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We measured the velocity of shock waves generated by the detonation of a high explosive in a stoichiometric (equimolar) mixture of Zn and S powders. The initial decrease in the velocity of the shock wave in a sample was then found to be followed by a remarkable increase in the velocity of shock wave propagation. This observation can be explained by the occurrence of the exothermic solid-state reaction $Zn+S \rightarrow ZnS$ in the zone of high dynamic pressure. The observed solid-state detonation represents a new type of transport phenomena in reactive media which may be expected to find important practical applications. © *2006 American Institute of Physics*.
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In conventional detonation, we are dealing with fast exothermic reactions of decomposition accompanied by vigorous gas evolution leading to the significant expansion of the reaction products. In this process, a released energy is spent on the compression of the unreacted matter in a layer adjacent to the reaction zone and on the initiation of chemical transformation within this layer. Such a mechanism of energy transfer induces the layer-by-layer chemical reaction and self-sustained wave propagation of the reaction zone at a supersonic velocity. But the presence of the gas phase is not a prerequisite for the occurrence of detonation. The classical theory of detonation (see, e.g., Ref. 1) imposes no limitations on the state of aggregation of matter neither before nor behind the front of detonation wave. The possibility of solid-state detonation has been predicted theoretically.[2,3] The formulated conditions for detonation were as follows: (i) exothermicity of chemical reaction; (ii) high reaction rate; and (iii) expansion of matter during the adiabatic process while the reaction products relax to the initial pressure. The last condition is most important, although the expansion of matter may be not as large. Even an insignificant change in a volume of condensed material during its compression requires exceedingly high pressure. That is why a relatively small increase in the specific volume of material in the zone of the solid-state reaction gives rise to a huge work on the compression of matter out of the reaction zone. This compression is sufficient for the initiation of chemical conversion in the material. Note that material heating does not play a key role in the acceleration of the chemical reaction. In solid-state processes, a key role belongs to the processes of crushing (activation) and mixing in contrast to gas- and liquid-phase reactions controlled by temperature and diffusion.

Earlier,[3] we carried out experiments with the T–C–Al-paraffin system: Al was added to the gasless T–C system as a substance with strong thermal expansion to satisfy condition (iii) and paraffin, in order to diminish the sample porosity. In this system, the shock wave (also generated by high explosives) was found to initially decay and then to accelerate. But the process in the earlier system can hardly be regarded as the solid-state one; at best, it can be classified as the low-gaseous detonation. The attempts to detect the solid-state detonation in the gasless Mn–S system *failed to demonstrate the existence of self-sustained detonation*.[4,5]

In this work, we used an equimolar powder mixture of Zn and S. The highly exothermic reaction $Zn+S \rightarrow ZnS$ (the reaction heat is 202 kJ/mol) proceeds without gas evolution and, *due to thermal expansion of the product* (the volume change is about 7%, see Ref. 6), satisfy the earlier conditions for detonability. The particle size of Zn and S powders was 3–5 μm while the sample density (ρ), 60%–70% of theoretical.

The experimental setup is shown in Fig. 1. A mixture was pelleted into cylinders 16.5 mm in diameter and 40–200 mm long. Samples 4 were placed in tubular container 5 made of a porous composite (with a low velocity of sound propagation) in order to exclude the effect of elastic waves in the container walls on the results of measurements. Shock waves were generated by detonation of charge 2 (TNT/RDX, 40 mm in diameter, 35 mm height, detonation velocity $D=7.85$ km/s). In the experiments, we measured the time interval τ between the arrival of the shock wave at sensors (contact gauges) 3 and 6. To avoid the sample discontinuity, the gauges were only placed on their top and bottom. The

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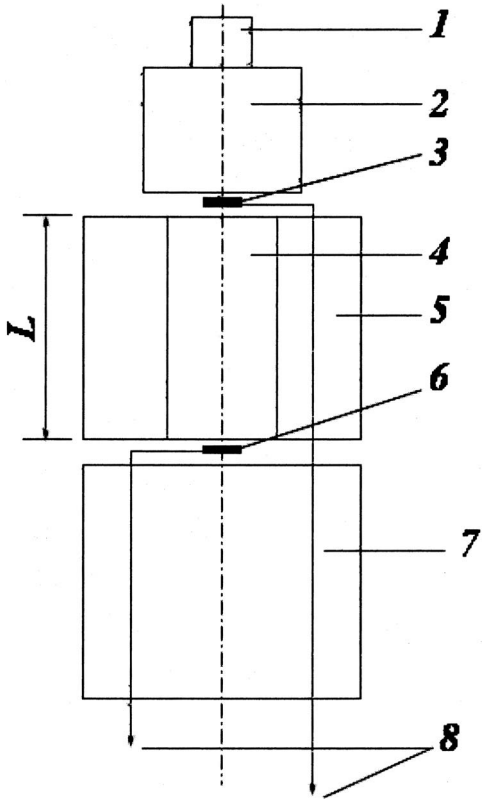

