

Correlation of shock initiated and thermally initiated chemical reactions in a 1:1 atomic ratio nickel-silicon mixture

Barry R. Krueger, Andrew H. Mutz, and Thad Vreeland, Jr.
W. M. Keck Laboratory of Engineering Materials, California Institute of Technology, 138-78, Pasadena, California 91125

(Received 11 March 1991; accepted for publication 19 August 1991)

Shock initiated chemical reaction experiments have been performed on a 1:1 atomic ratio mixture of 20- to 45- μm nickel and -325 mesh crystalline silicon powders. It has been observed that no detectable or only minor surface reactions occur between the constituents until a thermal energy threshold is reached, above which the reaction goes to completion. The experiments show the energy difference between virtually no and full reaction is on the order of 5 percent. Differential scanning calorimetry (DSC) of statically pressed powders shows an exothermic reaction beginning at a temperature which decreases with decreasing porosity. Powder, shock compressed to just below the threshold energy, starts to react in the DSC at 621 °C while powder statically pressed to 23% porosity starts to react at about 30 °C higher. Tap density powder starts to react at 891 °C. The DSC reaction initiation temperature of the shock compressed but unreacted powder corresponds to a thermal energy in the powder of 382 J/g which agrees well with the thermal energy produced by a shock wave with the threshold energy (between 384 and 396 J/g). (Thermal energies referenced to 20 °C.) A sharp energy threshold and a direct correlation with DSC results indicates that the mean thermal energy determines whether or not the reaction will propagate in the elemental Ni + Si powder mixture rather than local, particle level conditions. From this it may be concluded that the reaction occurs on a time scale greater than the time constant for thermal diffusion into the particle interiors.

I. INTRODUCTION

Shock initiated chemical reactions are currently of considerable interest.¹⁻⁶ With the high pressure and temperature associated with shock wave processing, it may be possible to concurrently synthesize and form near net shape parts of intermetallic compounds and other materials. Shock processing is also a viable technology for producing composite materials where it is necessary to control chemical reactions between the matrix and reinforcing particle since such reactions often have deleterious effects on the mechanical properties of the composite.

The chemistry and kinetics of intermetallic reactions have been explored by observing the behavior of multilayer thin films upon heating. It has been shown that in many multilayer composite structures, self-sustaining chemical reactions can be initiated upon heating.⁷⁻¹¹ Bordeaux, Yavari, and Desre⁸ place two basic criteria on whether or not such reactions are possible. Briefly, the first is that the heat of the reaction must be in excess of that required to melt the mixture, and the second is that the rate of heat generation due to the reaction must be greater than the rate of heat dissipation to the environment. Thermally initiated reactions which are not self-sustaining have been observed in Ni/Si multilayers as well as in a number of other metallic multilayers. The temperature at the onset of the reaction is observed to increase somewhat with the heating rate.¹¹ Ma *et al.*¹² observed an "explosive" reaction propagating at about 4 m/s in thin multilayers of Ni/Al and observed a layer thickness effect. Reactions did not propagate when the layer thickness exceeded a critical value,

and they suggested that the critical layer thickness is proportional to the ratio of the heat released by the reaction to the heat dissipated to the environment, which increases with ambient temperature.

Olowolafe *et al.*¹³ observed the growth of nickel silicide layers upon heating Ni films vacuum deposited on a single crystal, polycrystalline, and amorphous Si (*a*-Si) annealed from 200 to 325 °C. Only Ni₂Si formed on (111) and (100) Si and on polycrystalline Si while Ni₂Si and NiSi formed in two distinct sublayers on *a*-Si. Ma *et al.*¹⁴ observed solid state interdiffusion reactions in Ni film and *a*-Si bilayers, and observed only crystalline Ni₂Si formation with high purity *a*-Si. For the case where the *a*-Si contained about 5% carbon an amorphous Ni₂Si layer was also observed. Clevenger and Thompson,¹⁵ using isothermal and constant heating rate differential scanning calorimetry (DSC) of evaporated multilayer films of Ni and *a*-Si (2 Ni to 1 Si), found distinct exothermic peaks associated with the formation of amorphous nickel silicide and crystalline Ni₂Si.

