SHOCK SYNTHESIS OF NIOBIUM SILICIDES

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Elemental powder mixtures with two sizes (<5 μm and 15-45 μm) were shock compressed at 20, 46, and 70 GPa using a 20 mm-bore two-stage gun. Specimens were 10 mm in diameter and 0.5 mm thick. The powders were contained in a Cu capsule and impacted by a Cu projectile. The results for small <5 μm powder particles indicate that the experiments produced unreacted, partially reacted, and fully reacted $NbSi_2$, respectively, as predicted. Results for the larger 15-45 μm particles at 46 GPa indicate that reactions to form $NbSi_2$ did not occur during shock compression. This observation is consistent with the expectation that larger powder particles require more time to react. All the micrographs indicate that the powders are relatively mobile in the capsule and that some reactions are caused by plastic deformation after release of the shock.

INTRODUCTION

Following the first report by Batsanov, Deribas, and co-workers [1], a considerable amount of activity has taken place in the field of shock-induced chemical reactions. Recently, Vecchio *et al.* [2] and Meyers *et al.* [3] have attempted to develop a quantitative predictive understanding of shock-induced reactions in silicide systems. The results reported here represent the extension of this work. The particle size was varied in order to assess its effect on reaction kinetics.

EXPERIMENTAL TECHNIQUES

The niobium and silicon powders were obtained from CERAC and had sizes smaller than 44 μm (-325 mesh). The powders were separated in a vibrating microsieve, yielding two size ranges: <5 μm and 15-44 μm. The powders were mixed in the stoichiometric proportion $NbSi_2$ (twice the atomic composition for Si vs. for Nb). The powders were encapsulated in the LLNL capsule configuration shown in Figure 1(a) using a laser ruler, a microbalance, and a mechanical powder-tapping device. In this way, the initial specimen powder density (60% of theoretical) was obtained reproducibly in the specimens. The capsule diameter is 10 mm and thickness is 0.5 mm; this ensures a shock geometry that is close to one-dimensional (planar front propagating through powder) in contrast to the earlier experiments [2-4], in which the capsule geometry was such that two-dimensional effects dominated. Each Cu capsule was embedded in a steel recovery fixture and mounted in the target chamber of the 20 mm-bore two-stage gas gun at LLNL. The capsule recovery fixture assembly was impacted by copper flyer plate mounted in a plastic sabot [5, 6]. Three impact velocities of 0.96, 1.92, and 2.66 km/s yield shock pressures, in copper, of 20, 46, and 70 GPa, respectively. The pressure in the specimen powder "rings up" to the impact pressure. The first pulse traveling through the porous medium generates a lower pressure in the first wave, by virtue of the shock-impedance. The three pressures were chosen specifically to achieve unreacted, partially reacted, and fully reacted $NbSi_2$ from Nb + 2Si powder mixtures, based on previous shock melting calculations for Fe powders [7], a similar transition metal, which showed that about 50 GPa are required to achieve melting. Melting and temperatures close to it in the solid state are expected to produce rapid chemical reactions. To enhance the reaction rate in this fast experiment (~0.5 μsec), small particles (<5 μm) were used. Lower reaction rates were expected for larger particles, one experiment was done with 15-45 μm particles at intermediate pressure. To obtain relatively high quench rates to "catch" the high-pressure state, a thin (0.5 mm) specimen layer was used in a Cu capsule with a high cooling rate.

RESULTS AND DISCUSSION

Three impact experiments were conducted for the < 5 μm powder, at velocities of 0.96, 1.92, and 2.66 km/s. The objective of these experiments was to determine the threshold energy for shock synthesis, a concept proposed by Krueger *et al.* [8]. The unreacted, partially reacted, and fully reacted regions are shown in Figure 1(b). As shown in Figure 1, the elemental powder mixtures were essentially unreacted, partially reacted, and fully reacted at 20, 46, and 70 GPa, respectively. These observations are made by optical inspection of material near mid-radii where undesirable late-time edge effects on axis and on the outer boundary are ignored. The larger particles at 46 GPa are essentially unreacted on shock compression.

