

CHEMICAL REACTIONS IN CONTROLLED HIGH-STRAIN-RATE SHEAR BANDS

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Controlled high-strain-rate shear bands were generated in porous mixtures (Nb+Si, Ti+Si) using axially symmetric experimental configurations ("Thick-Walled Cylinder") method. Shear strains up to 100 and strain rates of approximately 10^7 sec^{-1} were generated inside shear bands. Particle fracture, melting, and regions of partial reaction were observed inside shear bands for the Nb+Si system. Under the same conditions of deformation, for the Ti-Si system the reaction initiated inside shear bands and propagated through the entire sample.

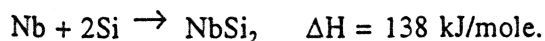
INTRODUCTION

The role of intense shear in the initiation of chemical reactions and phase transformations under mechanical deformation was emphasized by Bridgman[1], Dremine and Breusov[2], Graham[3], Batsanov[4] and others. Nesterenko et al.[5,6] developed an experimental technique providing conditions for controlled high-strain-rate shear bands. In this paper this method is applied for the comparative investigation of shear induced reactions in porous Nb+Si and Ti+Si mixtures.

EXPERIMENTAL SET-UP

The thick-walled cylinder method[6] was applied for Nb-Si (68-32% by weight), and Ti-Si(74-26% by weight) systems. The powders were purchased from CERAC and had sizes of -325 mesh (<44 μm).

These two systems have widely different enthalpies of reaction ΔH :



This results in widely different sensitivity to initiation and ease of propagation.

Two experimental configurations, shown in Figure 1, were used. In Configuration 1 (Figure 1a) porous mixtures with a density of 2 g/cm^3 for Nb-

Si and 1.87 g/cm^3 for Ti-Si (~50% of theoretical value) were initially densified by an explosive (explosive 1, Figure 1a) with a low detonation velocities (2.5 km/sec and 3.12 km/sec, respectively) up to a density of 3.2 g/cm^3 (~75% of theoretical value for Nb-Si) and 3.4 g/cm^3 (~90% of theoretical value for Ti-Si)).

In the next stage ($R_0=11\text{mm}$) these composite cylinders were collapsed by an explosive charge (explosive 2, Figure 1b) with a detonation velocity of ~4 km/sec, density of 1 g/cm^3 , and an outer diameter of 60 mm. It produced plastic deformation highly localized in shear bands. The measurements of the segment lengths of collapsed layer indicate that shear localization started in the first stage of material movement, at overall effective strain of ~0.1. The values of r and r_1 (radii of porous layer after collapse) for Nb-Si mixture were equal 5.9 and 7.5 mm; initial values are 8.1(r_0) and 9.35 mm (r_{10}). For Ti-Si mixture: $r = 6.05 \text{ mm}$ ($r_0 = 8 \text{ mm}$), $r_1 = 7.5 \text{ mm}$ ($r_{10} = 9.15 \text{ mm}$).

Conf. 2(Fig. 1c) was used for the same powders (density 2 g/cm^3 for Nb-Si and 1.78 g/cm^3 for Ti-Si) as in Conf. 1. The inner and outer diameters of tubular cavity were 16.4 mm and 21.7 mm, respectively, $R_0=11 \text{ mm}$. A few layers of amorphous ribbon were placed along the cylinder walls to initiate shear localization in the powder at an early stage of collapse. The average values of r and r_1 were equal to 6.5 and 8.1 mm (Nb-Si) and