Combustion synthesis (CS or SHS, self-propagating high temperature synthesis) of intermetallic and other systems employs a thermally initiated self-sustaining chemical reaction. In CS, the reaction is externally initiated in one section of a usually porous sample, with a specific contact area between particles much less than in multilayer films. The sample may be in either a vacuum or at atmospheric pressure. The reaction then propagates through the sample at a rate lower than that observed in the explosive reaction of multilayers, driven by the heat of reaction conducting and radiating into the unreacted material.¹⁶

The initiation of reactions by shock waves in chemically active powder mixtures is similar to thermal initiation in that the shock wave deposits a significant amount of thermal energy in the sample. The thermal energy is deposited through the plastic deformation associated with void collapse and relative interparticle motion, however the shock wave also produces conditions which have no counterpart in thermally initiated reactions. From a macroscopic point of view, the shock process is different in that the material in the shock front is very rapidly heated (with heating rates in excess of 10^{10} K/s) and raised to a pressure of typically several GPa for a duration on the order of microseconds, and the material behind the shock attains particle velocities on the order of hundreds of meters per second. SHS reactions typically propagate at velocities of less than 1 m/s. A shock wave which triggers a reaction typically travels at a velocity on the order of 1 km/s. Therefore substantial reaction may not occur in the shock front unless the powder particles are of submicron size, but the reaction will be initiated throughout the powder on a time scale much shorter than in the usual SHS reaction.

On the particle level, the shock process is also quite different from thermally initiated reaction. As a shock wave passes through a porous media, energy is deposited preferentially near the particle exteriors.¹⁷ In ductile powders the particle exteriors are deformed significantly more than the interiors in the closing of voids. The preferential deposition of shock energy results in a positive temperature gradient from interior to exterior of the particle. The time required for temperature equilibration is dependent upon the thermal properties of the materials, particle size, and melt pool size (when the shock energy is sufficient to cause melt to form). The homogeneous shock temperature is defined as the temperature of the shocked compact after local particle thermal equilibrium has been achieved, and before the compact conducts significant heat to the surrounding ambient. Assuming spherical particles, spherically homogeneous energy deposition and no melt pools, Schwarz *et al.*¹⁸ gave the time constant for temperature equilibration to be $r^2/16D$, where r is the particle radius, and D is the thermal diffusivity of the powder. Temperature measurements in shocked powders of Cu and constantan confirmed this relationship and excellent agreement between the measured homogeneous temperature and the homogeneous temperature calculated from the shock energy was demonstrated.¹⁹

Graham *et al.*,²⁰ Thadhani *et al.*,²¹ Batsanov *et al.*,²² and others have reported studies on shock initiated chemical reactions in a number of systems. They have put forth several qualitative reasons for why the shock initiated chemical reaction process might be very different from the other synthesis processes described above. These reasons are summarized in what Graham has coined "catastrophic shock" as opposed to "benign shock." Benign shock, as discussed by Horie *et al.*,²³ is a description of the shock process from the traditional viewpoint of the macroscopic conservation equations, with void collapse and the resulting inhomogeneous energy deposition and the normal processes of thermal equilibration and atomic diffusion. The

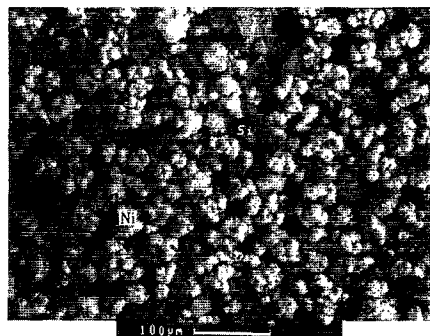


FIG. 1. Backscattered SEM micrograph of the Ni/Si powder mixture showing the morphology of the lumpy spherical Ni and the irregular Si.

catastrophic shock concept views the interaction of shock waves with chemically reactive media through the formation of activated complexes, nondiffusive transport of matter described as relative mass motion and fluidlike flow, and the critical involvement of crystal defects in chemical reactions.

We have recently reported the results of a series of shock initiated reaction experiments on two similar mixtures of 1:1 atomic ratio elemental nickel and silicon powders.²⁴ These experiments were conducted using a propellant gun and target design which results in highly one-dimensional shock conditions, and therefore, in uniform shock conditions over the majority of the sample. It was found that there exists a thermal energy threshold below which only minor surface reactions occur and above which the reaction goes to completion as evidenced by spherical voids in the recovered compacts indicative of bulk melting. These experiments show the threshold is crossed with an energy increase on the order of 5 percent. It was argued that the narrowness of the threshold indicates that the homogeneous temperature rather than the pressure effects and local inhomogeneities determine the initiation of the reaction forming NiSi. The current work provides further evidence that the thermal energy (or homogeneous temperature) is the critical parameter determining whether or not bulk reactions occur and that phenomena described as "catastrophic shock" must be of secondary importance in this chemical system.

II. EXPERIMENT

The mixture of 1:1 atomic ratio elemental Ni and Si (67.6 wt % Ni) consisted of 20- μm –45- μm nickel (Aesar Stock #10581) and –325 mesh crystalline silicon (Cerac Stock #S-1052). The powders were mechanically mixed in petroleum ether to avoid particle agglomeration and then dried. No special care was taken to remove or prevent the formation of oxides on the particle surfaces. A backscattered scanning electron microscope (SEM) micrograph of the starting mixture is shown in Fig. 1.

