

Shock-Induced and Self-Propagating High-Temperature Synthesis Reactions in Two Powder Mixtures: 5:3 Atomic Ratio Ti/Si and 1:1 Atomic Ratio Ni/Si

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The conditions for initiation and propagation of the reaction forming the intermetallic compounds Ti_5Si_3 and NiSi from mixtures of elemental powders of varying porosity have been investigated using shock waves of different pressure and at atmospheric pressure using hot wire ignition in air and in an argon atmosphere. In each case, the reaction either went to completion or the powder remained essentially unreacted. The conditions for the initiation of the reaction in Ti/Si are sensitive to the presence of air. Two regimes of porosity and shock pressure are found for the Ti/Si mixture which cause complete reaction. A low-energy regime with a high initial porosity (producing a low shock pressure) with 0.1 torr of residual air triggers the reaction, while no reaction is observed with a 128 pct higher shock energy and a lower initial porosity (producing a higher shock pressure) when the residual air is replaced with argon. Hot wire ignition of porous Ti/Si powder at room temperature initiates a self-propagating high-temperature synthesis (SHS) reaction more easily in air than in an argon atmosphere, while the Ni/Si powder must be heated to allow the SHS reaction to propagate in high- or low-porosity mixtures in air. These observations are compared to published work on self-sustaining reactions in multilayer films. Reasons for the difference in behavior of the two powder mixtures are discussed.

I. INTRODUCTION

A recently completed study of shock-initiated reactions in equiatomic Ni/Si powder found a threshold shock energy for the reaction forming NiSi.^[1] The threshold was determined to be between 384 and 396 J/g and was found to be insensitive to the shock pressure. The current study explores the shock conditions for the reaction forming Ti_5Si_3 from a mixture of the elemental powders, as well as the conditions for propagation of self-propagating high-temperature synthesis (SHS) reactions at atmospheric pressure in the two powder mixtures.

The chemistry and kinetics of intermetallic reactions have been explored by observing the behavior of multilayer elemental thin-film composites upon heating. It has been shown that in many composite structures, self-sustaining chemical reactions can be initiated upon heating. Bordeaux and Yavari place two basic criteria on whether or not such reactions are possible.^[2] Briefly, the first is that the heat of the reaction must be sufficiently in excess of that required to form melt in the mixture, and the second is that the mixing reaction time must be much shorter than the time for dissipation of the heat of reaction to the environment. Thermally initiated reactions which are not self-sustaining have been observed

in Ti/Si and Ni/Si multilayers as well as in a number of other metallic multilayers.^[2,3,4] Solid-state interdiffusion studies of Ni as well as Ti layers on high-purity amorphous and crystalline Si show the metal silicide phase forms upon deposition and extends upon annealing, with the compound phases forming as equilibrium is approached.^[4] Differential scanning calorimetry scans show at least two exothermic peaks, the first due to the amorphous silicide formation and the second due to crystallization of the silicide.

Self-propagating high-temperature synthesis reactions in elemental powder mixtures have been extensively explored at atmospheric pressure. They may be initiated at one end of a porous sample and may propagate in a homogeneous or heterogeneous mode. Analytic expressions describing the propagation of SHS reactions have been developed.^[5,6] Relevant parameters are the rate of heat release in the reaction front and the rate of heat loss by thermal conduction and radiation. Reaction fronts typically propagate at velocities less than 1 m/s. A shock wave which triggers a reaction typically travels at a velocity on the order of 1 km/s in a powder mixture, reduces the porosity, and deposits shock energy in powder particles in times on the order of 10 ns (for particles of about 20- μ m diameter).^[7] 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 reactions.

The initiation of SHS reactions at atmospheric pressure in Ni/Si and Ti/Si powder mixtures were compared in the present study. The observations suggest possible explanations for the different initiation conditions found for reactions in shocked Ni/Si and Ti/Si powder mixtures.

