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DETONATION-LIKE PHENOMENA IN Al/S MIXTURE

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INTRODUCTION

Solid-phase chemical reactions caused by shock wave compression have been much investigated during last forty years. [1-3]. Contrary to static loading, shock waves drastically accelerate running of physical-chemical processes. Shock waves when propagating in reactive mixtures initiate a variety of the processes promoting chemical reactions. These processes could be the following: moving and intermixing of the components; heterogeneous heating-up of particles; plastic deformations, generation of fresh surfaces; disintegration of the initial component structure; phase transitions etc.

Previously with the help of optical pyrometry, there were observed shock-induced exothermic reactions in sulphur-metal (Mg, Al, Ti, Sn, Cu, and Fe) mixtures [4-7]. Pressed samples of the mixtures with porosity less than 10% were tested. Radiation of shocked samples emitted through transparent window was recorded by optical pyrometer. Within first 0.1 – 0.3 μ s there were obtained relatively high brightness temperatures for the mixtures of sulphur with Mg, Al, and Ti (2800 K, 3000 K и 2250 K respectively). The conducted calculations have allowed estimating a degree of chemical transformation. The comparison with experimental data has shown that for mixtures Mg/S 43/47 and Al/S 55/45 the completeness of reacting is of ~0.2 and ~0.5 respectively. The mixture Al/S can be considered as the most reactive among tested ones. This mixture was taken for further studies.

MATERIALS TESTED

Aluminium sulphide is produced according the reaction:

$2\text{Al} + 3\text{S} = \text{Al}_2\text{S}_3(\text{solid}) + 172.9 \text{ kcal/mol}$ [8]
Stoichiometric composition of initial mixture corresponds to the mass ratio 36% Al and 64% S. Theoretical maximum density (TMD) of the mixture is 2.26 g/cc. The reaction proceeds with increase of specific volume, Al_2S_3 density 2.02 g/cc (20 °C) [9]. Of course, in the reaction zone Al_2S_3 can be not in the solid phase and the heat effect could decrease. Non-reacted components can also undergo phase transition when heated. This is particularly true for sulphur having low melting (112.8 °C) and boiling (444.6 °C) temperatures.

For pyrometric studies dense samples were manufactured by cold pressing from preliminary mixed sulphur powder and Al ones. Al content was varied from 35 to 75 % wt. Mean particle size of sulphur was 10 μ m. There were used different Al powders: spherical Al – coarse (~ 600 μ m), fine (~ 6 μ m – ASD-4), ultra-fine (<100 nm - UDA) and flaked Al pyrotechnic powder – PP-1, PP-2 and PAP-2 with flakes 1-2 μ m of thick and cross-sectional sizes 50-120 μ m and 20 – 80 μ m respectively. Porosity of the pressed samples depended both on Al mass content and particle size, but it did not exceed 10%. The samples were 40-mm diameter and 3-3.5-mm thick. For comparison there were conducted experiments with non-reactive mixtures S/LiF. Mean particle size of LiF was 20 μ m. There were also tested low-dense samples with porosity up to 80%.

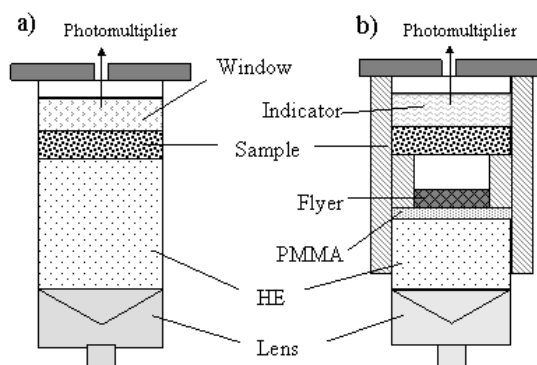


FIGURE 1. Experimental assemblies for temperature and pressure measurement

OPTICAL PYROMERY RESULTS

The pressure-time histories as well as temperature ones were obtained with the help of dual-channel optical pyrometer. Brightness temperatures were measured applying so-called window technique. The indicator technique [10] was used for measuring of pressure profiles. Thus the tests were performed with two types of the experimental assemblies. They are shown in Fig. 1.