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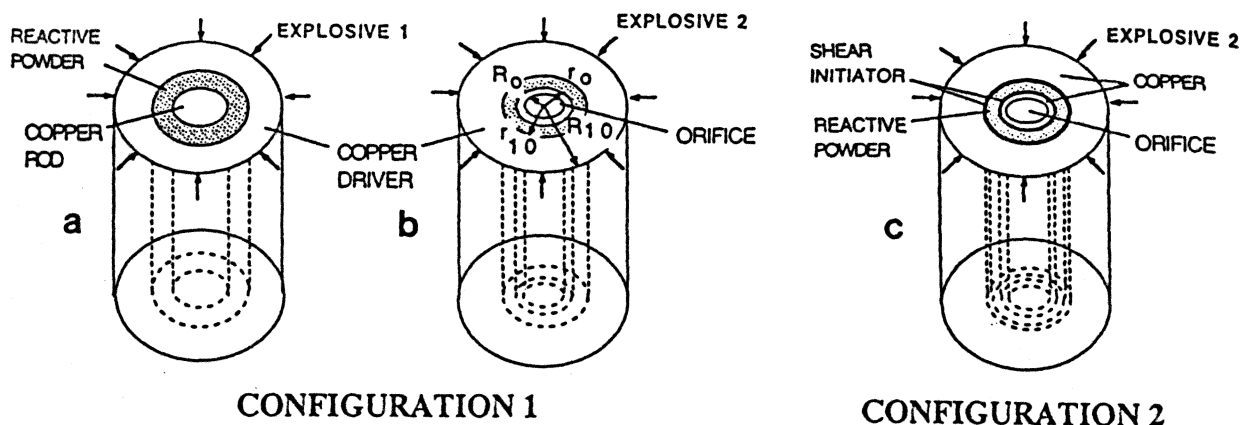


FIGURE 1. Geometry and sequence of deformation events in thick-walled cylinder method.

6.05 mm, 8.4 mm for Ti-Si mixture. The comparison between the data for the two mixtures indicates that overall strains were close.

EXPERIMENTAL RESULTS

Nb-Si mixture: Fig. 2 shows the cross-section of specimen tested in Configuration 2. The overall shear strain γ inside the shear zone (simple shear) is the ratio of the shear displacement, Δ and thickness of shear band, δ . The former is in the range $\Delta \sim 100$ -600 μm and δ varies between 5 and 10 μm for Conf. 1, and 10-20 μm for Conf. 2. The strains γ inside shear bands are found to be in the range 10-100 and shear strain rates $\dot{\gamma}$ are 10^6 - 10^7 s^{-1} [5,6].

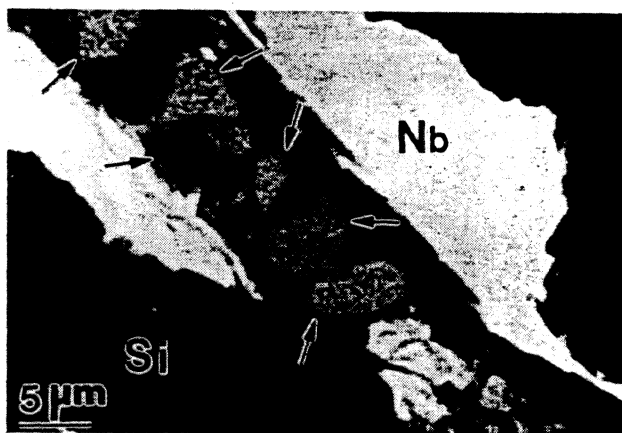


FIGURE 2. Shear band with reacted material inside (shown by arrows), Nb-Si mixture

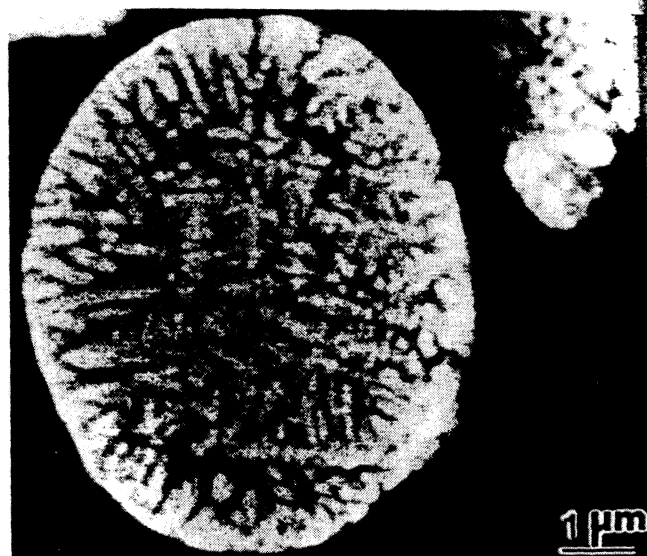


FIGURE 3. The structure of reaction product for Configuration 2, Nb-Si system.