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II. EXPERIMENT

Aesar -325 mesh Ti powder (99.5 pct nominal purity) was wet mixed in 1,1,2-trichloro-1,2,2-trifluoroethane with CERAC* -325 mesh crystalline Si powder

*CERAC is a trademark of Cerac, Inc., Milwaukee, WI.

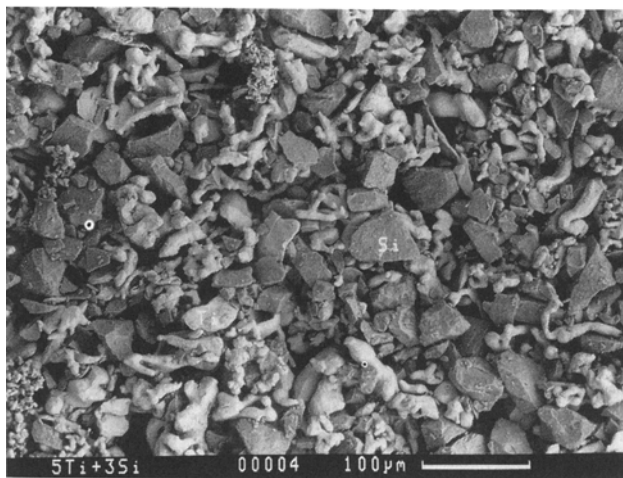
(99.5 pct nominal purity) in a 5:3 atomic ratio and dried in vacuum. The 1:1 Ni/Si powder was similarly prepared. Figure 1(a) is a scanning electron microscope (SEM) image of the Ti/Si powder, and Figure 1(b) is an SEM image of the Ni/Si powder, which has Ni particles (Aesar stock no. 10581) more spherical than the Ti and the CERAC -325 mesh Si.

Shock experiments were conducted using propellant-driven stainless steel flyer plates and a target which produces well-controlled plane-wave shock geometry.^[1] The barrel and powder were evacuated to 0.1 torr just prior to each experiment. In one set of shock experiments, the Ti/Si powder was evacuated, backfilled with argon, and evacuated again. Others contained residual air.

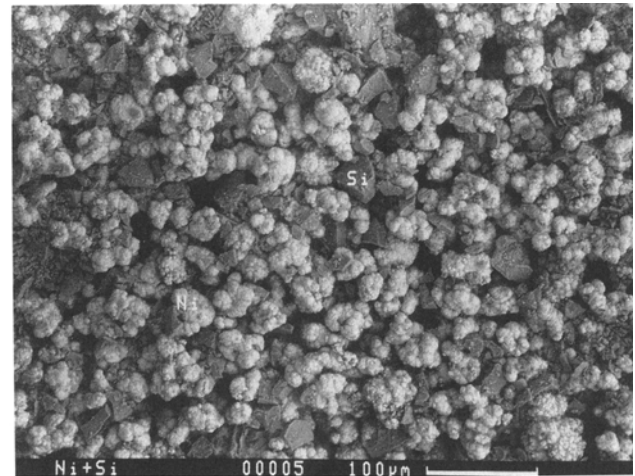
III. RESULTS

Table I lists the results of the experiments on Ti/Si powders pressed to different initial porosity. Shock pressures and energies for the powder mixture were calculated using averaged properties for an inert elemental mixture, as in Reference 1.

The shocked samples were examined by X-ray diffraction, and only Ti_3Si_3 diffraction peaks were observed in the reacted samples. Only Ti and Si diffraction peaks were observed in the unreacted samples. An optical micrograph of a polished surface of the recovered sample shocked to 0.8 GPa and mounted in plastic is shown in Figure 2. The highly porous spongelike structure is typical of SHS material which melted at atmospheric pressure or in vacuum with the evolution of gases.^[8] Figure 3 is a backscattered SEM image of the unreacted shock-consolidated Ti/Si mixture shocked to 2.29 GPa. The Si particles show extensive fracture and no evidence of local mixing or melting. Nickel/silicon powder shocked to just below the reaction threshold is shown in the



(a)



(b)

Fig. 1—Backscattered SEM micrograph of (a) the Ti/Si powder mixture and (b) the Ni/Si powder mixture.