Using first one (see Fig. 1a), there were recorded time histories of radiation emitted by shocked mixtures through transparent material – window. Handling radiation histories, there were obtained brightness temperatures averaged over two effective wavelength 720 and 420 nm. Optical LiF crystals and water were used as the windows. Their shock Hugoniot lies above and below shock Hugoniot of tested mixture in pressure–particle velocity plane, respectively. Reflected shock wave, in one case, and rarefaction in another affected the measured temperature histories.

Using another type of experimental assembly, there was recorded radiation emitted by shocked liquid indicator placed in-contact with tested sample. Two indicators were used - tetrachloride carbon and bromoform. For them, there are known

shock Hugoniot, isentrope of compressed state and temperature–pressure relationships. Hence one can transform time history of radiation measured from the shock front propagating through an indicator to pressure history nearby interface.

Shock waves in samples were generated either by impact of Al flyer accelerated by detonation products of booster charge or by detonation products of HE charge placed in-contact with the tested sample. Shock pressures given below in Figures were obtained basing on the known shock Hugoniot and parameters of shock wave generators. Hugoniot of the tested samples were calculated as for non-porous mixtures of non-reacting components assuming additivity of specific volumes of the components.

In Fig. 2, there are given brightness temperature time-histories obtained with LiF as the window. Both Al content and particles' size were varied. Shock wave was generated by RDX charge. Closed symbols are for the mixtures with coarse Al, open ones - for the mixtures with PP-1; the same symbols are used for the compositions with the same Al content. (These notations are used everywhere below.) As one can see for all mixtures measured temperatures lie above 2400 K - the temperature observed in shocked pressed sulphur samples in 0.5 μ s after shock wave had entered LiF window.

In the tests with PP-1, one can observe slow temperature decrease after first 0.2 μ s. Variation of the composition from stoichiometric one results to temperature decrease, but the range within it is varied is not large. In case of 35/65 and 55/45 compositions, there is a slight temperature increase within 0.2–0.3 μ s. For compositions with coarse Al, there was observed sharp luminosity flash-up within first 0.15 μ s followed by slow radiation increase. Contrary to mixtures with fine Al, measured temperatures grow with Al content increase

though variation of the composition from the stoichiometric one increase too. For compositions 75/25 of different particles' sizes, temperatures level off by 0.8 μ s (see curves 3 and 4, Fig. 2).

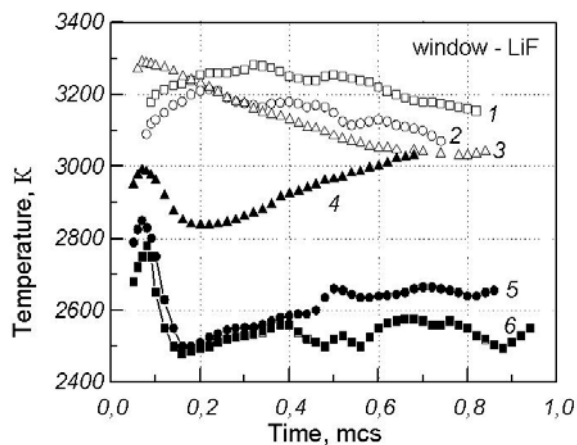


FIGURE 2. Temperature-time history for Al/S 55/45 measured at the interface with LiF-window. 1, 6 - Al/S 35/65 P=33.0 (40.7); 2, 5 - Al/S 55/45 P=34.6 (40.3); 3, 4 - Al/S 75/25 P=36.4 (39.8); (open symbols Al – PP-1; close symbols – Al coarse; pressure values of incident waves and reflected ones (in brackets) are given in GPa)

If the components were non-reacting behind shock front, radiation intensity would be dictated by the temperature of shocked sulphur and the specific area it occupies in the sample surface. (We eliminate heterogeneous heating-up from the consideration.) From this viewpoint temperature of mixed samples could not exceed the temperature of sulphur samples shocked to the same pressure and it should decrease with increase of Al content. In the course of chemical reaction energy release is controlled by specific contact surface. For samples with fine Al one could expect temperature decrease with increase of Al content and its variation from stoichiometric composition. For samples with fine Al specific contact surface is larger than that with coarse Al, thus from this standpoint increase of Al content enhance reaction

proceeding at the initial stage. This is the situation we did observe in the conducted experiments.