The shock facility used is the Keck Dynamic Compactor which employs a 35-mm smooth bore launch tube. In our target, the flyer plate, carried by a nylon sabot, strikes the sample directly and does not strike the sample contain-

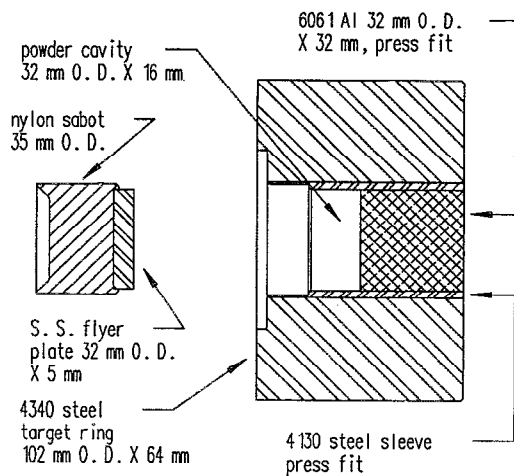


FIG. 2. Schematic drawing of the sabot with flyer plate and the target design. The left surface of the target ring is "O" ring sealed to the barrel and the right surface is pressed against a momentum trap.

ment fixture, a schematic of which is shown in Fig. 2. There exists strong evidence that the target assembly and impact conditions result in highly one-dimensional, and therefore well-defined, shock conditions as discussed below.

Figure 3 shows metallic glass ($\text{Ni}_{76.4}\text{Cr}_{19.7}\text{B}_{2.3}\text{Co}_{0.08}$, Allied MBF 50) which has been shock consolidated with a 5 mm thick 304 stainless steel flyer at a velocity of 1 km/s.²⁵ The sample has been cut with a low speed diamond saw, polished and etched with Marbles reagent. The shock propagated from left to right in (a) and (b) of the figure. A macrophotograph of the recovered compact is shown in Fig. 3(a), and an optical micrograph of the region of changing contrast is shown in Fig. 3(b). X-ray diffraction has confirmed that the darkened region crystallized while the light region remained amorphous. Although the properties of this metallic glass are not well characterized, the transition region occurs at a distance from the flyer/sample

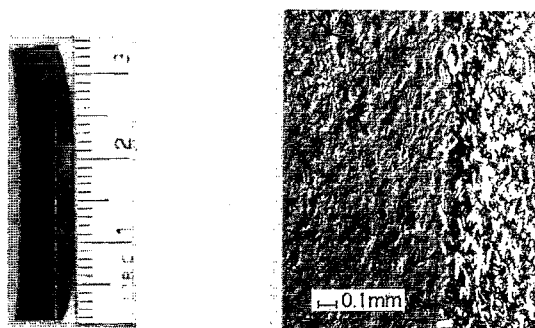


FIG. 3. A macrophotograph of the sectioned compact, (a) and an optical micrograph of the consolidated metallic glass powder, (b). The shock wave propagated from left to right, and the region on the left of the compact is crystalline. Note the planar shape of the transition region between the crystalline phase (darker phase) and the glass phase (non-etching) which is located at the position where the release wave from the back of the flyer caught the shock wave.

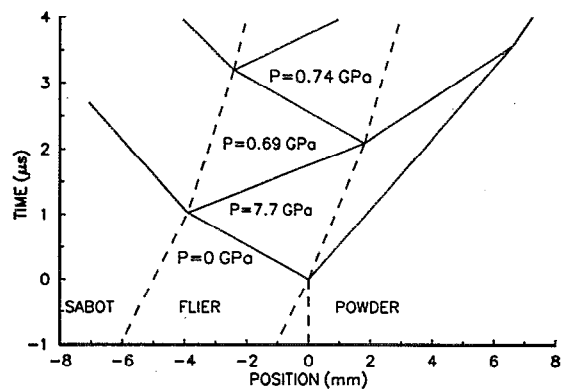


FIG. 4. The one-dimensional plane wave time-displacement history calculated for the consolidation experiment of metallic glass (sample of Fig. 3.). Solid lines are shock waves, dashed lines are surface positions. Note the shock pressure drops from 7.7 to 0.74 GPa when the rarefaction wave from the back of the flyer catches the shock wave.

interface at which a release wave from the rear of the flyer is expected to overtake the initial shock. Figure 4 shows the results of a one-dimensional plane wave time-displacement calculation for this consolidation experiment. The release wave catches the shock wave at about 3 mm into the consolidated powder, beyond this point the powder is effectively consolidated by the nylon sabot at considerably lower pressure as indicated in the figure. These observations strongly imply that the shock energy heated the compact to a temperature in excess of the crystallization temperature (the entire sample remained amorphous at lower shock energies). This sample's salient feature is the highly planar interface between the crystalline and glass regions indicating nearly one-dimensional shock conditions.