Figure 1 shows that the capsules underwent considerable deformation with increasing pressure, with material being pushed into the periphery, and by the formation of a central jet along the axis of the disk. On the periphery, the material was pushed into the threaded area of the capsule by the high hydrostatic stresses and, most probably, pressure gradients due to shock wave convergence along the axis of the disk. Figure 1(b) shows that there is a strong preference for reaction in the regions where the material underwent intense late-time plastic deformation (periphery and central axis) on release. Whereas the material was virtually unreacted at the 0.96 km/s impact, it was fully reacted after 2.66 km/s impact. Figure 1(b) does not show any marked effect of particle size at the 1.9 km/s impact velocity. The only difference is that the central jet is partially reacted for the large particles. Scanning electron microscopy observations show the observed differences.

Figure 2 shows unreacted (a) and trace amounts of partially reacted (b) regions from the

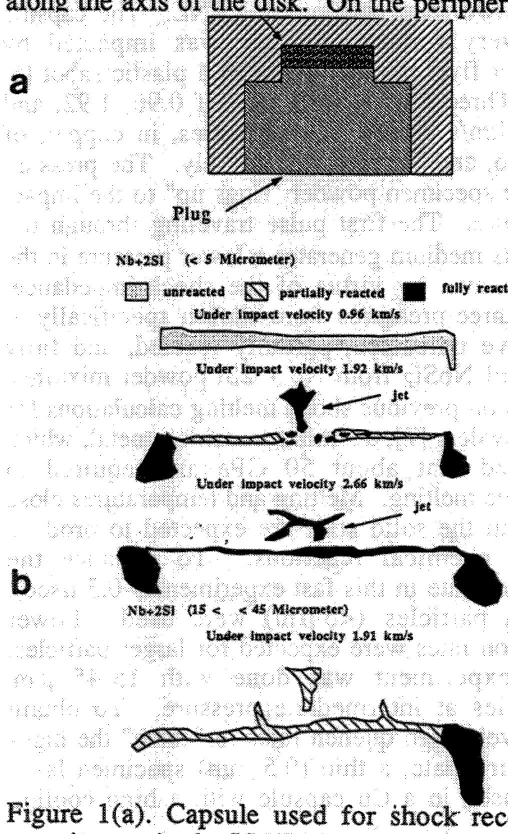

Figure 1(a). Capsule used for shock recovery experiments in the LLNL 6.5-meter-long 2-stage gas gun. (b). Unreacted, partially reacted, and fully reacted regions for capsules; notice late time formations of central jet and lateral extrusions, probably caused on release.

