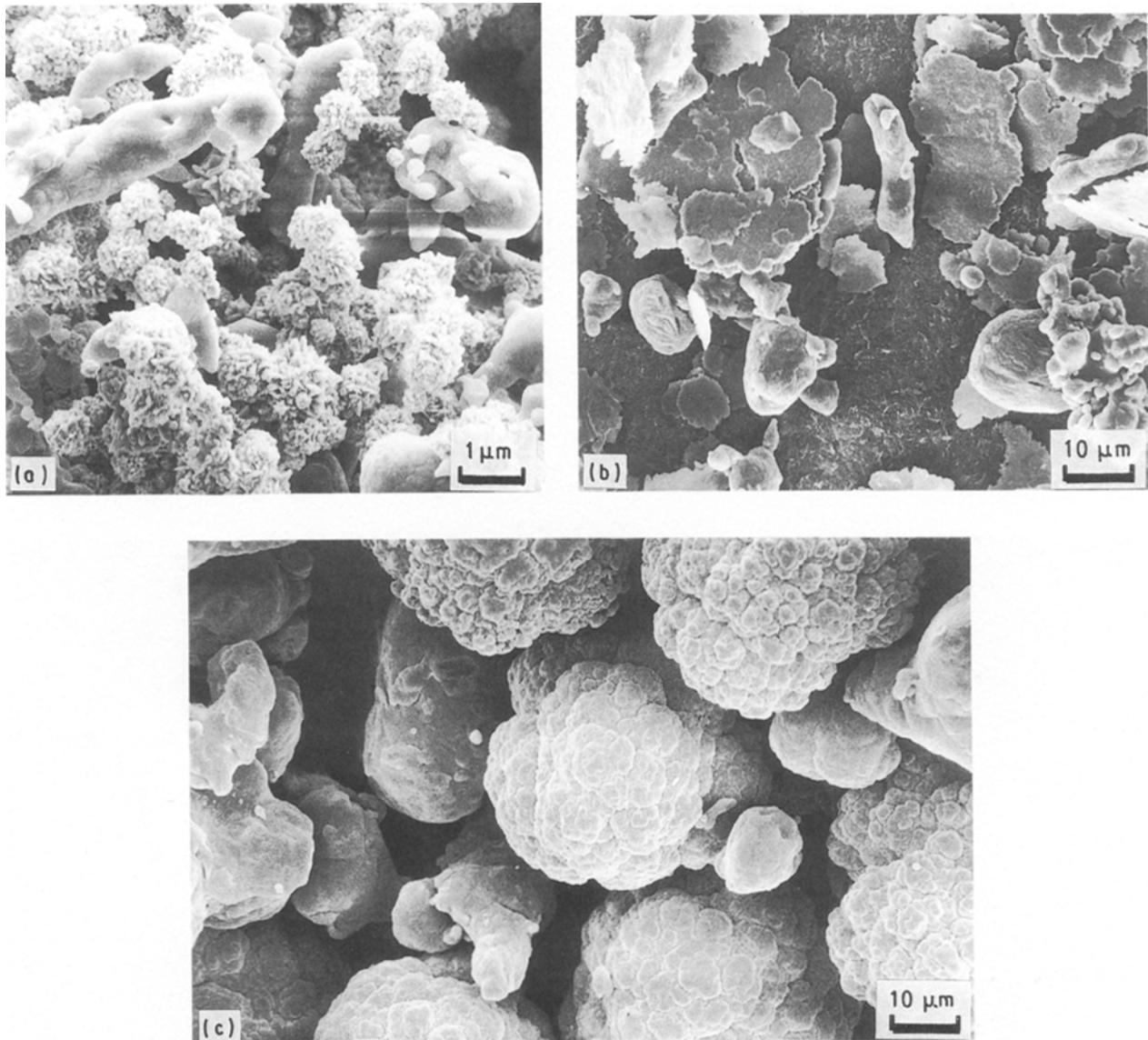


Figure 4 Scanning electron micrographs showing morphologies of (a) fine, (b) flaky and (c) coarse Ni-Al powder mixtures.

4. Results

The shock-processed Ni-Al powder mixture compacts were recovered from the copper capsules and cross-sectioned longitudinally. The cross-section surfaces were polished to reveal the contrast of the reactants and the products. Metallography and scanning electron microscopy were performed to characterize the shock-compression features in the various compacts. Differential thermal analysis was then performed to evaluate the reaction behaviour of unreacted regions of the compacts. Results of these investigations will be discussed next.

4.1. Microstructural characterization

Optical microscopy of the shocked compacts was carried out to identify reacted and unreacted regions of the compacts, based on contrast between individual unreacted particles and the reacted region, as well as porosity, as shown in Fig. 5. In the unreacted regions (Fig. 5a, b and c), the dark contrast of Al particles and bright contrast of Ni particles is clearly visible. In the reacted regions (Fig. 5d) only a uniform contrast with

voids generated due to melting and subsequent solidification can be discerned. Melting is the thermochemical result of the large heat of reaction, thus it is always associated with the products of reaction.