Table I. Shock Reaction Experiments on 5Ti + 3Si Powder Mixtures

Flyer Velocity (m/s)	Porosity (Pct)	Shock Energy (J/g)	Shock Pressure (°C)	Reaction (GPa)
480	48.7	104	0.80	yes*
487	49.2	108	0.80	no
693	46.0	206	1.76	no
757	42.9	237	2.29	no
837	44.4	293	2.61	yes
915	48.7	350	2.67	yes
965	48.7	386	2.95	yes

*Powder with residual O_2 (not backfilled with argon and evacuated before shock treatment)

**Data for calculation of shock energy and shock pressure were obtained from Refs. 9 through 12 using Reuss averages for elastic properties of the mixture as in Ref. 1. Variations in the property values between different references and different averaging methods for the elastic properties of the mixture^[13] give rise to calculated values of shock energy and shock pressure which are within 1 pct of the values listed in the table. Uncertainties in flyer velocity and initial porosity give rise to 1% uncertainty in shock pressure and 2 pct uncertainty in shock energy.

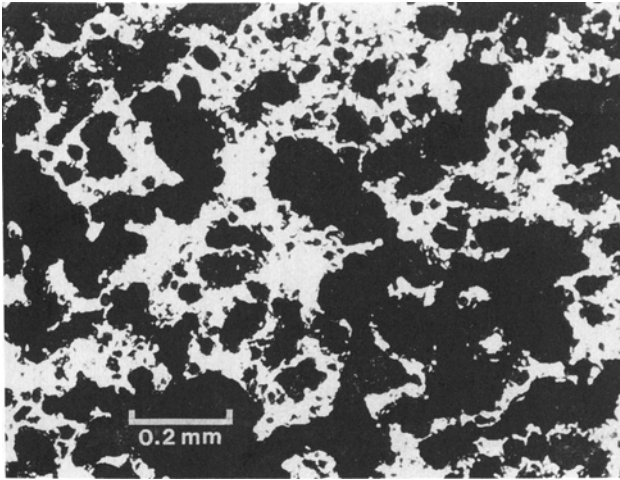


Fig. 2—Optical micrograph of the recovered Ti/Si powder mixture which was shocked to 0.8 GPa showing a spongelike structure identified as Ti_5Si_3 by X-ray diffraction.

backscattered SEM image of Figure 4. The Si particles have fractured, and isolated regions of a mixture of Ni and Si are observed in what appear to have been melt pools. The mixed region in Figure 4 was found to be 21 at. pct Ni and 79 at. pct Si by energy-dispersive X-ray (EDX) analysis.

The SHS ignition behavior of both equiatomic ratio Ni/Si powders and 5:3 atomic ratio Ti/Si powders of high porosity (about 55 pct) and low porosity (near zero, shock consolidated but unreacted) was observed. A 0.13-mm Ta wire was placed in contact with the sample, and a voltage which brought the wire to a white heat was applied to the ends of the wire. The powders were tested in air as well as in Ar. The low-porosity powders did not ignite. The high-porosity Ti/Si ignited more readily in air than in Ar, and the high-porosity Ni/Si did not react. An SHS reaction in high-porosity Ti/Si in contact with low-porosity Ti/Si resulted in complete re-