Although a numerical simulation has not been conducted for our target fixture, a recently presented simulation of a similar target indicates that the target assembly and impact conditions used should result in highly one-dimensional shock conditions.²⁶ For the simulation, a thick cover plate was assumed, and to achieve one-dimensional conditions, it was determined that the ratio of the flyer to sample diameters should be slightly greater than one. With our target and impact conditions, no cover plate is used and the flyer to sample diameter ratio is equal to one. Although the precise effect of these differences has not been investigated, the similarity in the two target designs indicates that deviations from one-dimensional shock conditions should be small.

Finally, a simple argument shows that shock parameters calculated assuming one-dimensional conditions give the maximum pressure and shock energy in the sample, given that the release wave from the rear of the flyer overtakes the initial shock within the powder sample (the thickness of the powder sample was adjusted to assure this in the present investigation). Since the sample containment fixture is not impacted, the pressure at the sample edges releases radially in the target and containment fixture, and there is no increase of pressure or shock energy due to the "wrap-around" waves which occur when the sample as

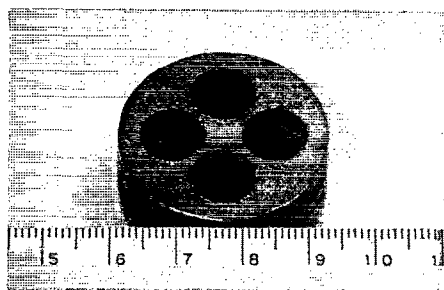


FIG. 5. Porous bronze insert machined with four cavities for powder samples.

well as the target fixture is impacted by the flyer.²⁷⁻²⁹

In all the experiments, a 5-mm-thick 303 stainless-steel plate was used as the flyer. Flyer velocities were measured by timing the interruption of two light beams just prior to impact. The distance between the light beams is 40 mm, and a counter records the number of oscillations of a 10-MHz crystal during the time interval between the interruption of the light beams. A doppler radar system was used to verify that the flyer achieves a nearly constant terminal velocity before it reaches the light beams. Flyer velocities were measured to within 1% by this system. As discussed above, the geometry of the target assembly limits the maximum shock duration in the powder by the reflection from the back of the flyer plate, and therefore the maximum shock duration is governed by the material and thickness of the flyer and the shock wave velocity in the powder. The effects of shock duration were not explored in this investigation. The launch tube and target were evacuated to about 0.1 Torr prior to impact.

Preliminary shock experiments were conducted using porous bronze inserts, with four separate powder cavities, pressed into a target fixture (Fig. 5).³⁰ These experiments have the advantage of identical impact conditions for each of four samples per shot. A disadvantage is some impedance mismatch between the insert and samples due to a difference in porous and solid density and wave speed between the samples and porous bronze. This impedance mismatch will give rise to some two-dimensional effects. To check that the two-dimensional effects were not governing the reaction initiation in the four cavity experiments, critical experiments were repeated using targets filled with only the powder mixture. The results of full and four cavity experiments presented below were in good agreement.

The differential thermal analysis experiments were performed on a DSC 2000 manufactured by Setaram Corporation, France. DSC samples were pressed in a simple cylinder and die assembly made of C350 maraging steel to allow static pressures as high as approximately 1.5 GPa.

III. RESULTS

The shock conditions were determined using an averaging method which assumes the shock pressure and particle velocity of the two constituents are equal; the mixture's bulk modulus is linear with pressure, and the

TABLE I. Thermodynamic parameters used to determine the Hugoniot of the Ni/Si mixtures. The isentropic bulk modulus of Ni and the Grüneisen parameters for Ni and Si were taken or calculated from Ref. 31. The pressure derivative of the isentropic bulk modulus of Ni was determined by fitting solid Ni Hugoniot data. Silicon's isentropic bulk modulus and its pressure derivative were taken from Ref. 32. The heat capacity coefficients were taken from Ref. 33. The units of a , b , and c are J/(mol-K), J/(mol-K²), and J-K/mol, respectively.

Density (g/cm ³)	β_S (GPa)	$\frac{\partial \beta_S}{\partial P}$	γ_0	a	b	c
Ni (α) 8.90	192.5	3.94	1.91	17.00	29.48	0
Ni (β) 8.90	192.5	3.94	1.91	25.12	7.54	0
Si 2.33	97.9	4.19	0.74	23.95	2.47	-4.14

mixture's Grüneisen parameter to specific volume ratio is constant. With these assumptions, the Rankine-Hugoniot relationships and the known Hugoniot of the flyer, the mass averaged shock conditions can be determined. The properties were averaged according to the following formulas. Reuss averages were used for the elastic properties of the powder mixture.