Optical microscopy conducted on the 3Ni + 1Al distribution mixtures showed that with the coarse and fine morphology, a reaction occurred in only top corner (periphery) areas of the samples, as observed along the cross-section surface. The flaky Ni morphology sample of the 3Ni + 1Al mixture appeared to have the entire bottom (non-impact) half fully reacted, as observed from the uniform contrast of the polished cross-section. The top part of the sample was unreacted and showed the flaky Ni being aligned perpendicular to the direction of shock wave propagation. The shock conditions were such that the top part of the sample experienced lower shock conditions than the bottom part of the sample.

The 1Ni + 1Al samples showed a range of regions that appeared to be reacted depending on the powder morphology. The coarse Ni mixture showed no evidence of reaction, while the fine Ni sample showed reaction occurring only in the corner regions, and the

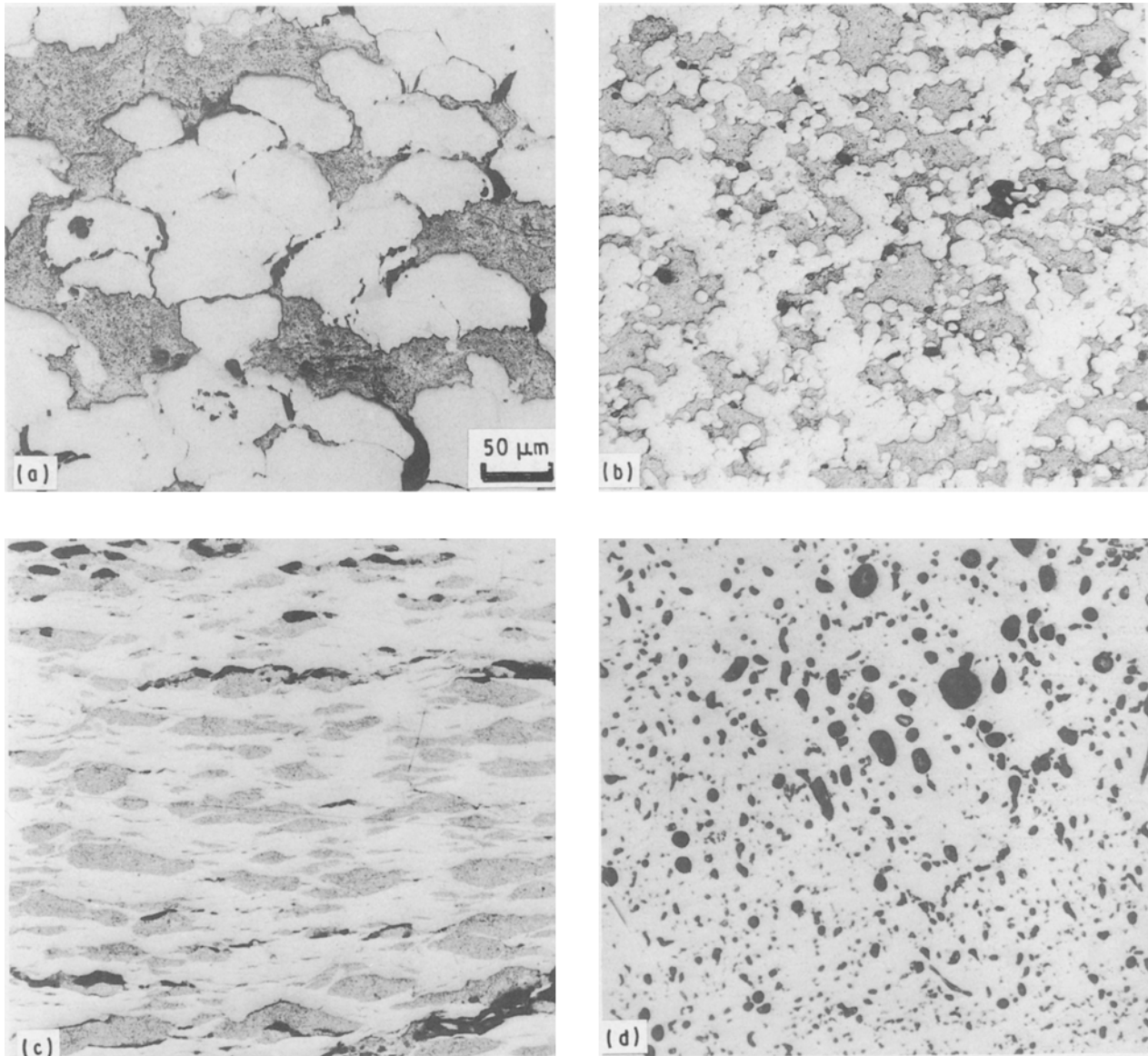


Figure 5 Optical micrographs of compacts showing unreacted region in (a) coarse (spherical), (b) fine (spherical) and (c) flaky powder mixture compacts, and (d) a typical fully reacted region.

flaky Ni sample showed evidence of complete reaction.

