

SYNTHESIS REACTIONS BEHIND SHOCK FRONTS

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Data on the shock compressibility of stoichiometric mixtures of tin and sulfur and tin sulfide indicate that SnS synthesis reactions take place behind a shock front in a mixture of its components. In studies of the effect of shock waves on reactive compositions the time and conditions under which a reaction takes place are the fundamental questions. The shock compressibility of tin and the corresponding mixture of tin and sulfur is studied here in order to examine this problem.

The shock adiabat of a mixture of nonreacting substances is determined as an additive quantity from the shock adiabats of the components [1-3]. If a reaction takes place behind the shock front, then the location of the experimentally determined shock compressibility of the mixture plotted on pressure-specific volume (p - V) axes will differ from the computed curve after some threshold value p^* . If the specific volumes of the mixture and reaction product are close and the reaction itself is highly exothermic, then the experimental curve will deviate to the right (toward lower compressibility) owing to thermal back pressure. This must be the case for the reaction $\text{Sn} + \text{S} = \text{SnS}$ where the interaction will occur in a compressed state, since the specific volumes of SnS and Sn + S are close (0.194 and 0.213 cm^3/g , respectively) and the thermal yield of the reaction is $\Delta H_0 = 727 \text{ kJ/kg}$ [4].

Test samples were prepared in the form of disks with a diameter of 50 and height of 5 mm. The mixture samples were pressed from carefully mixed powders of tin and sulfur with particle sizes of 5-10 μm . The average initial specific volume of the samples of tin sulfide was $0.216 \pm 0.002 \text{ cm}^3/\text{g}$ and of the mixture samples, $0.229 \pm 0.004 \text{ cm}^3/\text{g}$. Thus, the porosity of the prepared samples was 1.12 and 1.06 for tin sulfide and for the Sn + S mixture. The shock adiabats were determined by the modified reflection method proposed by Altshuler. A shock wave was introduced into the sample from a screen made of material with a known shock adiabat chosen such that its dynamic rigidity was somewhat lower than that of the test material. A manganin probe was placed in the screen a distance of 1-2 mm from the test material to measure the pressure in the incident and reflected shocks. The parameters of the shock wave in the test sample were calculated from the pressure-mass velocity U diagram under the assumption of mirror reflection in the shock adiabat for secondary compression of the screen material. This method makes it possible both to determine the parameters as the discontinuity decays and to evaluate the processes taking place in the sample from the pressure profile. Teflon disks, with a shock adiabat of the form $D = 2.180 + 1.584 U$, where D is the shock front velocity [5], were used as screens in all the experiments.

A shock wave was excited in the screen by an 84-mm-diameter, 100-mm-high plated explosive charge. Initiation was by means of a plane wave generator. The pressure in the screen and in the sample, which was mounted in a Teflon holder, was measured by the manganin probe. The pressure was varied by using different explosives. A correction was introduced in the location of the experimental points on the p - V and p - U diagrams for the deviation in the pressure profile from rectangular owing to the trailing unloading wave.

A typical oscilloscope trace (x is the coordinate, t the time) and p - U diagrams for calculating the shock parameters in a test sample are shown in Figs. 1a-c. The origin in the x - t diagram corresponds to the time the shock front reaches the probe. The pressure in the incident shock front in the screen corresponds to point 0 on the oscilloscope trace. As the shock front propagates the distance h_0 from the probe to the test sample the parameters in the front may drop owing to the action of the unloading wave moving from the back surface of the explosive charge. The pressure in the front at the moment it reaches the sample surface is equal to the pressure recorded by the probe at time t_1 and corresponds to point 1 on the oscilloscope trace. Since the distance h_0 is small, all the characteristics on the diagram may be regarded as straight lines. Then the interval t_1 can be determined by jointly

Moscow. Translated from *Fizika Goreniya i Vzryva*, Vol. 22, No. 6, pp. 134-137, November-December, 1986. Original article submitted December 16, 1985; revision submitted July 11 1986.