$$V_{0AB} = \sum_i x_i V_{0i} \quad (1)$$

$$\left[\frac{V}{\gamma} \right]_{0AB} = \sum_i x_i \left[\frac{V}{\gamma} \right]_{0i} \quad (2)$$

$$\beta_{0SAB} = V_{0AB} \left[\sum_i \frac{x_i V_{0i}}{\beta_{0Si}} \right]^{-1} \quad (3)$$

$$\beta'_{0SAB} = \left[\frac{\beta_{0SAB}^2}{V_{0AB}} \sum_i x_i V_{0i} \left(\frac{1 + \beta'_{0Si}}{\beta_{0Si}^2} \right) \right] - 1 \quad (4)$$

The subscript AB refers to the mixture. The subscript i refers to the individual components. The subscript 0 refers to standard conditions, and V , γ , β_{0S} , β'_{0S} are the specific volume, Grüneisen parameter, isentropic bulk modulus, and the pressure derivative of the isentropic bulk modulus at constant entropy, respectively.

Table I lists the thermodynamic parameters used in the calculations. Thermal energies of powder mixtures heated in the differential thermal analysis experiments presented below were calculated using the mixture's heat capacity of the form $C = a + 10^{-3}bT + 10^5c/T^2$, where C is the heat capacity and T is temperature.³³ The impact conditions and calculated shock parameters of the experiments bounding the energy threshold discussed below are listed in Table II.

A four cavity shock experiment was then performed where the initial porosity of the samples and flyer velocity (Table II) were chosen to give shock energies either just below or just above the reaction onset energy found in preliminary experiments. It should be noted that with a given flyer velocity, the shock energy *increases* with powder porosity while the shock pressure and the shock and particle velocities *decrease* with porosity. The two lower energy compacts recovered showed no evidence of chemical reactions with either optical or x-ray diffraction analy-

TABLE II. The shock conditions of the Ni + Si shock initiated reaction experiments. Shock energies are calculated without chemical reaction energy or volume change, presuming chemical reaction proceeds slowly compared to shock front passage. The column headings correspond to the mixture porosity, flyer velocity, pressure, total energy, thermal energy, and whether or not the reaction occurred, respectively. An asterisk indicates a four cavity experiment. The enthalpy of formation of NiSi at 298 K is -43.1 kJ/mol or -593 J/g from Oelsen and von Samson-Himmelstjerna, Mitt. K.-W.-I. Eidenforsch., Dusseldorf 18, 131 (1936). The ratio of energy input from the shock plus the energy generated by the reaction to the energy needed to heat and melt NiSi is 1.23 for the lowest shock energy which triggered the reaction.

Porosity (%)	Velocity (m/s)	P (GPa)	E (J/g)	E_T (J/g)	React. (Y/N)
37.5	1020	5.60	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

sis, and the compacts were poorly bonded. In the two higher energy samples, the reaction apparently went to completion as evidenced by large spherical voids throughout the compact, indicative of bulk melting. The threshold was found to lie between thermal energies of 384 and 396 J/g, corresponding to homogeneous temperatures of 631 and 648 °C, or a total energy difference of less than 3 percent. Full cavity experiments confirmed the energy threshold to be at the same level and that the separation in total energy between no and full reaction was less than 10 percent. No attempt was made using full cavities to further narrow the threshold width.

X-ray diffractions scans of the Ni/Si powder mixture shocked to just below and just above the energy threshold were made. Only Ni and Si diffraction peaks were observed in the samples shocked to just below the threshold, and optical as well as SEM examination of polished sections revealed no porosity. All diffraction peaks observed in the sample shocked to just above the threshold were indexed as orthorhombic NiSi indicating that the reaction goes to completion once the energy threshold is crossed. It is important to note that in these experiments no compacts were recovered in an intermediate condition between no and full reaction.

DSC experiments were performed on statically pressed powders. It was found that the onset temperature of the first significant exothermic reaction was dependent upon the porosity of the DSC samples. Four DSC scans on statically pressed powder are shown in Fig. 6 corresponding to 50% porosity (tap density), a porosity of 32%, a porosity of 27%, and a porosity of 23%. As can be seen, the onset temperature increases with increasing porosity. The magnetic transformation at 360 °C is seen on all of the scans.