The 1Ni + 3Al samples also showed similar results: the coarse sample showed no evidence of reaction; the fine Ni samples had reaction in general lesser than for the corresponding mixtures of 1Ni + 1Al and 3Ni + 1Al; and the flaky mixtures indicated complete reaction. In summary, the flaky-type morphology mixtures reacted almost completely in all three volumetric mixtures. The fine morphology powder mixtures underwent partial reaction (of varying degree) in each of the three mixtures. The coarse (rounded) morphology powder mixtures showed the most dominating volumetric distribution effect, such that unlike the Ni-rich mixture stoichiometry, the Al-rich mix showed no evidence of chemical reaction.

For those compacts that did not react, the change in configuration can be seen in the optical and SEM micrographs in Figs 5 and 6 (morphology effect) and also in the optical micrographs of coarse powders showing volumetric distribution effect in Fig. 7. The coarse and fine powders compact well together, with the harder Ni powder retaining the rounded shape,

and the softer Al particles deforming around the Ni (Figs 5, 6 and 7). The deformation of Al allows a high surface-area contact to be established with the Ni. However, since the fine powders have more surface-area contact after the powders are compressed, they subsequently tend to react more readily than the coarse powders. There are areas in between the Ni where Al was mixed with the Ni, creating an intimate mixture in the coarse powder (Fig. 6), as determined by energy-dispersive spectroscopy (EDS). The large Ni spheres, which do not deform easily, act as anvils against which the smaller Al particles are deformed. In contrast, the flaky Ni particles undergo extensive deformation and cause entrapment of Al particles. Thus, with continued deformation the Al smears out (thereby increasing its overall surface area) and mixes with any protrusions on the Ni surface. Fresh clean surfaces and fine-scale mixing are then generated as shown in Fig. 6.

In the case of the flaky morphology mixture, fine strands of pure Al as well as Al containing Ni are also observed. Such a state with intimate (fine-scale) mix-

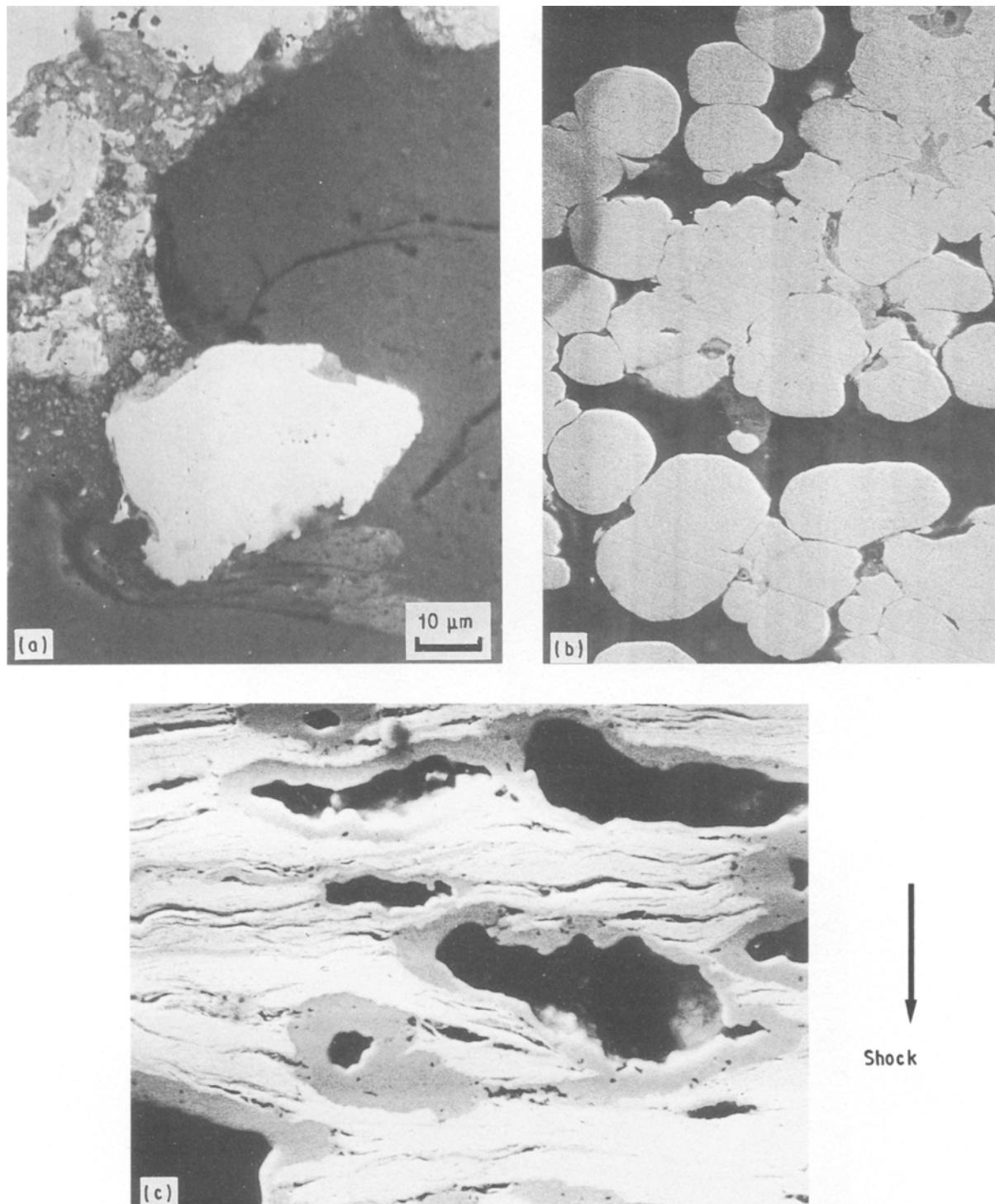


Figure 6 Scanning electron micrographs of (a) coarse, (b) fine and (c) flaky mixtures showing evidence of mixing.