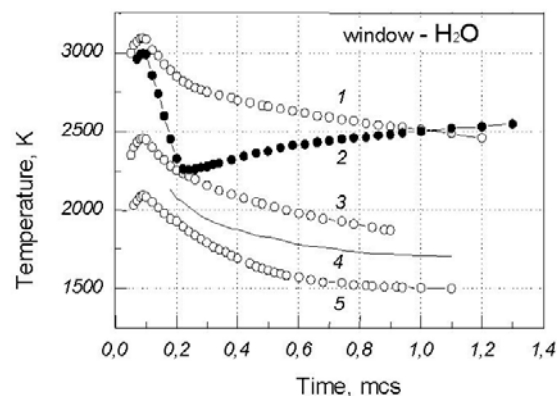


FIGURE 3. Temperature-time history for Al/S 55/45 measured at the interface with water-window. 1, 2 - P=34.6 (18.2); 3 - P=27.6 (14.7); 5 - P=21.7 (11.5); 4 - LiF/S (35/65) – P=26 (15) (see notations in Fig. 2).

Temperature histories measured nearby water-sample interface are shown in Fig. 3. Rarefaction reflected from the water-sample interface decrease pressure inside the sample noticeably. It changes temperatures histories of samples containing fine Al powder. Except first 0.1 μ s, one can observe just temperature decrease after shock wave has entered the interface. Maximum temperatures measured with water-window lie below those obtained with LiF window at the same initial pressure. For samples containing coarse Al, it is seen temperature growth after temperature decay at the initial part of the records. In approximately 1 μ s, it leads to the same temperature values as in the case of fine Al. It seems that such temperature behaviour is related with the rarefaction effect on the macroscopic kinetics of shock-induced reactions in tested mixtures.

In Fig. 3 it is also shown the temperature history obtained for non-reactive LiF/S 35/65 composition. Parameters of incident wave and reflected one are close to those occurred in experiments with Al/S 55/45 (see

curve 3 in Fig. 3). In spite of larger sulphur content in LiF/S samples the measured temperatures are 200 K less.

Experimental pressure histories obtained with CCl_4 and CHBr_3 used as indicators are shown in Figs. 4 and 5. Measurement of pressure history from shock front in indicators can give some information on macroscopic kinetics of transformations taking place in Al/S mixtures under shock loading.

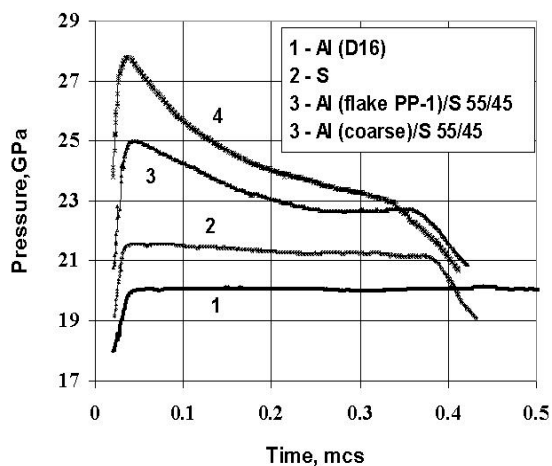


FIGURE 4. Pressure-time history in CCl_4
 Samples: 1 – Al (D16); 2 – S (pressed); 3 - Al/S 55/45 (Al – PP-1); 4 - Al/S 55/45 (Al – coarse).

Shock waves in samples were generated by impact of Al(D16) flyer (1.9 mm of thick) accelerated to the final velocity $w = 3.61$ km/s. Thickness of the samples was 3.0 – 3.5 mm. There were also tests with flyer velocities $w = 3.2$ and 4.51 km/s. In general, pressures transmitted through composite samples to the indicator liquids exceed those transmitted through Al or sulphur. The distinctive feature of the pressure histories obtained for composite samples of Al/S is the presence of clearly defined pressure peak at the beginning of the records; its value depends on the Al powder dispersity. It should be mentioned that for other tested sulphur mixtures with Mg, B, Fe, Ti, and Cu under the same experimental conditions no pressure peak was observed.

Shock-wave pressure variation in the range from 20 to 50 GPa does not lead to qualitative changes in the pressure histories. The effect of Al powder dispersity on the shape of pressure history and transmitted pressure is more noticeable than variation of Al content in the mixture within the range 35% - 75% wt. Possibly the peculiarities of pressure histories could be explained by formation of aluminium sulphide which has less density than TMD of mechanically mixed initial components.