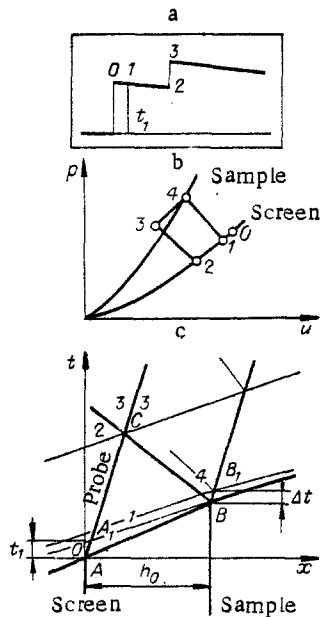


Fig. 1

Fig. 1. A typical $x-t$ oscilloscope trace and $p-U$ diagram for calculating the shock parameters in a test sample.

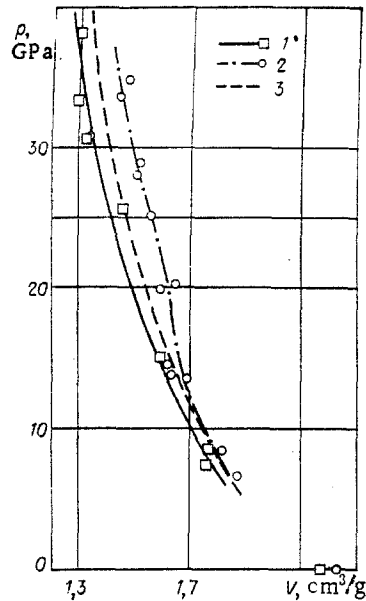


Fig. 2

Fig. 2. The shock adiabat of tin sulfide (points 1) and of a stoichiometric mixture of Sn + S (points 2). (Points 3 denote the shock adiabat of an inert Sn + S mixture.)

solving the equations for the shock front (AB) and the characteristic (A_1B) which catches up with the front during the time it approaches the sample:

$$t_1 = (U_0 + c_0 - D_0) / D_0 c_0 \cdot h_0,$$

where c_0 is the post-shock sound speed in the screen (calculated in the acoustic approximation).

Before the reflected shock wave reaches the probe (point C in Fig. 1) the pressure ahead of the shock front corresponds to point 2 and that behind the front corresponds to point 3. These quantities are read directly from the oscilloscope trace. The pressure and mass velocity in the test material at the boundary with the screen are determined from the $p-U$ diagram at point 4, where the isentrope 3-4 intersects the shock adiabat 1-4 for secondary compression of the screen. It should be noted that this yields the state of the material at the screen-sample interface at point B_1 (see Fig. 1c). The shock-compressed material arrives at B_1 after a time interval Δt following the emergence of the shock front at the boundary (B). This method, therefore, makes it possible to determine the parameters of the state of the test material a time Δt after the shock front has passed through it. We determine Δt from a joint solution of the equation for the trajectory of the front of the incident AB and reflected BC shock waves in the screen, the trajectory of the probe AC and the screen-sample interface, and the trajectory of the characteristic B_1C which catches up with the front of the reflected shock at the moment it reaches the probe:

$$\Delta t = \frac{h_0}{D_0 c_4^2} (U_0 - U_4) (c_4 + D_0 - U_0)$$

(U_4 and D_4 are the mass velocity and shock front velocity in the screen at the interface with the sample and c_4 is the sound speed behind the shock in the screen).

Experimental data on the shock compressibility of SnS and a stoichiometric mixture of sulfur and tin are shown in Fig. 2. The smooth curve denotes the shock adiabat of tin sulfide, given by the equation $D = 2.370 + 1.156 U$ and the dashed curve denotes the shock adiabat of an unreacted Sn + S mixture calculated with the porosity taken into account. (The shock adiabats of sulfur and tin were taken from [5].) The dot-dashed curve shows the experimentally-measured shock compressibility of this mixture. Up to $p \approx 13-15$ GPa the exper-

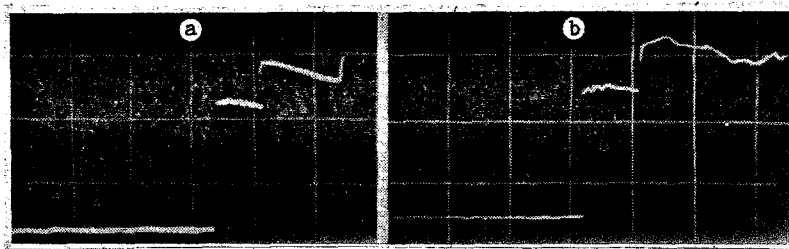


Fig. 3. Oscilloscope traces of the pressure in shock waves recorded by a manganin pressure probe. (One division corresponds to 1 μ sec.)