tures and contacts between cleansed surfaces, along with large amounts of defects introduced into the particles, cause the compressed mixtures to react easily during subsequent heating (e.g. in DTA). However, as the amount of Ni decreases, there is less intense mixing of the elements, as shown in the optical micrographs of the three volumetric distributions of the powders in Fig. 7. With decreasing Ni, there are fewer particles present as hard anvils to deform the Al, thereby decreasing the amount of mixing. On the other hand, small ($< 5 \mu\text{m}$) pieces of Ni are also seen in the Al up to $50 \mu\text{m}$ away from the nearest Ni particle in the 1Ni + 1Al and 1Ni + 3Al mixtures,

indicating that deformation, scuffing and fracturing of Ni was taking place rather than the deformation and mixing of Al with hard Ni particles.

4.2. Differential thermal analysis of shocked compacts

DTA was conducted on samples from unreacted regions of the shock-treated compacts of the various Ni-Al powder mixtures. In general the results were consistent with the prior observations of Hammett *et al.* [5] and Thadhani *et al.* [6]. The most revealing effects of powder morphology and volumetric ratio on

the reaction behavior are shown in the DTA traces in Figs 8 and 9. Fig. 8 shows the DTA traces for the 3Ni + 1Al mixtures of coarse, flaky and fine morphology, and Fig. 9 shows the DTA traces for coarse morphology powders mixed in the three different volumetric ratios corresponding to the stoichiometry of the 3Ni + 1Al, 1Ni + 1Al and 1Ni + 3Al atomic compounds.

The DTA traces in Fig. 8 indicate that all three morphologies of the 3Ni + 1Al mixture exhibit an exothermic pre-initiation event (forming NiAl_3) at $\sim 550^\circ\text{C}$ prior to the expected main exotherm (forming Ni_3Al) at 650°C . However, the magnitude of the pre-initiation exothermic event is strongly dependent on morphology. The coarse morphology powder mix-