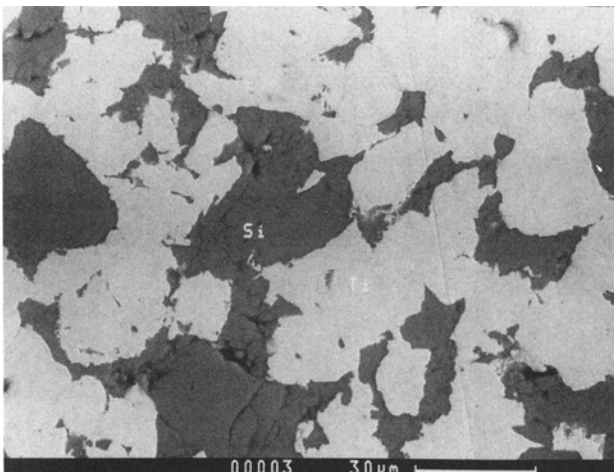


Fig. 3—Backscattered SEM micrograph of unreacted Ti/Si shocked to 2.29 GPa. No titanium silicides were found in X-ray diffraction or EDX analyses.

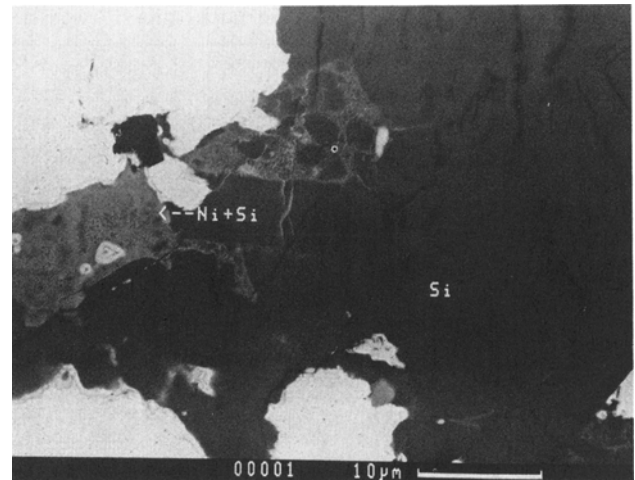


Fig. 4—Backscattered SEM micrograph of a Ni/Si powder mixture (1:1 atomic ratio) shocked to an energy just below that for bulk reaction. Some thin interfacial mixed regions are observed as well as isolated pools of a mixture of Ni and Si. The more typical interfaces show no mixing.

action. The low-porosity Ni/Si was not ignited by contact with an SHS reaction in high-porosity Ti/Si.

IV. DISCUSSION

The shock-initiated reaction in the Ti/Si mixture shows a more complex energy dependence than the Ni/Si mixture. The Ti/Si mixture exhibits reaction behavior which depends upon shock energy and residual gas. A shock energy of 104 J/g initiated the reaction to Ti_5Si_3 with residual air, while no reaction was observed at a shock energy of 237 J/g with residual Ar. The heats of reaction for the formation of Ti_5Si_3 and NiSi are given in Table II for the purpose of comparison with the shock energies for initiation of the reactions. Also given in the table are the energies to heat and melt the reactants and the melting temperatures. Oxidation of Ti in both the shock- and SHS-initiated reactions can account for the relative ease of initiation in Ti/Si powder mixtures compared to Ni/Si mixtures. The critical conditions for the self-sustaining reaction according to Bordeaux and Yavari^[2] are: (a) the heat of mixing must be sufficiently in excess of the energy to form melt in the mixture and (b) the mixing reaction time must be much shorter than the time required for dissipation of the heat of reaction to the surrounding material to prevent quenching of the reaction. The critical condition (a) is met in both systems under shock loading, when the minimum shock energy observed for reaction initiation is added to the reaction energy. Condition (a) is met for SHS reaction of Ti/Si but for not for Ni/Si at 20 °C. Thermal conductivities of Ni, Ti, and Si at ambient conditions are 0.91, 0.22, and 1.49 W/(cm-K), respectively. The rate of heat dissipation is greater in the Ni/Si system and the reaction energy is smaller. Both conditions (a) and (b) favor SHS reactions in the Ti/Si mixture, as observed in this investigation. The effect of residual air on both shock and SHS initiation may be explained by the energy from the

