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REPRINTED FROM:

SHOCK COMPRESSION OF CONDENSED MATTER - 1991

Proceedings of the American Physical Society Topical Conference held in Williamsburg, Virginia, June 17-20, 1991

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1992

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SHOCK COMPRESSION OF CONDENSED MATTER 1991
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SHOCK SYNTHESIS OF SILICIDES

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Niobium, molybdenum, and titanium silicides were synthesized by shock waves travelling through mixtures of elemental powders; the explosively generated impact experiments were carried out on powders at ambient temperature and pre-heated to 500°C. The unreacted, partially reacted, and fully reacted regions were mapped and correlated with pressure and energy levels predicted from computations. Characterization of the partially reacted regions (for Nb-Si) showed that melting of silicon is a critical requirement for the initiation of the reaction; niobium dissilicide spherules nucleate and grow at the Nb-Si interface and eventually detach themselves. Concurrently, solid state diffusion of Si into Nb creates Nb_5Si_3, which acts as a barrier for further reaction. In parallel experiments on Nb-Si diffusion couples heated to 1200°C, it is found that the same reaction sequence occurs ($NbSi_2 \rightarrow Nb_5Si_3$). A preliminary analysis is conducted based on the requirement for silicon melting for reaction to occur. This analysis predicts critical melt pool sizes for reactions, which can be correlated to shock energy. Two important parameters in this analysis are: the heat of reaction and the thermal diffusivity of the components.

1. INTRODUCTION AND EXPERIMENTAL METHODS

Shock-induced chemical reactions have been studied since the 1960's. The bibliography by Graham *et al.* [1] lists all the relevant work prior to 1983. It is well known that full reaction can occur in time scales of microseconds. In this paper, we characterize and analyze shock-synthesized silicides. The experimental systems and conditions are described elsewhere by Ferreira *et al.* [2] and Yu and Meyers[3]. The synthesis was carried out in the Sawaoka system[4] using impact velocities of 1.2 and 1.9km/s. Pre-heating of the system to 500°C was accomplished using a discardable furnace. The elemental powder mixtures (sizes <44μm) were compacted to densities of approximately 60% (40% porosity) prior to shocking. After the shock experiments, capsules were sectioned for mapping the reacted regions. Scanning and transmission electron microscopy was conducted to fully characterize the microstructures of the unreacted, partially-reacted, and fully-reacted regions.

2. RESULTS AND DISCUSSION

Figure 1 shows the maps of the cross-sections for the Nb-Si system, in which fully-reacted, partially-reacted, and unreacted regions are shown. Upon recovery and sectioning, portions of the specimens were lost, since they were considerably cracked. The Ti-Si specimens had apparently completely reacted in a highly energetic manner, perforating the capsule along the disc axis with loss of the material. The following qualitative statement can be made: increases in impact velocity, at ambient temperature, and in pre-shock temperature, from 20 to 500°C, result in an increase in the extent of reaction.

The energy contours predicted from CSQ simulations conducted at Sandia National Laboratories by Norwood and Graham[5] are shown in Figure 2. These simulations were conducted using rutile at ~60% theoretical density as a model material. These energy levels are not isochronal, but rather correspond to the maxima at each point. A central spike evident along the axis of the disk is due to the convergence of waves. Comparing the energy profiles to the profiles of the three regions in Figure 1, in a semi-quantitative manner, it is possible to establish energy (or pressure) levels required for shock-induced reactions to occur. Since the correlation with the energy levels is clearer, it is possible to speculate that an energy of ~700J/g

is required for the initiation of the reaction. For the 500°C experiment, on the other hand, the enhanced reaction produced by this additional thermal energy can be incorporated by adding the term $E_{th}=c_p \Delta T = 220J/g$ to the energy curves; the temperature-corrected curves are shown in Fig. 2(c).

The thermodynamics of the process is simply modeled by adding the energy of reaction (approximately equal to the heat of reaction) to the conservation equation:

$$E_2 - E_{00} = \frac{1}{2} P_1 (V_{00} - V) + Q$$

Figure 3 shows pressure vs. specific volume curve. This treatment predicts an increase in pressure, particle velocity, and shock velocity with reaction. Implied in these results is the assumption that the reaction is completed instantaneously, at the front. The approach delineated above has been introduced by Boslough[6], Horie and Kipp[7], and Yu and Meyers[4] The shifting of the P-V curve to the right with reaction was first experimentally established by Batsanov *et al* [8]. The threshold energy of 700J/g is also shown.