A DSC run of the mixture shocked to an energy just below the threshold where the reaction occurs is also plotted in Fig. 6. It can be seen that the onset of the reaction occurs at a temperature 30 °C below that found in powder statically compressed to 23% porosity. Apparently, the unreacted powders were not significantly modified by the shock process except that the porosity was reduced. Table

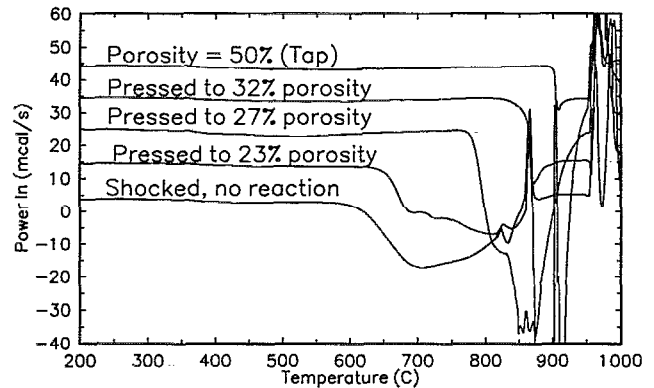


FIG. 6. DSC scans of Ni/Si powder statically pressed to four different porosities and a shock compressed but unreacted powder (porosity near zero). Note that the onset temperature of the exothermic reaction increases with porosity. Heating rate was 10 K/min, and scans are successively displaced by 10 mcal/s from the scan below.

III lists the reaction initiation temperatures and calculated reaction initiation energies for the five DSC scans shown in Fig. 6.

Scanning electron microscopy of a full cavity compact shocked to just below the reaction threshold revealed that isolated mixing had occurred which was not detected optically or with x-ray diffraction. The mixing occurred in regions which appear to have been shock-induced melt pools. As can be seen in the backscattered electron image shown in Fig. 7, the extent of the mixing was very limited. A higher magnification backscattered electron image of a mixed region is shown in Fig. 8, which was found to be 21% Ni and 79% Si by dispersive x-ray analysis.

IV. DISCUSSION

Clemens *et al.*³⁴ observed an energy threshold for the formation of an amorphous alloy from layered nickel-zirconium films which were heated by microsecond current pulses. The sudden onset of reaction at the threshold energy was attributed to chemical energy of the reaction, and the change in diffusion kinetics as the sample temperature

TABLE III. Quasistatic reaction initiation conditions for statically and dynamically compressed Ni + Si mixtures. All but the 0% porous sample were statically compressed. Reaction initiation temperatures were determined from DSC data presented in Fig. 6. Energy required to heat the mixtures from room temperature to reaction initiation temperatures was calculated using thermodynamic data in Table I; the DSC runs are not as accurate for integrated energy calculations. The phase transition enthalpy for Ni α to Ni β , 6.56 J/g (Ref. 33), was included in the energy calculation.

Porosity (%)	Reaction initiation temperature (°C)	Calculated reaction initiation energy (J/g)
50	891	566
32	867	549
27	783	491
23	651	402
0	621	382

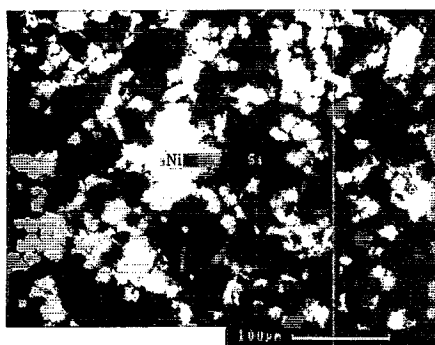


FIG. 7. SEM backscattered image of the Ni/Si powder mixture shocked in a full cavity experiment to an energy just below where bulk reaction occurs. At this magnification, there is little evidence of any interaction between the Ni and Si.

exceeded the glass transition temperature of the amorphous alloy. We postulate that in the shocked Ni-Si powder the shock energy and the released chemical energy cause the sample temperature to exceed the NiSi melting temperature when the threshold shock energy is exceeded.

Bordeaux *et al.*⁸ observed a small increase in reaction temperature with an increase in DSC heating rate in Pd-Sn and Zr-Al reactions triggered by melting of one component of the mixture. The small increase in reaction temperature with heating rate observed for Ni-Si mixtures (going from 621 °C at 10 °C/min for shock compacted but unreacted powder to between 631 and 648 °C at about 10¹⁰ °C/s for shock reacted powder) is comparable to that observed by Bordeaux *et al.*⁸ in Pd-Sn and Zr-Al for only a 60-fold rate increase.

The rapid temperature rise in the shock prevents buildup of diffusion barriers by solid-state reactions which can occur at typical DSC scan rates. The mixing reaction time is thereby decreased without significantly changing the time for dissipation of the heat of reaction to the environment. This leads to a self-sustaining reaction in the shocked mixture when the heat of mixing is sufficiently large as Bordeaux *et al.*⁸ have postulated. Static pressing brings more particle surface area into contact and also

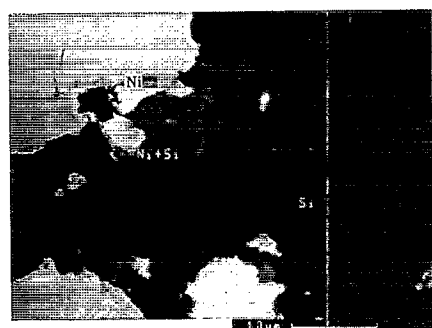


FIG. 8. SEM backscattered image of the Ni/Si powder mixture shocked in a full cavity experiment to an energy just below where bulk reaction occurs. At this magnification, some small interfacial mixed regions are observed as well as isolated pools of a mixture of Ni and Si. The more typical interfaces show no mixing.

tends to break up oxide layers which leads to lowered onset temperatures for the reaction.