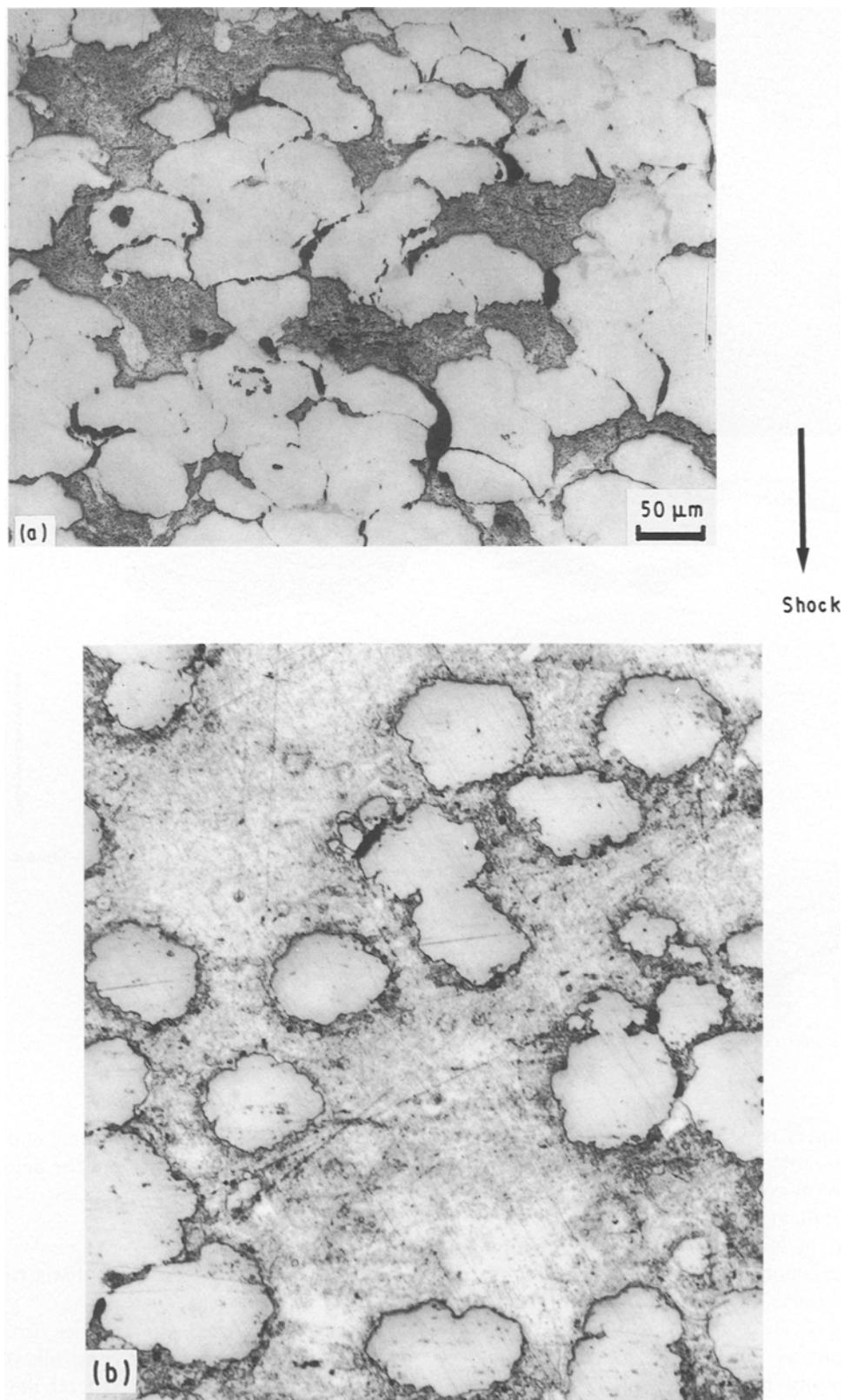


Figure 7 Optical micrographs of the coarse morphology mixtures of the different volumetric distributions of (a) 3Ni + 1Al, (b) 1Ni + 1Al and (c) 1Ni + 3Al.

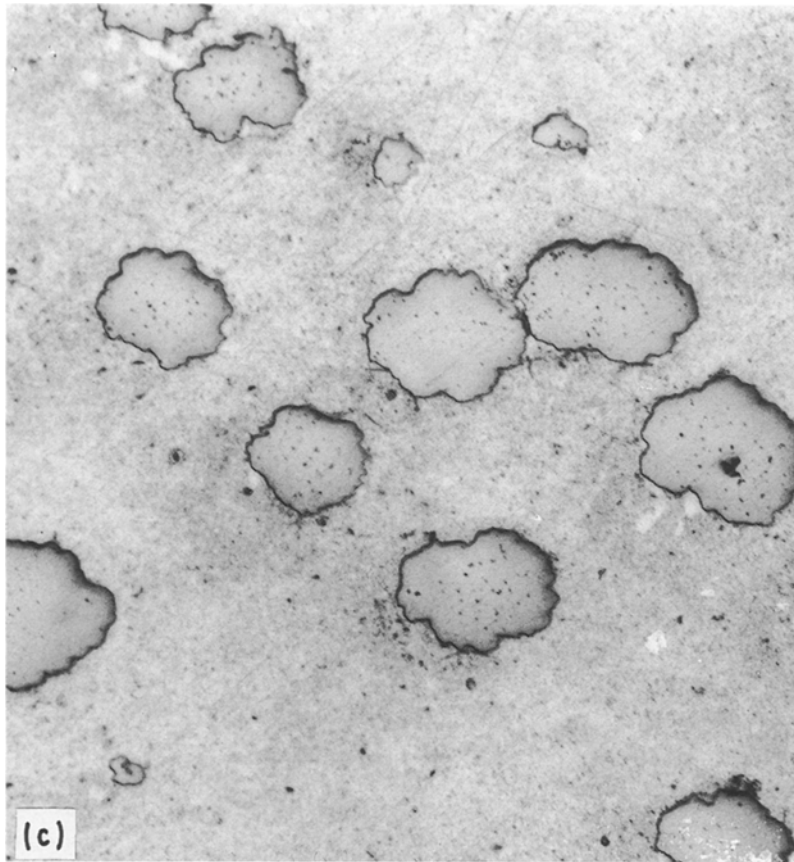


Fig 7 (continued)

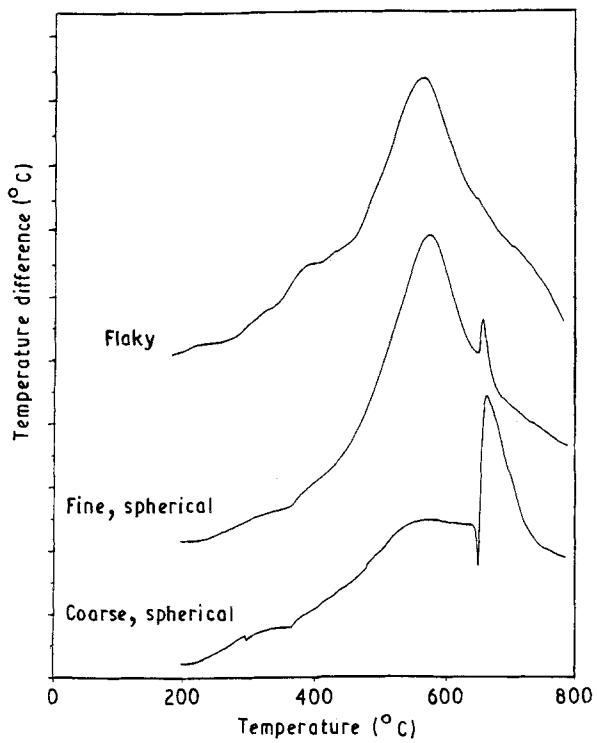


Figure 8 DTA traces for the atomic ratio mixture 3Ni + 1Al, showing the effect of powder morphology.