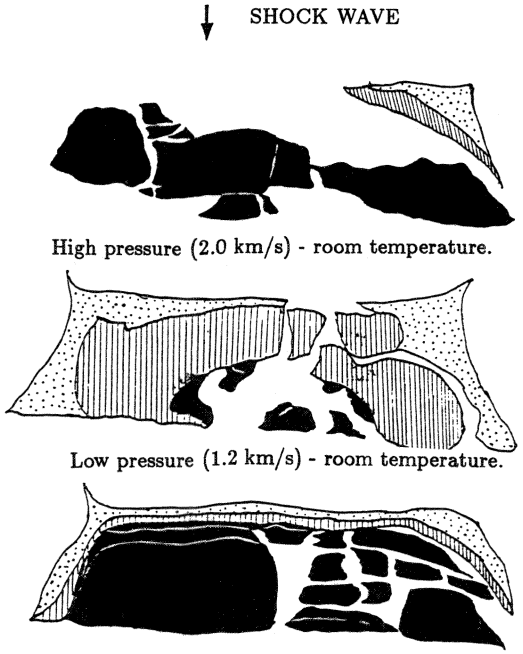
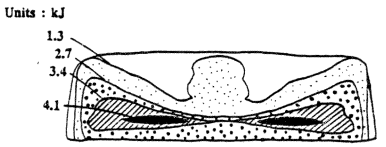
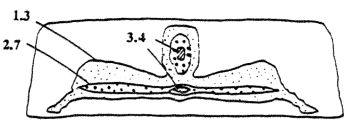


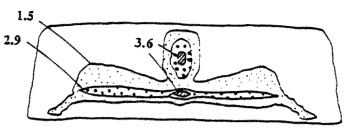
FIGURE 1
Mapping of unreacted, partially-reacted, and fully-reacted regions for Nb-Si subjected to impacts at 1.2km/s(20°C), 1.2km/s(500°C), and 2.0km/s(20°C).



(a)
Energy contours for impact velocity 1.3 km/s at room temperature.



(b)
Energy contours for impact velocity 1.3 km/s at room temperature.



(c)
Energy contours for impact velocity 1.3 km/s at 500 C.

FIGURE 2
Maximum energy contours for Nb-Si subjected to impacts at 1.9 and 1.3km/s (results replotted from computations by Norwood and Graham[5]).

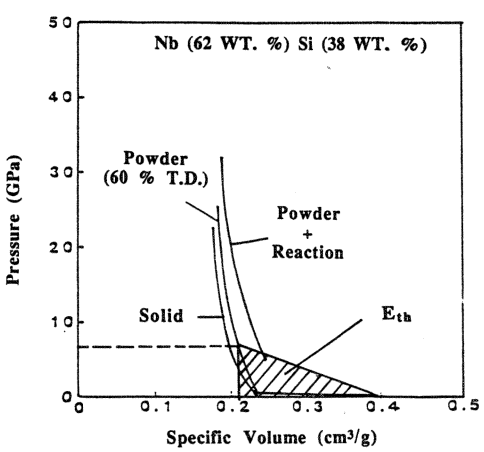


FIGURE 3
Pressure-specific volume Hugoniot for Nb(62wt.%)-Si(38wt.%) powders (60%TD) with and without reactions.

At the microstructural level, the sequence of events leading to shock synthesis in niobium silicides was analyzed by examining the partially reacted regions. Figure 4(a) shows a scanning electron micrograph of a partially reacted region. The niobium particle shows an external

shell into which diffusion of silicon has occurred. The silicon particles melt and totally surround the niobium particles. At the solid/liquid interface, small $NbSi_2$ crystals nucleate and then detach themselves from the interface, "floating" into the molten silicon. Transmission electron microscopy [Figure 4(b)] was used to identify these silicide particles, which are monocrystalline, and possess a shape determined by the surface energy growth kinetics. The picture that emerges from these observations is that silicon plastically deforms to a much larger extent than the niobium particles and eventually melts due to this preferential energy deposition process. The chemical reaction initiates at different points along the interface with the nucleation and growth of solid $NbSi_2$. The pressure gradients are such that the molten silicon is in a state of agitation for the duration of the shock pulse. The disilicide particles detach themselves from the interface once they reach a critical size, and subsequently dragged into the liquid silicon. After the pulse decays, silicon solidifies and the particles remain embedded in it.