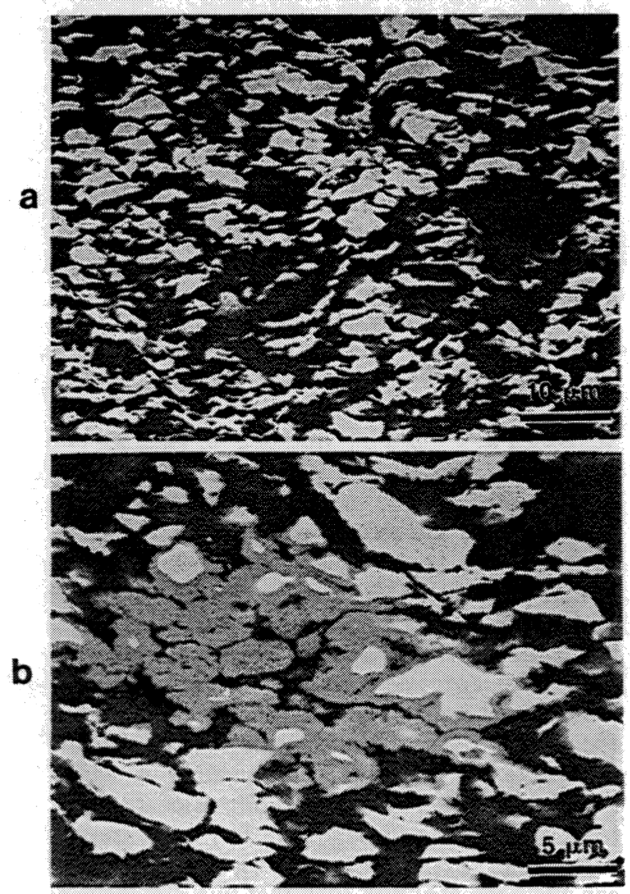

Figure 2. Fine (<5 µm) powder impacted at 0.96 km/s; (a) unreacted area; (b) partially reacted area (possibly, after shock-wave passage).

fine powder impacted at 0.96 km/s. The partially reacted region shown in Figure 2(b) represents only trace amounts. It is probable that the partial reaction occurred after shock-wave passage, through diffusive processes. As the impact velocity is increased to 1.92 km/s, the material (fine powder) was either partially or fully reacted. The periphery and core were fully reacted, and the imtermediate region was partially reacted, as can be seen from Figure 1(b). The fully reacted region probably caused by release at late time showed profuse evidence of full-scale melting and some capsule melting (Figure 3(a) and (c)). Dendritic growth is evident in Figure 3(c) showing the edge of the capsule, while the center shows particulate $NbSi_2$ in (probably) a Si matrix. The partially-reacted region (Figure 3(b)) shows $NbSi_2$ spherules (gray) in the silicon matrix and along the Nb-Si interfaces. This mechanism of reaction is shown in Figure 4 [2, 3]. Reaction is initiated at the Nb (solid)-Si (liquid) interface (a). After it has proceeded to a certain extent (c), surface (interfacial) forces become dominant, and the liquid reaction product agglomerates, forming spherules (d). These spherules then solidify and are extracted from the interface by the motion of the liquid silicon or by forces exerted by the next generation of spherules that is being formed.

At 2.66 km/s impact velocity, the fine powder is fully reacted, with the morphology of the product consisting of a mixture of particulate silicides (center) and dendritic growth (corners).

The 15-45 μm powder exhibited, at the impact velocity of 1.91 km/s, features similar to the <5 μm powder (see Figure 5). The principal difference is the larger Nb particles; see Figures 5(a) and 3(b). The total Nb-Si interface available for reaction is greater for the <5 μm powder, aiding the reaction. The kinetics are accelerated for the small powder size. In the fully reacted region (periphery), massive Nb particles can still be seen for the 15-45 μm powders (Figure 5(b)), whereas they are totally consumed for the <5 μm powder (Figure 3(c)).

An additional surprising effect was established. Dremin and Breusov [9] and Al'tshuler [10] suggested that local heating of material in zones of intense slip could influence the kinetics of reaction, and Yu [11] and Shang