ture exhibits primarily the main exotherm at 650°C, with a small pre-initiation peak preceding the endotherm (corresponding to the melting of Al). The fine morphology powder mixture exhibits a large pre-

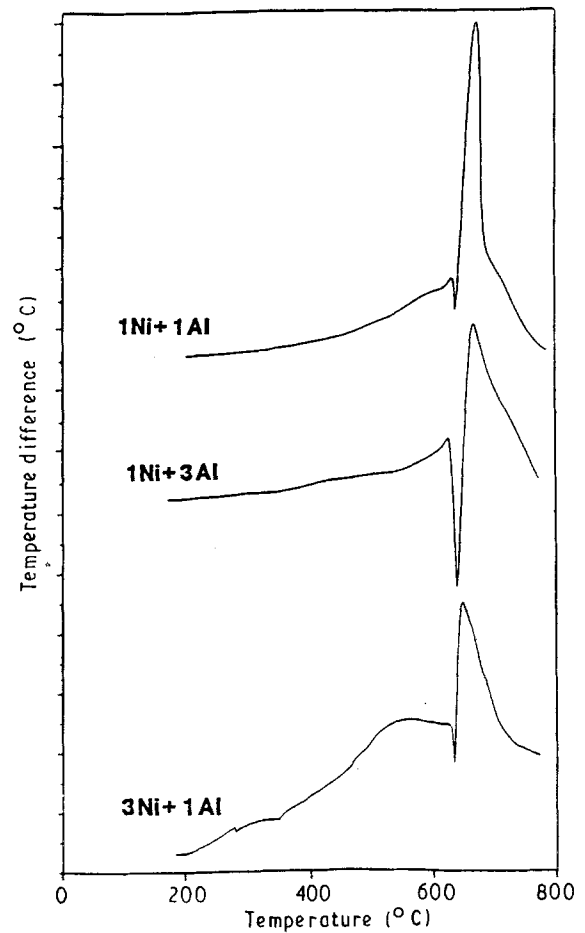


Figure 9 DTA traces for the coarse (spherical) powder mixture, showing the effect of volumetric distribution.

initiation peak that is much larger than the main exotherm, which considerably decreases in magnitude, while the flaky powder mixture shows only a broad pre-initiation exothermic event. These DTA results clearly indicate that the reaction behaviour of the shock-treated 3Ni + 1Al powder mixture is significantly affected by the starting powder particle morphology.

The effect of morphology on the degree of chemical reaction as seen in the DTA traces can be explained in terms of the evidence of configuration changes leading to mixing of the elements and introduction of large amounts of defects as seen in the micrographs in Fig. 5a, b and c. For the coarse morphology (Fig. 5a) not much mixing is seen, except in some small areas. The overall surface contact of the powder is high, but not as much as in the compacts of the other two morphology mixtures. This yields a smaller magnitude of the pre-initiation peak for the case of the coarse morphology mixture.

The magnitude of the pre-initiation peak for the fine powder morphology mixture is much larger than that for the coarse powder. This is due to a larger surface area having clean and more intimate contacts between the Ni and Al powders.

The flaky powder mixture undergoes the greatest configuration change, most intimate mixing and largest surface-area contacts between cleansed surfaces. Such a state thus shows the largest pre-initiation event, with the reaction being completed even before the compact reached the expected final reaction initiation temperature, so no main exotherm was seen. In fact, with a little more intense shock conditions, the configuration change, mixing and activation can cause the flaky powder mixtures to undergo complete chemical reaction even during the shock-loading state. This result was seen in most regions of the flaky mix compact which, due to more intense shock conditions, reacted fully.

The DTA traces for the coarse morphology powders mixed in volumetric distributions corresponding to 3Ni + 1Al, 1Ni + 1Al and 1Ni + 3Al atomic proportions are shown in Fig. 9. It can be seen that only the 3Ni + 1Al mixture exhibits clear evidence of the pre-initiation event. In the 1Ni + 3Al powder mixture the melting of Al, indicated by the large magnitude of the endotherm, overrides any possible pre-initiation event due to the large volume of Al in the sample. The 1Ni + 1Al coarse powder mixture shows results similar to those of the 1Ni + 3Al mixture, except that the Al melting endotherm is not as large because of the lesser amount of Al. These results indicate that the reaction behaviour of the shock-treated coarse morphology powder mixed in the 3Ni + 1Al ratio is different from that of the 1Ni + 1Al and 1Ni + 3Al mixture ratios.

It can be seen from Fig. 7 that the amount of Al relative to the Ni in a given area changes as the mixture goes from 3Ni + 1Al to 1Ni + 3Al. The presence of the pre-initiation peak for the 3Ni + 1Al mixture was explained above. The lack of any pre-initiation event in the other two ratios was due to the lack of mixing and the smaller surface-area contact

between dissimilar particles. Fig. 7 shows the lack of mixing between Ni and Al due to the deficiency of Ni relative to the amount of Al in the mixture. There was some evidence at higher magnifications that showed small ($< 5 \mu\text{m}$) Ni particles in the Al which are up to $50 \mu\text{m}$ away from the Ni particles. However, the amount of surface-area contact and cleansing is significantly reduced due to the lack of Ni available in the mixture relative to the amount of Al.