From the existence of a sharp shock energy threshold and its correlation with the thermal energy threshold level at the onset temperature of the reaction in the DSC (for zero porosity powder), it can be reasoned that the shock parameter governing whether or not bulk reactions occur in a 1:1 mixture of the Ni + Si powder is the thermal energy of the mixture. The experiments rule out the possibility that the threshold is a pressure or elastic energy effect since the more porous compacts react but are shocked to a lower pressure and elastic energy.

One may argue that local particle level conditions change significantly across the threshold, however any such explanation is suspect since it must exclude the possibility that the same local conditions exist anywhere at lower shock energies. For example, the occurrence of shock initiated chemical reactions has been explained by local mass mixing due to local differences in the particle velocities of the constituents.²² However, as can be seen in Figs. 7 and 8, there is no evidence of mass mixing outside of melt pools and thin isolated surface layers, and it is unlikely that increasing the energy by as little as 3 percent will greatly enhance mass mixing, especially combined with a lower shock pressure and particle velocity, as one would expect less constituent mixing as these shock parameters decrease.

Another local condition which may arguably change as the threshold is crossed is that a critical melt pool size is attained, however this is also not likely. Since the energy difference between practically no and full reaction is small, there is a high probability that there exists some local pre-shock particle configuration in the less porous green which will result in a "critical" melt pool size upon compaction. Another argument may be that a critical density of melt pools is attained above the threshold, however this cannot be true since, in the time it takes to "communicate" between melt pools through heat conduction, the melt pools no longer exist. It is possible to argue other particle level explanations, but a necessary feature of such an approach would be that the same local conditions cannot exist in samples shocked to slightly lower energy.

The experimental findings and the above arguments are fully consistent with recent work on self-sustained reactions in metal-metal multilayer composites by Bordeaux, Yavari, and Desre,⁸ and their description of these reactions is analogous to what we believe is occurring in the Ni/Si mixtures used here.

We therefore conclude that the homogeneous temperature determines whether or not reactions occur in 1:1 atomic ratio Ni/Si mixtures of the particular morphologies used here. Since the thermal energy and corresponding homogeneous temperature determines whether or not bulk reactions occur, one can also conclude that the reaction kinetics are slower than kinetics of temperature equilibration in the particles. Therefore, the reaction proceeds on a time scale greater than several microseconds when the particle size exceeds about 10 μm.

V. CONCLUSION

Experiments on shock compacted mixtures of 1:1 atomic ratio Ni and Si powders reveal the existence of a sharp energy threshold below which no significant reactions occur and above which the reaction goes to completion as evidenced by SEM and x-ray diffraction results and voids indicative of bulk melting. The level of the thermal energy threshold corresponds to the thermal energy at the onset temperature of the reaction in zero porosity but unreacted powder in a DSC scan. From the existence of a sharp energy threshold and the correlation with DSC results, it can be reasoned that the homogeneous shock temperature determines whether or not the bulk reaction occurs rather than particle level conditions. These results are consistent with experiments in multilayer metal-metal composites, and we believe the phenomenological criteria put forth by Bordeaux *et al.*⁸ for these reactions adequately explains the basic nature of the shock reaction process in the Ni/Si mixtures and morphologies used here. One can also conclude that the reaction occurs on a time scale greater than several microseconds.

ACKNOWLEDGMENTS

This work was supported under the National Science Foundation's Materials Processing Initiative Program, Grant No. DMR 8713258. We would like to thank Phil Dixon, formerly at the New Mexico Institute of Technology, for preparing the powder mixture, and Zezhong Fu of Caltech for her help with the DSC experiments. Barry Krueger died on October 29, 1990 as a result of injuries received in a motorcycle accident. His family, friends, and scientific colleagues mourn the loss of a truly gifted individual.

- ¹S. S. Batsanov, S. Doronin, S. V. Klochdov, and A. I. Teut in *Combustion, Explosions and Shock Waves* **22**, 765 (1986).
- ²R. A. Graham, B. Morosin, Y. Horie, E. L. Venturini, M. B. Boslough, M. Carr, and D. L. Williamson, in *Shock Waves in Condensed Matter*, edited by Y. M. Gupta (Plenum Press, New York, 1986), p. 693.
- ³N. N. Thadhani, M. J. Costello, I. Song, S. Work, and R. A. Graham (to be published).
- ⁴N. N. Thadhani, A. Advani, I. Song, E. Dunbar, A. Grebe, and R. A. Graham, in *Proceedings of the International Conference on High Strain-rate Phenomena in Materials*, UCSD.
- ⁵M. B. Boslough, *J. Chem. Phys.* **92**, 1839 (1990).