Table II. Thermochemical Properties of Titanium and Nickel Silicides and Oxides

Reactants	Product	Formation Enthalpy (kJ/mole)	Energy to Heat and Melt Reactants (kJ/mole)	Melting Temperature (°C)
Ti/Si	Ti ₅ Si ₃	579.8	558	Ti: 1668 Si: 1410 Ti ₅ Si ₃ : 2130
Ti/O ₂	TiO ₂	944.0	65	TiO ₂ : 1840
Ni/Si	NiSi	89.6	134	Ni: 1453 NiSi: 992
Ni/O ₂	NiO	240.7	55	NiO: 1984

*Formation enthalpy, $-\Delta H_f$, referenced to solid at 25 °C,^[9] energy to heat and melt reactants (from 20 °C) for a mole of product, and melting temperatures in the Ti/Si, Ti/O₂ and Ni/Si, Ni/O₂ systems. For comparison, the lowest shock energy found for reaction to Ti₅Si₃ is 38 kJ/mole with residual O₂ and 100 kJ/mole with residual Ar. The lowest shock energy found for reaction to NiSi is 34 kJ/mole.

oxidation of Ti. The spongelike structure of the shock-reacted material indicates the presence of a liquid phase after the shock pressure was removed.

V. CONCLUSIONS

1. The shock-induced reaction forming Ti₅Si₃ from the stoichiometric elemental powder mixture of Ti and Si exhibits a dependence on shock energy and residual oxygen. Oxidation of Ti triggers the reaction at significantly lower shock energies than that required in the absence of oxygen.
2. Self-propagating high-temperature synthesis reactions are more readily initiated in the Ti/Si mixture than in equiatomic Ni/Si powder mixtures with comparable particle sizes.
3. High shock and chemical reaction energies and low thermal conductivity appear to favor self-propagating reactions in shocked powders, as proposed by Bordeaux and Yavari for thin-film elemental composites.^[2]
4. The shock-initiated reaction produces a spongelike structure, indicating that the reaction initiated by the shock formed solid Ti₅Si₃ after the shock pressure was removed.

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REFERENCES

1. B.R. Krueger, A.H. Mutz, and T. Vreeland, Jr.: *J. Appl. Phys.*, 1991, in press.
2. F. Bordeaux and A.R. Yavari: *J. Mater. Res.*, 1990, vol. 5, pp. 1656-61.
3. R. Sinclair: *Mater. Trans. Jpn. Inst. Met.*, 1990, vol. 31, pp. 628-35.
4. K. Holloway and R. Sinclair: *J. Appl. Phys.*, 1987, vol. 61, pp. 1359-64.
5. A.A. Zenin, A.G. Merzhanov, and G.A. Nersisyan: *Combust. Explos. Shock Waves*, (Engl. Trans.), 1981, vol. 17, pp. 63-71.
6. T. Boddington, P.G. Laye, J. Tipping, and D. Whalley: *Combust. Flame*, 1986, vol. 63, pp. 359-68.
7. R.B. Schwarz, P. Kasiraj, and T. Vreeland, Jr.: in *Metallurgical Applications of Shock-Wave and High-Strain-Rate Phenomena*, L.E. Murr, K.P. Staudhammer, and M.A. Meyers, eds., Marcel Dekker, New York, NY, 1986, pp. 313-27.
8. W.F. Henshaw, A. Niiler, and T. Leete: ARBRL-MR-03354, Ballistics Research Laboratory, Aberdeen Proving Ground, Aberdeen, MD, 1984.
9. *Smithell's Metals Reference Book*, 6th ed., E.A. Brandes, ed., ch. 8, pp. 24-27.
10. O.L. Anderson: *J. Phys. Chem. Solids*, 1966, vol. 27, p. 547.
11. *LASL Shock Hugoniot Data*, P.S. Marsh, ed., University of California Press, Berkeley, CA, 1980.
12. A.L. Ruoff: *J. Appl. Phys.*, 1967, vol. 38, pp. 4976-80.
13. J.P. Watt: *Rev. Geophys. Space Phys.*, 1976, vol. 14, pp. 541-63.