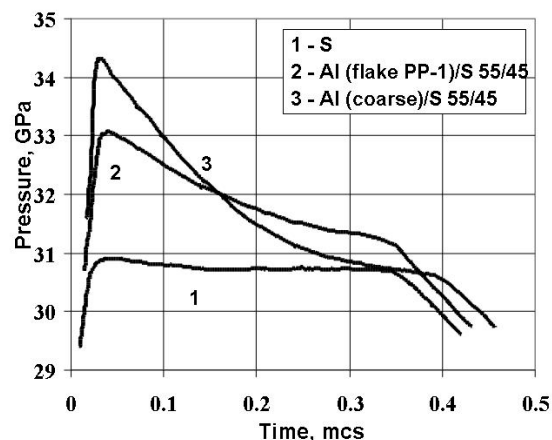


FIGURE 5. Pressure-time history in CHBr_3
 Samples: 1 – S (pressed); 2 - Al/S 55/45 (Al-PP-1); 3 - Al/S 55/45 (Al-coarse).

Analysing both the results on pressure and temperature profiles, one can suppose sufficient completeness of the reaction resulted in formation of aluminum sulphide within first 0.5 μs . However, it is difficult to estimate the proper value of reaction completeness basing only on experimental data and not making some additional assumptions, which also need for experimental verification. Besides, it should be mentioned some contradiction between temperature and pressure data on the influence of Al dispersity on reaction proceeding. Pressure peak measured in indicator in case of coarse Al is higher than that measured for fine Al. By contrast, temperatures of the mixtures with coarse Al are lower. One of the possible explanations

of this disagreement is the different time wanted for particles of different sizes and materials to be involved in flow behind the shock front; this effect has been previously observed for mixtures of non-reacting components [11].

VELOCITY MEASUREMENTS

Basing on the results of the pyrometric studies it was supposed that self-sustaining detonation-like process could propagate in Al/S mixture under certain conditions. There was conducted a number of experiments in order to measure shock wave velocities in Al/S mixtures of different densities.

In first series of the experiments, there were tested samples of pyrotechnic powder PP-1 mixed with sulphur: Al/S (55/45; 40/60) the density of which was 2.17 and 2.10 g/cc. Samples were initiated by HMX (1.80 g/cc) or RDX/TNT (1.65 g/cc) charges 40 mm in diameter, 20-50 mm in height supplied by plane-wave generator made of RDX with wax. Total weight of initiating assembly was about 60 g. Shock wave propagation was recorded by streak camera from lateral and end-on surfaces. In all tests the lateral luminosity damped out within first 5-10 mm of propagation, the luminosity from end-on surfaces was not observed. Thus the experiments with dense composite samples showed decaying character of the reaction initiated by HE. Under powerful initiation the components have no time to react completely enough to support self-sustaining regime and rarefaction waves disperse non-reacted components. So-called "over-initiation" is observed for weak commercial explosives, e.g. ammonium nitrate, for which intense initiation results to detonation decay when propagation conditions are close to failure ones [12].

In second series, there were tested low-dense charges of Al/S mixture placed in thick steel tubes of different internal diameters. Experimental assembly is shown in Fig. 6. AP/PMMA mixture was used for

shock wave initiation. Weak initiation was made in order to prevent over-compaction of the mixture. Mean size of AP particle was 15 μm and that of PMMA - 3 μm . Both initiating and tested explosive mixtures were prepared by mechanical mixing in rolling mill with porcelain balls. AP/PMMA mixture was initiated by electrical detonator. In all shots, except first one, initiating system was supplied by thin layer of RDX (1.5 g) placed between detonator and AP/PMMA mixture. The velocity was measured with the help of 4-6 contact gages over several bases (3-5 in each shot).

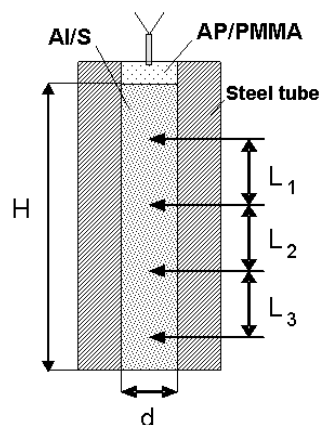


FIGURE 6. Experimental assembly for velocity measurements in low-dense Al/S mixture.

Data of some shots are given in the Table, in which there are made the following notations: m (g), d^* (mm), ρ (g/cc) – are consequently mass, diameter and density of AP/PMMA charge; H is the height of tested charge; d – are and internal diameter of steel tube; ρ_0 – initial density of tested mixture (in brackets it is referred to TMD in per cents) L_i – are measuring base; D_i – average velocity.