- ⁶L. H. Yu and M. A. Myers, *J. Chem. Phys.* **92** (1990).
- ⁷L. A. Clevenger, C. V. Thompson, and R. C. Cammarata, *Appl. Phys. Lett.* **52**, 795 (1988).
- ⁸F. Bordeaux, A. R. Yavari, and P. Desre, *Rev. Phys. Appl.* **22**, 707 (1987).
- ⁹J. A. Floro, *J. Vac. Sci. Technol.* **A4**, 631 (1986).
- ¹⁰F. Bordeaux, Doctoral thesis, Institut National Polytechnique de Grenoble, October, 1989.
- ¹¹F. Bordeaux and A. R. Yavar, *J. Mater. Res.* **5**, 1656 (1990).
- ¹²E. Ma, C. V. Thompson, L. A. Clevenger, and K. N. Tu, *Appl. Phys. Lett.* **57**, 1262 (1990).
- ¹³J. O. Olowolafe, M-A. Nicolet, and J. W. Meyer, *Thin Solid Films* **38**, 143 (1976).
- ¹⁴E. Ma, W. J. Meng, W. L. Johnson, and M-A. Nicolet, *Appl. Phys. Lett.* **53**, 2033 (1988).
- ¹⁵L. A. Clevenger and C. V. Thompson, *J. Appl. Phys.* **67**, 1325 (1990).
- ¹⁶J. B. Holt, *Mater. Res. Bull.* **XII**, 60 (1987).
- ¹⁷W. H. Gourdin, *Prog. Mater. Sci.* **30**, 39 (1986).
- ¹⁸R. B. Schwarz, P. Kasiraj, T. Vreeland, Jr. and T. J. Ahrens, *Acta Metall.* **32**, 1243 (1984).
- ¹⁹R. B. Schwarz, P. Kasiraj, and T. Vreeland, Jr., in *Metallurgical Applications of Shock-Wave and High-Strain-Rate Phenomena*, edited by L. E. Murr, K. P. Staudhammer, and M. A. Myers (Marcel Dekker, New York, 1986), p. 313.
- ²⁰R. A. Graham, B. Morosin, Y. Horie, E. L. Venturini, M. B. Boslough, M. Carr, and D. L. Williamson, in *Shock Waves in Condensed Matter*, edited by Y. M. Gupta (Plenum Press, New York, 1986), p. 693.
- ²¹N. N. Thadhani, M. J. Costello, I. Song, S. Work, and R. A. Graham, in *Solid State Powder Processing*, edited by A. H. Clauer and J. J. DeBarbadillo (Minerals, Metals and Materials Society, Warrendale, PA, 1990).
- ²²S. S. Batsanov, G. S. Doronin, S. V. Klochdov, and A. I. Teut, *Combust., Explos. Shock Waves (USSR)* **22**, 765 (1987).
- ²³Y. Horie and M. E. Kipp, *J. Appl. Phys.* **63**, 5718 (1988).
- ²⁴B. R. Krueger and T. Vreeland, Jr., in *Shock Waves and High-Strain-Rate Effects in Materials*, edited by M. A. Myers, L. E. Murr, and K. P. Staudhammer (Marcel Dekker, New York, 1990) (in press).
- ²⁵J. Bach, B. Fultz, and B. R. Krueger (research in progress).
- ²⁶T. Thomas, P. Bensussan, P. Chartagnac, and Y. Bienvenu, source cited in Ref. 4.
- ²⁷R. A. Graham and D. m. Webb, in *Shock Waves in Condensed Matter*, edited by J. R. Asay, R. A. Graham, and G. K. Straub (Elsevier, Amsterdam, 1984), p. 211.
- ²⁸G. E. Korth, J. E. Flinn, and R. C. Green, see Ref. 19, p. 129.
- ²⁹T. Akashi and A. B. Sawaoka, U. S. Patent No. 4 658 830 (April 7, 1987).
- ³⁰A. H. Mutz and T. Vreeland, Jr., see Ref. 26.
- ³¹V. N. Zharkov and V. A. Kalinin, in *Equations of State for Solids at High Pressures and Temperatures* (Consultants Bureau, New York, 1971).
- ³²O. L. Anderson, *J. Phys. Chem. Solids* **27**, 547 (1966).
- ³³*Smithells Metal Reference Book*, 6th ed., edited by E. A. Brandes (Butterworth and Co., Washington, DC, 1983), pp. 8-42.
- ³⁴B. M. Clemens, R. M. Gilenbach, and S. Bitwell, *Appl. Phys. Lett.* **50**, 495 (1987).