Based on these observations, we can propose a simplified model for the initiation and propagation of shock-induced reactions. Figure 5(a) shows the shock energy required to melt silicon for both homogeneous and heterogeneous energy deposition exclusively in the silicon; the change in melting point of Si with pressure has been incorporated in the calculation. By adding the energy of reaction (900J/g) to the shock energy, the curve shown in Figure 5(b) is obtained. Clearly, the energy required to completely react the specimen is lower than the energy required to initiate it, and as such, the reaction should self-propagate (under shock) once initiated. A certain critical molten fraction of silicon (E_{th} ~700J/g, which corresponds to 0.2 - 0.5 melting fraction in Fig. 5(a)) is needed to initiate the reaction. This threshold melting fraction results from a balance between heat generation and heat loss, and these two competing mechanisms determine the arrest or propagation of the reaction. A formal treatment will use the simplified configuration shown in Figure 6(a). The heat transfer equation is:

$$\dot{Q} + \rho c_p \frac{\partial T}{\partial t} = k\left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r}\frac{\partial T}{\partial r}\right)$$

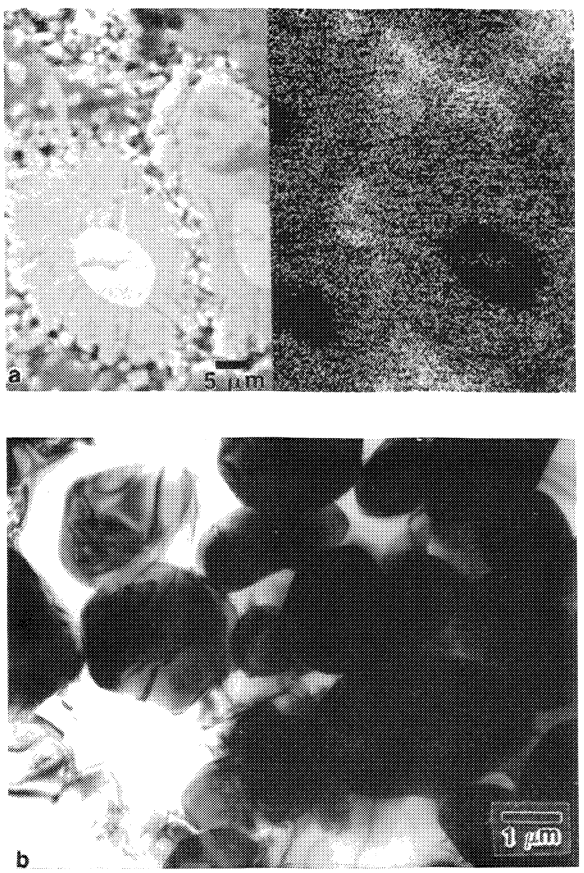


FIGURE 4
(a) SEM and (b) TEM of partially-reacted region showing monocrystalline $NbSi_2$ particles nucleated along interface.

where ρ is the density, c_p the heat capacity, k the thermal conductivity, r the radius of the molten pool at time t=0, and $\dot{Q}$ is the heat generation rate; the above equation is for a centrosymmetric problem. The heat evolution, from the reaction, can be described by:

$$\dot{Q} = 4\pi r^2 K H_r \exp\left[-\frac{\Delta H}{RT} H(T - T_m)\right]$$

where $4\pi r^2$ is the surface of the molten region over which reaction occurs, K is a pre-exponential kinetic factor, H_r is the enthalpy of reaction, ΔH the activation energy for the reaction, and $H(T - T_m)$ a Heaviside function (reaction rate = 0 at $T<T_m$, where T_m is the melting point). A simpler approach, taken from the "hot spot" theory of Rideal *et al.*[9], was implemented and is shown in Figure 6(b). The heat losses from spherical molten pools of varying radii as