High porosity of the samples tested in the second series facilitates relative motion of the components and escalates heterogeneous heating-up – the processes promoting shock-induced reactions. Thus, the experiments with low-dense samples seem to be much more permissible than those performed in first series. However in the most tests, there

were just recorded the shock-induced processes of decaying character with average velocity through the last base equals to 300 – 400 m/s (see the Table). Stability of the process strongly depends on the amplitude of initiating impulse and sample structure. Slightly variation in Al/S mixture density or in intensity of initiating impulse resulted either to process attenuation with formation of the “plug” consisted of compacted mixture of products and reagents at the end of the tube or to its transition into regime of slow burning. In the Table they are noted as “P” and “B” respectively. In the conducted experiments the reaction rate was not enough to support self-sustaining detonation-like regime. One can see several ways for reaction intensification. First one is in preliminary mixture activation. It can be achieved by introduction of more

chemically active Al particles. Both mechanically activated and nano-size Al particles were added. Enhancing of components mixing under shock loading is another possible way of reaction acceleration. Adding of more heavy particles such as particles of Fe, Fe₂O₃; or presence of Al particles of different batches in the mixture can facilitate relative movement of components.

All the aforementioned ways of reaction intensification and some other are just under investigation. At present, none of them can be preferred to. Detonation-like process, if it could, run within narrow region of variation of experiments' conditions and mixture parameters. The best result was obtained for the Al/S 40/60 mixture with PP-2 Al powder measured velocity was about 1.3 km/s.

Table. Velocities of reaction propagation in low-dense Al/S mixture.

№	AP/PMMA m/d*/ ρ	Al % wt.,	ρ ₀ , g/cc (%TMD)	H, mm	d, mm	L ₁ , mm D₁ , m/s	L ₂ , mm D₂ , m/s	L ₃ , mm D₃ , m/s
1	85/15 3/16/0.8	40, PP-2	0.75 (33%)	200	16	50 720	50 360	50 “P”
2	85/15 4/20/0.8	40, PP-2	1.10 (48%)	155	20	35 1200	35 300	35 “P”
3	97/3 3/20/0.55	40, PP-2	0.75 (33%)	155	20	35 470	35 -	35 “B”
4	97/3 6/29/0.55	40, PP-2	0.72 (32%)	120	29	30 -	30 1260	30 1330
5	97/3 7/30/0.55	27 - PP-2 + 13 - PAP-2	0.62 (27%)	375	34	70 450	140 250	140 “B”
6	95/5 8/29/0.55	40, ASD-4	0.72 (32%)	180	29	30 530	60 410	60 280
7	85/15 10/29/0.55	43 - ASD-4 + 14 - Fe ₂ O ₃	0.60 (24%)	180	29	30 1160	60 650	60 440
8	85/15 10/29/0.55	38 - ASD-4 + 17 - Fe	0.75 (29%)	180	29	30 1020	60 640	60 410
9	95/5 10/29/0.55	45, UDA	0.45 (20%)	150	29	30 770	30 610	60 460
10	95/5 10/29/0.55	40, PP-2 (activ.)	0.53 (23%)	150	29	30 730	30 560	60 420

CONCLUSION

Performed pyrometric studies of high-dense metal-sulphur mixtures under shock compression showed that shock-induced reaction significantly increase the temperature of Al/S, Ti/S, and Mg/S mixtures. For Al/S mixtures there were observed complicated shock pressure histories looking like detonation ones. Such pressure profiles could be explained by formation of aluminium sulphide with larger specific volume than initial components. The obtained data provided some reasons to suppose the possibility of the proceeding self-sustaining chemical reaction in Al/S mixture in detonation-like regime. Experimental verification of this assumption showed that the reaction completeness is not enough to support self-sustaining regime in dense samples of 40-mm diameter. There was observed only quasi-stationary detonation-like process in low-dense charges of Al/S mixture. Detonation-like process could run within narrow region of variation of experiments' conditions and mixture parameters, such as: intensity of initiating impulse; Al content and mean particle size; charge diameter and its density etc. The experiments demonstrate principal ability for detonation-like processes to occur in solid non-explosive mixtures. It is anticipated that experimentation currently in progress will lead to clearing the conditions under which reactions in solids are able to propagate in detonation-like regime.

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