5. Discussion

In this section the microstructurally characterized configuration of the shock-processed Ni–Al powder mixtures will be discussed and correlated with the mechanisms identified in the CONMAH model. This will be followed by evaluation of the reaction behaviour to provide additional support for the correlation of the microstructure with the shock-compressed configuration.

5.1. Shock-induced chemical reactions in powder mixtures

Shock synthesis studies done to this point have included the effects of starting powder morphology on shock-induced chemical reactions in order to conduct a comparative study of events thought to be important in or leading to chemical reactions. These studies have shown that the starting powder particle morphology plays a significant role in influencing the extent of shock-induced reactions, and also the type of reaction product formed. Furthermore, it has also been reasoned that the pre-initiation phenomenon is a direct illustration of the enhancement in reactivity due to shock compression loading. These results, consistent with the present observations, indicate that an irregular type of powder morphology (flaky powders) reacts more readily than a regular, more uniform type of powder morphology (i.e. rounded or spherical type). With the increased flow and mixing seen in the irregular morphology, the tendency for reaction is increased.

The results of Hammett *et al.* [5] also show that the morphology of the powders significantly influences the reaction behaviour as analysed in the DTA experiments. In addition to the morphology effect, present results prove that if the volumetric distribution of the starting powders is so lopsided that one species is deficient, then the mixing that takes place is insufficient to cause bulk chemical reaction in the shock state. In such cases, although the reaction may initiate at localized regions, its slow propagation allows thermal conductivity to take the required heat away, thereby quenching the reaction [20]. On the other hand, if there are a number of mixed, activated areas, then the reaction will propagate much faster, not allowing for thermal quenching, and spread over the bulk of the compact.

Several other studies on intermetallic forming systems have been performed in order to understand the mechanism of shock-induced chemical reactions in elemental powder mixtures. Krueger *et al.* [21–23] have included shock-induced reaction energetics to

explain the reaction mechanisms in Ni–Si and Ti–Si systems. Their interpretations imply the importance of a shock energy threshold and the accompanying shock-compression heating for reaction initiation, assuming thermodynamic equilibrium conditions. Accordingly, the threshold shock energy corresponds to the bulk homogeneous temperature, which must be above that required to initiate ambient-pressure reactions.

Krueger *et al.*'s results, however, pertain to only one type of morphology of starting powders. On the other hand, the present results as well as those of Hammetter *et al.* [5] and Thadhani *et al.* [6] show that a change in starting powder morphology (or other starting powder mix characteristic) alters the energy threshold criterion in powder mixtures shock-compressed under otherwise identical peak pressure and bulk temperature conditions. In fact, with irregular (flaky) morphology powders, shock-induced chemical reactions initiate at energy levels corresponding to bulk temperatures which are much below those required for initiating chemical reactions in unshocked powder mixtures. Thus, it can be argued that the resulting effects cannot be simply explained by interpretations of shock energetics but rather with the mechanochemical aspects characterized by the CONMAH model.

5.2. Adiabatic reaction behaviour of shock-compressed powder mixtures

The results of the present study, consistent with the prior results of Hammetter *et al.* [5] and Thadhani *et al.* [6], reveal that the adiabatic reaction behaviour of shock-treated elemental powder mixtures is different from that of simply mechanically mixed powder mixtures. Unlike the latter case where chemical reactions are triggered at a temperature close to the melting point of the lower-melt temperature constituent, the shock-treated mixtures show varying behaviour depending on the effects or changes caused during shock-compression. These effects lead to reaction initiation in the shock-compressed mixtures at temperatures much lower than those in mechanically mixed powder mixtures.

A reduction in the reaction initiation temperature in the shocked (but unreacted) powder mixture compact, in contrast to the unshocked powder mixtures, has also been observed by Krueger *et al.* [21–23] in Ni–Si and Ti–Si. Combustion (SHS-type) chemical reaction can be made to occur at lower than usual temperatures in green compacts pressed to high densities, or alternatively, in compacts heated at slow rates. These conditions promote a significant degree of solid-state diffusion, which in some cases may even inhibit subsequent reaction occurring at the melt temperature of one of the constituents.