Experimental points for the mixture correspond to the calculated shock adiabat without a reaction. For $p > 15$ GPa the points deviate to the right, providing evidence of energy release from a reaction in the shock-compressed mixture immediately adjacent to the shock front. This is also indicated by the shape of the pressure profile recorded by the manganin probes.

Figures 3a and b show oscilloscope traces of the pressure for compression of tin sulfide and of an Sn + S mixture. In both cases, the pressure of shock compression lies in the neighborhood of 75 GPa. As can be seen from Fig. 3b, a pressure rise is observed behind the shock front in the mixture. This may indicate that synthesis of tin sulfide is taking place with energy release. In this experimental setup the probe receives information on processes taking place at the sample-screen boundary $\approx 0.05 \mu$ s after the shock enters the sample. Judging from the location of the experimental points for Sn + S, this time is quite sufficient for the reaction to take place to a considerable extent. Knowing the mutual location of the shock adiabats of the inert and reacting mixtures, it is possible to determine the specific heat released during the reaction:

$$Q_v = E_2 - E_1 = 1/2 \cdot (p_2 - p_1) (V_{00} - V),$$

where E_1 , p_1 and E_2 , p_2 are the energy and pressure, respectively, on the shock adiabats of the inert and reacting mixtures compressed to the same volume V . V_{00} is the initial specific volume of the mixture. Calculations based on this scheme for $V = 0.156 \text{ cm}^3/\text{g}$ show that $Q_v = 136.7 \text{ kJ/kg}$.

If we assume that the reaction yield is independent of the pressure and temperature, then it is possible to estimate the extent of the reaction. Using the standard value of ΔH_0 , we find that after $\Delta t = 0.05 \mu$ s a fraction $\alpha = Q_v/\Delta H_0 = 0.27$ has reacted, i.e., a quarter of the material has been transformed immediately adjacent to the shock front. An analysis of these experiments shows that if the relative error in determining the parameters of the shock adiabat of the reacting mixture is 5%, the accuracy in calculating the inert shock adiabat is 5%, and the mean scatter in the initial density of the samples is 1.6%, then the maximum relative error in determining the specific heat of the reaction and the fraction of reacted material is $\sim 30\%$, i.e., the determination of the fraction of reacted material has the character of an estimate.

These experiments, therefore, indicate that tin sulfide is synthesized from the solid components during dynamic compression near the front of shocks with $p > 15$ GPa. This suggests that diffusion processes proceed at a high rate during shock compression of the test mixture.

The physical explanation for the high rates of diffusion processes during shock compression of mixtures of materials with different dynamic rigidities is that the difference in the mass velocities of the components may reach values on the order of kilometers per second. (For Sn + S at $p = 10\text{--}40$ GPa, $\Delta U = 0.7\text{--}2.0 \text{ km/sec}$.) With such huge velocities particles of one type will be pressed through particles of the other type, thereby ensuring rapid mixing of the materials.

This model also explains the threshold character of reactions under shock compression; the reaction begins at a pressure for which the forced diffusion velocity (relative velocity of the particles) is sufficient to penetrate through a particle of a given size. In our case, the threshold diffusion velocity $v_d = 0.9 \text{ km/sec}$ ensures passage over a distance of $10 \mu\text{m}$ (the mean particle size) in $0.1 \mu\text{sec}$, which is of the same order of magnitude as the experimentally measured chemical reaction time. Here it is clear that the reaction time with shock compression will depend on the mechanical properties of the components and their degree of dispersion.

The authors thank E. V. Lazareva and N. N. Shevtsova for preparing the test samples.

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