a function of time are shown. The heat generated (instantaneously) by the reaction in the molten pool is also shown. Thus, when the heat of reaction exceeds the heat loss from the molten pool, the reaction propagates; when it is lower, the reaction stops. This is a mechanistic complement to the "threshold energy" model of Krueger and Vreeland[10], and Krueger *et al.*[11]. Further development of this analysis is ongoing, and comparison with other shock-synthesis reactions is underway.

This research was supported by the National Science Foundation Materials Processing Initative Grant CBT 87 13258. Discussions with Drs. R. A. Graham and N. N. Thadhani are gratefully acknowledged.

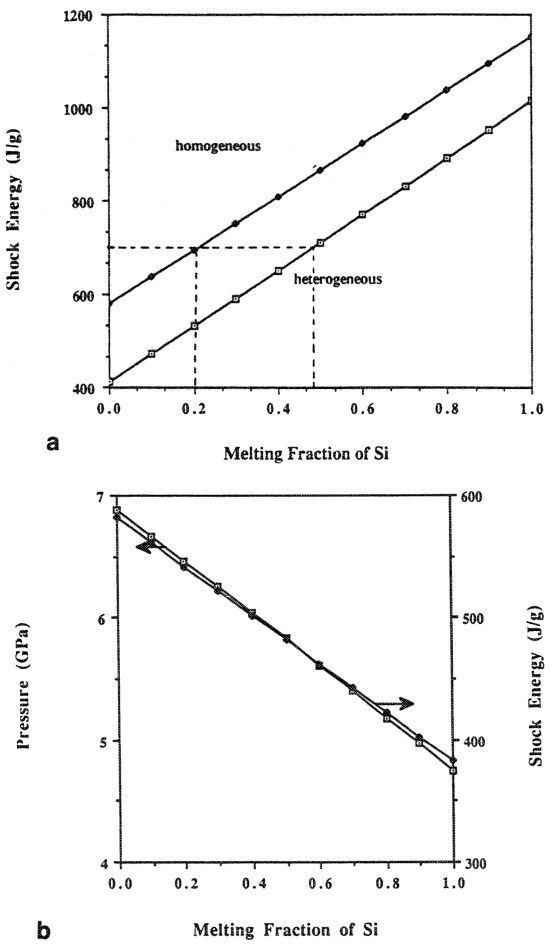


FIGURE 5
Shock energy vs. melting fraction (a) without and (b) with incorporation of heat of reaction (melting fraction determines reacted fraction).

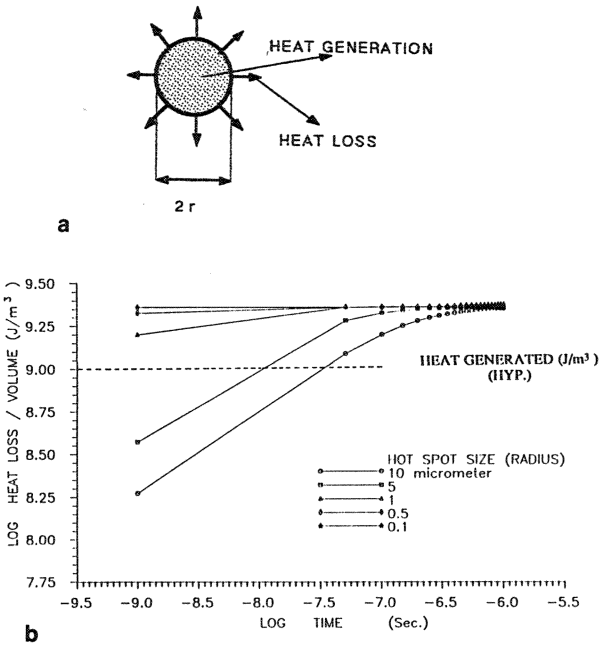


FIGURE 6
(a) "Hot spot" model and (b) calculated heat losses for different sizes and heat generation (instantaneous) from synthesis.

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