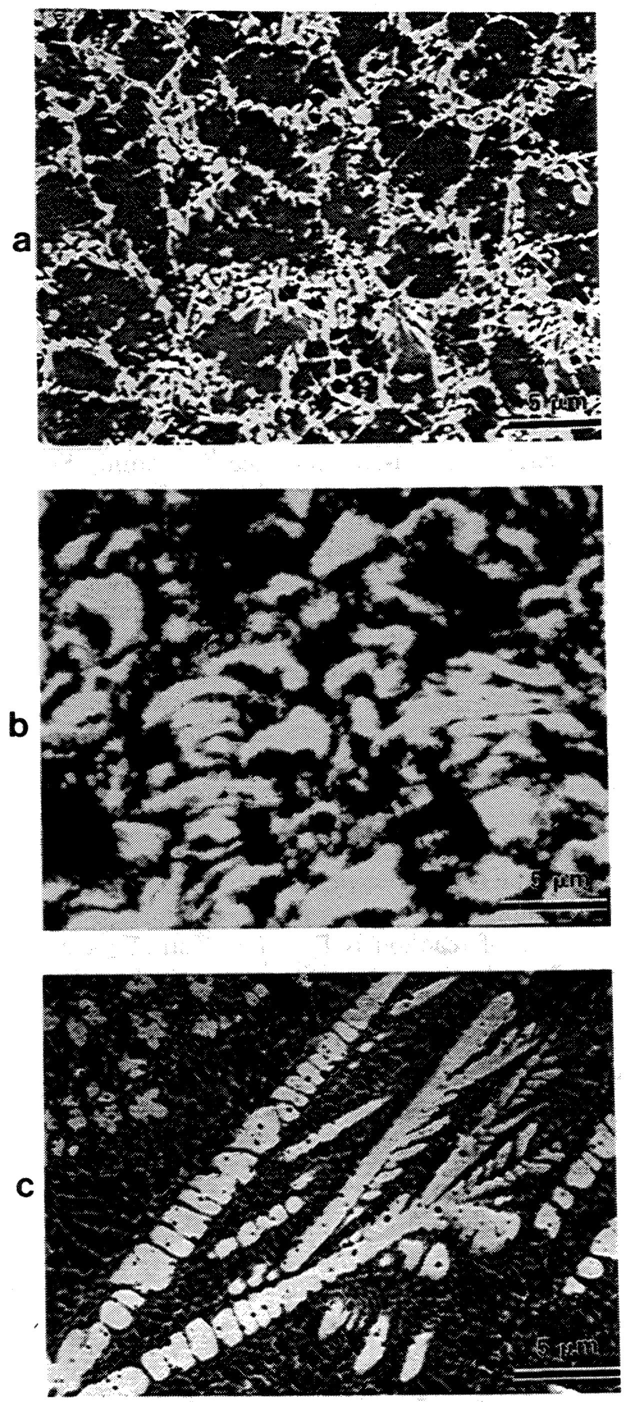

Figure 3. Fine (<5 μm) powder impacted at 1.91 km/s; (a) fully reacted area in center region; (b) partially reacted area; (c) fully reacted area from extruded peripheral region.

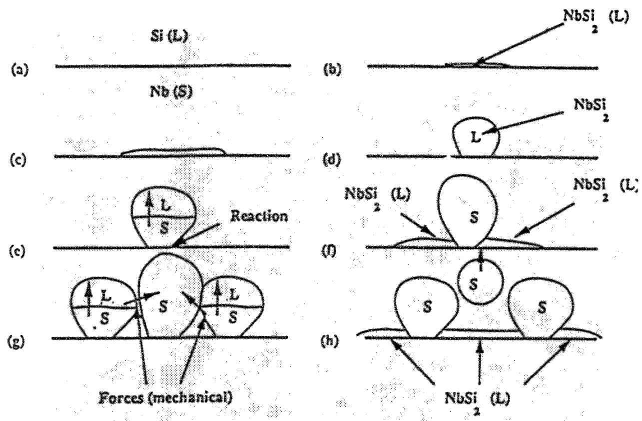

Figure 4. Idealized representation of propagation of reaction at Si-Nb interface (Nb-solid; Si-liquid).