FIG. 1. Experimental setup: (1) detonator, (2) charge of high explosive, (3, 6) contact sensors, (4) Zn–S sample, (5) container (made of porous composite), (7) stand, (8) wire leads to oscilloscopes; and L is the gauge length.

gauge length L was measured prior to experiment. The average velocity of shock wave propagation through a sample was determined from the expression $\bar{D}=L/\tau$. At the sensor thickness 200 μm, the contact gap was 100 μm. The estimated measurement error (δ) was 0.6% at $L=40$ mm and diminishes with increasing gauge length down to 0.1% at $L=200$ mm. Signals from sensors 3 and 6 were recorded with two storage oscilloscopes Tektronix TDS 1012 (main and doubling ones). Experiments were carried out at 14 °C. The data obtained are collected in Table I.

In the absence of a chemical reaction, the shock wave generated in the sample could be expected to decay at a distance of 1.5–2 diameters from the top due to side rarefication. Experimental shock wave velocity measured in a corresponding inert system (final product ZnS) drops to zero at a distance of 25–30 mm from the sample top. So, a minimal sample length (40 mm) was chosen such that, in the absence of chemical replenishment, sensor 6 would give no signal altogether. Experimental data for the trials when both the sensors gave their signals are presented in Table I. This implies that the process of shock wave propagation was supported by the energy released in the chemical reaction taking place in the zone of high dynamic pressure.

TABLE I. Experimental data.

Experimental run	L(mm)	$\bar{D}$(km/s)	ρ(%)	δ(%)
1	40	2.27	68.1	0.6
2	60	1.30	63.0	0.2
3	75	1.64	71.6	0.2
4	90	1.39	60.7	0.2
5	100	2.55	62.4	0.2
6	150	2.195	63.5	0.1
7	150	1.915	62.4	0.1
8	200	2.169	59.4	0.1

As follows from Table I, the shock wave velocity $\bar{D}$ initially drops sharply from starting 7.85 km/s (at a charge of high explosive) down to 1.30 km/s (at $L=60$ mm) and then grows up to above 2 km/s (for $L=100-200$ mm). Some scattering can be attributed (a) to a random character of detonation initiation in some points behind the shock wave front, (b) possible occurrence of several detonation modes and transition processes between them,[7] and (c) some variation in the induction period for chemical reaction. Theoretical estimation for an ideal detonation in the monolith matter under study was calculated[8] from experimental Hugoniot of ZnS using a corresponding heat reaction (see earlier) and Grunaisen coefficient. It gives value of $D=2.486$ km/s. If we take into consideration that in our experiments $\rho=60\%-70\%$ theoretical (monolith), the measured $\bar{D}$ values well agree with the theoretical prediction for the detonation process. Longitudinal sound velocity in the initial powder mixture of Zn and S at the mentioned density was measured as well. It was about 0.6 km/s. If we take into account that volumetric sound velocity is always less than longitudinal, than the wave process we observed is supersonic.

The data of x-ray diffraction analysis of the products taken at the bottom of container 5 (Fig. 1) show a virtually complete conversion of a starting mixture into zinc sulfide (ZnS) (only trace amounts of Zn were detected), which confirms the occurrence of a chemical reaction in the shock wave. The action of the high temperature was also noticed on the surface of sensor 6 (it was charry), that indirectly supports the presence of highly exothermic reaction.

The observed acceleration of the shock wave can be regarded as experimental evidence for the occurrence of solid-state detonation in the system under study. Note that when we record a steady propagation of the shock wave, there always exists a probability that the observed process is weakly decaying and, hence, not self-sustained but the experimental accuracy is not sufficient for noticing this on a limited gauge length. In contrast, the observation of acceleration (as in our experiments) leaves no grounds for doubt in the occurrence of the detonation in the material under study.

The phenomenon of solid-state detonation represents a new type of transport phenomena in reactive media. The phenomenon may find its application, e.g., in mining where the shattering action of explosives is being used while the presence of gaseous products is not desirable. Just like solid-state synthesis by combustion, detonation-mediated synthesis in the solid state may also turn out useful in the preparation of various compounds and materials.

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