Shear localization seems to produce partial melting of one component (Si), as in shock wave loading, as shown by Meyers et al. [7]. The multiple fracturing of the Nb particles due to shear localization, at the mesolevel, leads to a decrease of the initial particle size from 44 μm to 0.1 - 2 μm , resulting also in intense heating of the newly created thin particles. Material flow inside the shear band is unstable and results in vortex formation [5,6]. The combination of these effects (melting of Si, fracturing of Nb and

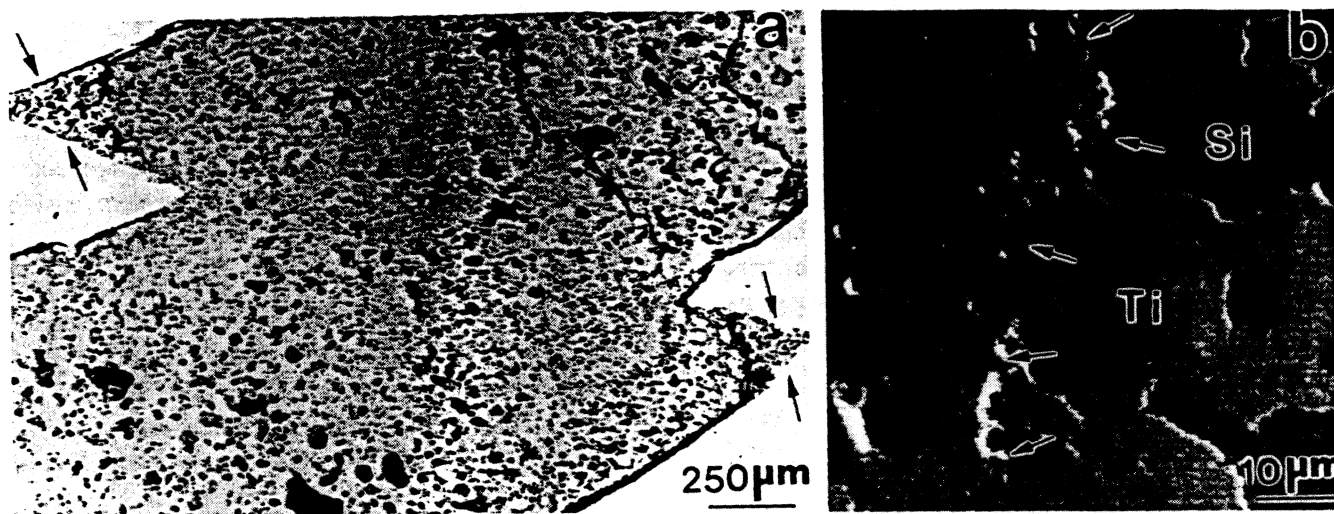


FIGURE 4. (a) - Overall view of shear band in Ti-Si mixture (Configuration 1); (b) - structure of reacted-unreacted material interface (shown by arrows) near inner copper wall.

vorticity) provides the reaction product inside shear band with the sizes up to 8 μm (Figs. 2,3) for Configuration 2.

Ti-Si mixture: The deformation of this mixture also resulted in localized plastic flow, Fig. 4a. However, unlike in the Nb-Si mixture, the reaction propagated throughout most of the specimen. Small triangular regions, adjacent to the copper wall (shown by arrows in Fig. 4a) remained unreacted. The structure of reacted compact is depicted in the Fig. 4b. The evaluation of shock pressure in the first wave (< 2GPa) allows to conclude that shock did not play an essential role in initiation of chemical reaction[8] and that shear bands are the main reason for it.

The average values of Vickers microhardness, measured in mixtures after different stages are: 177 (Conf. 1, stage 1), 914 (Conf. 1, after collapse), and 970 (Conf. 2). They demonstrate that reaction took place for Conf. 1(after collapse) and Conf. 2.