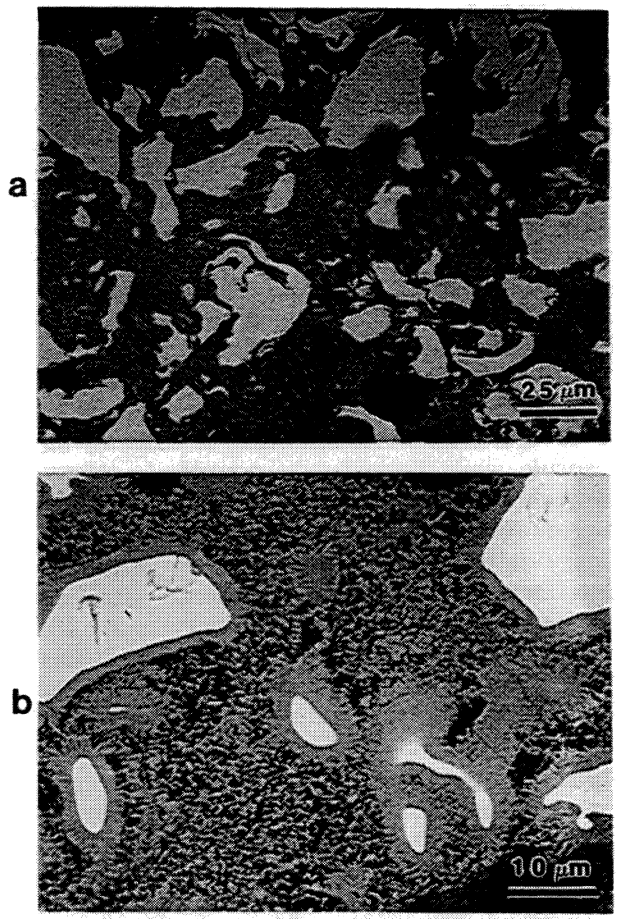

Figure 5. Coarse (5-44 µm) powder impacted at 1.91 km/s; (a) partially reacted area; (b) fully reacted area showing remnants of Nb particles.

[12] observed a reaction enhancement in regions of localized shear. The results reported herein strongly suggest that shear strains play an important role in shock-induced chemical reactions, confirming suggestions [9, 10] and observations [11, 12]. The peripheral and central regions experienced more extreme reaction because the additional plastic strains on release at late time. The energy deposited into the powders by the shock can be expressed as $E_1=1/2\ P(V_{00}-V)$, whereas the plastic deformation energy can be taken as $E_2=\tau\gamma$, where τ and γ are shear stress and strain. The total energy contributing to initiation of reaction is $E_1 + E_2$. Thus, E_2 can contribute significantly to process.

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REFERENCES

1. S. S. Batsanov, A. A. Deribas, E. V. Dulepov, M. G. Ermakov, V. M. Kudinov, *Comb. Expl. Shock Waves USSR* **1**, p. 47 (1965).
2. K. S. Vecchio, L.-H. Yu, and M. A. Meyers, *Acta Met. et Mat.*, in press (1993).
3. M. A. Meyers, L.-H. Yu, and K. S. Vecchio, *Acta Met. et Mat.*, in press (1993).
4. L. H. Yu and M. A. Meyers, *J. Matl. Sci.*, **26**, p. 601 (1991).
5. C. L. Seaman, E. A. Early, M. B. Maple, W. J. Nellis, J. B. Holt, M. Kamegai, and G. S. Smith, in *Shock Compression in Condensed Matter - 1989*, Elsevier, 1990.
6. A. J. Gratz, W. J. Nellis, J. M. Christie, W. Brocious, J. Swegle, and P. Cordier, *Phys. and Chem. of Min.*, **19**, p. 267 (1992).
7. W. J. Nellis, W. H. Gourdin, and M. B. Maple, in *Shock Waves in Condensed Matter*, Elsevier, 1987.
8. B.R. Krueger, A. H. Mutz, and T. Vreeland, Jr., *J. Appl. Phys.* **70**, p. 5362 (1991).
9. A. N. Dremin and O. N. Breusov, *Russian Chem. Rev.* **37**, p. 392 (1968).
10. L. V. Al'tshuler, *J. Appl. Mech. Tech. Phys.* **19**, p. 496 (1978).
11. L. H. Yu, Ph.D. Thesis, NMIMT (1992).
12. S. S. Shang, Ph.D. Thesis, UCSD (1992).