Bordeaux and Yavari [24] have conducted a DTA study on mechanically formed metal multilayer composites. They observed a pre-initiation exotherm (corresponding to reaction by solid-state diffusion) and a main exotherm (close to the melting temperature of Sn) while heating a Pd–Sn composite at a rate of $40^\circ\text{C min}^{-1}$, as shown in Fig. 10. The mechanically

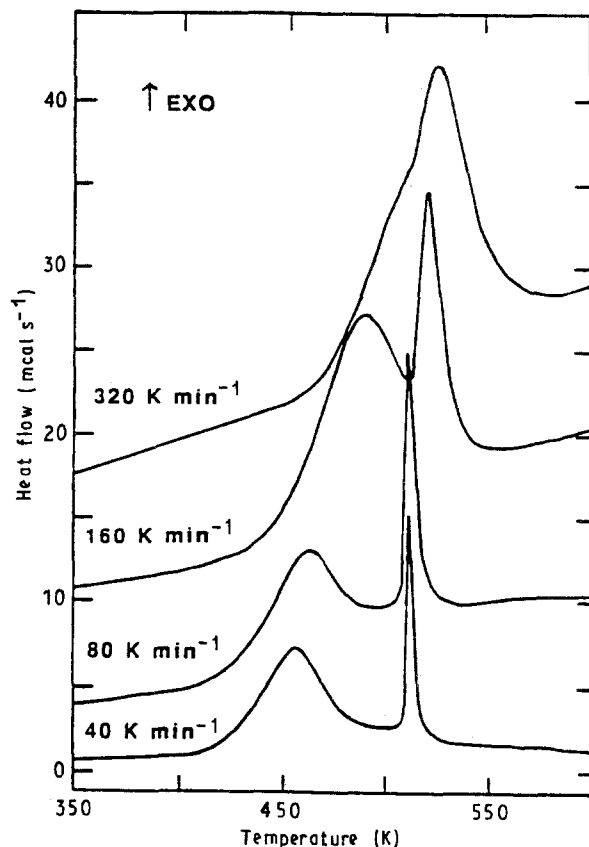


Figure 10 DSC thermograms for Pd–Sn composite powder, showing the effect of heating rate on the pre-initiation and main exotherm (from Bordeaux and Yavari [24]). $1 \text{ cal} = 4.19 \text{ J}$.

formed multilayer composites of Bordeaux and Yavari (made by repeated rolling together of thin layers of Pd and Sn) are in principle similar to the shocked (but unreacted) Ni–Al mixtures of the present study. The micrographs of their rolled Pd–Sn layers show the same type of intimate contact between the elements as is seen in our shock-compressed Ni–Al mixtures (Fig. 5). Likewise, the pre-initiation exothermic event observed in the Ni–Al powder mixtures in the present study occurs due to the shock-compression enhanced diffusion occurring at heating rates of $10^\circ\text{C min}^{-1}$ in the DTA. Furthermore, different reaction behaviours are observed in otherwise identically shock-compressed samples heated at similar heating rates in the DTA. Thus, such differences can be attributed to shock-compression effects alone, and not packing density or heating-rate effects.

Considering that all the different types of powder mixture used in the present study were shock-compressed under identical conditions (two-dimensional), the reaction effects should then correspond to the differences between individual starting powder mixtures. Thus, one can conclude that powder particle morphology and volumetric distributions of powder mixtures (the two starting powder characteristics varied in the present study) significantly affect the reaction behaviour of shock-compressed materials. The effect of powder particle morphology on the control of the pre-initiation event is due to the greater degree of surface-area contact achieved in an intimately mixed powder mixture. Such a degree of mixing and surface

contact is particularly seen in the case of irregularly shaped (flaky) and fine powder morphologies, in contrast to the coarse rounded powder morphologies.

The differences in the reaction behaviour when powder mixtures of three types of volumetric distribution of Ni and Al used are also most significant with coarser and more rounded powder particle morphologies. The volumetric distribution effects arise because of the similar underlying reasons, mainly differences in the configuration change (degree of mixing and intimacy of contacts between reactants) accomplished during shock compression. Due to the large density difference between Ni (7.896 g cm^{-3}) and Al (2.70 g cm^{-3}), the 3Ni + 1Al mixture has almost 67 vol % Ni and balance Al, the 1Ni + 1Al mixture has 40 vol % Ni and balance Al, while the 1Ni + 3Al mixture has only 18 vol % Ni and 82 vol % Al on a volumetric scale. Thus, in the 1Ni + 3Al mixture there is very little Ni available which can participate in the mixing and form an intimate mixture with Al, thereby promoting the tendency for chemical reaction.

The present results show that shock-compression of powder mixtures results in a configuration change leading to the formation of a close-packed, intensively deformed, and intimately mixed and activated state, consistent with the mechanisms of the CONMAH model [7]. With subsequent external thermal simulation or even by the thermal environment generated during shock compression, a chemical reaction is easily initiated at temperatures much lower than those at which normal combustion reactions occur. The characteristic nature of the activated state is determined by the intensity of the shock conditions, and material factors such as the relative powder morphologies as well as the proportions in which the two ingredients are mixed.

6. Conclusions

Shock-compressed but unreacted nickel and aluminium powder mixtures of varying particle morphology and volumetric distributions exhibit different adiabatic chemical reaction behaviours. Powders mixed in equimolar volumetric distributions and those having more irregular (flaky) type particle morphologies undergo a significant extent of configuration change, macroscopic mechanical mixing and activation during shock-compression, in contrast to powders of more regular morphologies and those mixed in other volumetric distributions. Such a chemical reaction is easily initiated at temperatures lower than those occurring in simply mechanically mixed powders. These type of "mechanochemical" effects, in addition to the thermal environment provided by shock-compression, lead to complete reaction in the duration of the shock state.

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