MECHANISM OF REACTION INSIDE SHEAR BAND: COMPARISON WITH SHOCK WAVES

On the basis of the observations a mechanism of *shear-assisted* chemical reaction can be proposed. The main stages are:

(1) Nb particles are split into foils with thickness on the order of magnitude of 0.1-1 μm by

localized mesoshear. They are heated as a result of intense shear deformation which precedes their formation and have "fresh" surfaces.

(2) Reaction begins due to the extensive relative flow of Nb particles and Si inside the shear band, which is accompanied by melting. The reaction proceeds along the Nb(silver)-Si interfaces, with thickness l_r up to 1 μm as mentioned by Thadhani[9].

(3) Instability of gradient flow on another, larger scale inside shear band, results in vorticity and the coiling of partially reacted Nb foils (as snow balls) together with adjacent Si into rounded particles with diameters up to 8 μm. Vorticity can also promote the collection of partially reacted small particles to the center of rotation, providing typical sizes of reaction product on the order of 1 μm.

(4) Reaction continues up to the scale length D_r in places where temperatures are sufficiently high and is then quenched by the surrounding material. This mechanism enables the evaluation of the size of final reaction product D_r [6]:

$$D_r \approx l_r \gamma. \quad (1)$$

It is important to emphasize that Equation (1) represents the connection between the size of reaction region at the microlevel and the dimensions of reacted particles at the macrolevel determined by mechanical shear movement of material.

The reaction inside shear band for Ti-Si mixture develops in the same manner. The propagation of the reaction in this case throughout the entire sample is mainly accomplished due to the differences in enthalpy of reaction.

The main differences between shear and shock assisted(induced) chemical reactions are due to essential differences in displacements of neighboring particles. Under shock-wave loading the relative displacements of particles are comparable or less than the particle sizes at normal porosities close to 50 % and cannot induce essential particle fracture, as is observed inside shear band[5,6]. This is also responsible for flow instabilities, enhancing the reactivity of mixtures.

EVALUATION OF THE REACTION TIME

The time of reaction can be evaluated from the time of shear band quenching. For the Nb-Si system reaction was quenched as a result of heat removal to the relatively cold material outside shear band. Taking the thermal diffusivity for surrounding material as $k \sim 0.1 \text{ cm}^2/\text{s}$, $\delta \approx 10 \text{ }\mu\text{m}$, the quenching time τ_q and \dot{T} are obtained:

$$\tau_q \sim \delta^2 / \kappa \sim 10^{-5} \text{ s} \quad (2)$$

$$\dot{T} \sim \Delta T / \tau_q \sim 10^3 \text{ K} / 10^{-5} \text{ s} \sim 10^8 \text{ K/s} \quad (3)$$

Reaction products can have either a microdendritic or a microcrystalline(Fig. 3) structure[5,6]. The secondary dendrite-arm spacings of the reaction product $\lambda \approx 0.1 \text{ }\mu\text{m}$ (Fig. 3) enable independent evaluation of cooling rate. The value is of the same order of magnitude as Eqn. 3: $\dot{T} \approx 10^8 \text{ K/s}$ [6]. This confirms that the reaction products inside the shear bands were formed during 10^{-5} s .

It is worthwhile to mention that only the beginning of spherule formation is noticeable in Figs. 11a, 12[6], being very well developed for shock assisted chemical reactions for the same materials[7]. The mechanism of their formation can be connected with the instability of planar reaction-diffusion front[10].

CONCLUSIONS

The thick-walled cylinder method was successfully applied to generate controlled, high-rate localized reactive shear bands in heterogeneous, porous materials with overall parameters inside shear bands up to $\gamma = 100$, $\dot{\gamma} = 10^7 \text{ sec}^{-1}$. A mechanism of *shear-assisted* chemical reaction, qualitatively different from the one observed for shock-wave loading, is proposed. It predicts a linear dependence of the reaction product size on shear strain. For Nb-Si mixtures, reaction was restricted to shear bands, but for Ti-Si system(with the heat of reaction three times higher) the reaction, initiated inside shear bands, propagated throughout the entire specimen, with exception of small regions, adjacent to copper driver tube, where it was arrested due to rapid heat transfer.

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