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Detonation properties of tetranitromethane-methanol mixture

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Abstract. An experimental study of the reaction zone structure and stability of detonation waves was performed for tetranitromethane-methanol (TNM-M) mixture using a velocity interferometer system for any reflector (VISAR). At the near stoichiometric concentration of methanol, it was observed that the amplitude of Von Neumann spike decreases significantly, whereas the detonation parameters increase. The instability of detonation waves in TNM-M mixture was shown, both with respect to one-dimensional longitudinal perturbations and to the curvature of the front leading to the formation of the cellular structure. The dependence of detonation velocity of TNM-M on the diluent concentration and limits of detonation propagation were found.

1. Introduction

The chemical reaction in shock-compressed liquid high explosives (HE) has a thermal character, and rate of reaction is a function of activation energy. An effective method of changing the thermodynamic and kinetic properties of liquid HE is the use of various additives. This makes it possible to obtain important information on the effect of the kinetics of chemical reactions on the structure of detonation waves and critical detonation regimes. The object of research in this work is a mixture of tetranitromethane (TNM) with methanol (M), the interest in which is due to several reasons. First, TNM is a strong oxidant with a positive oxygen balance which is equal to 49%. Therefore, the addition of methanol, which is combustible, allows in a wide range to change the heat of explosion, and, consequently, the detonation parameters of the mixture [1]. It can be expected that this will lead to a significant change in the structure of the reaction zone. Secondly, the authors [1–3] note poor reproducibility of experimental data in mixtures of TNM with nitrobenzene and methanol in the vicinity of the stoichiometric concentration of diluents. The reasons for this phenomenon remain unclear, and in this situation, an experimental study of the influence of various factors (charge diameter, shell material, mixture preparation conditions) on the reproducibility of wave profiles is relevant. Thirdly, one of the distinguishing features of liquid HE is the possibility of the propagation of both stable and unstable detonation waves into them [4]. The implementation of one or another nature of the flow is determined primarily by the kinetics of a chemical reaction. This work is devoted to the study of these patterns.

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Figure 1. Scheme of experiments: 1—the TNT–RDX charge; 2—the water window; 3—Al foil; 4—the shell of the HE charge; 5—the ionization gauge.

2. Experimental setup

The scheme of experiments is shown in figure 1. The HE charge was placed into the shell from polypropylene, polymethylmethacrylate (PMMA) or steel. The length of charge varied from 50 to 260 mm, the internal diameter of the tube varied from 26 to 50 mm. Shock waves in the investigated mixture were created by the charge of TNT–RDX. The velocity of the HE–water boundary was recorded using a velocity interferometer system for any reflector (VISAR). To determine the absolute value of the velocity, two interferometers with velocity fringe constants of 280 and 1280 m/s were used simultaneously. A laser beam (532 nm) was reflected from an aluminum foil with a thickness of 7 μ m which was placed between the investigated mixture and water window. In each experiment, the gauge recorded the entry time of the detonation wave, which allowed us to determine the value of the detonation velocity D using interferometric data. The accuracy of determination of D is higher than 1%.

3. Experimental results

In the experiments, TNM (C[NO₂]₄) with an initial density of 1.64 g/cm³ and detonation velocity of 6.32–6.48 km/s [1,4–6] and methanol (CH₃OH) with an initial density of 0.793 g/cm³ [7] were used. The difference in values of detonation velocity of TNM is due to the dependence of this on the charge diameter, which was found in previous work of authors [6].

Particle velocity profiles on the TNM-M—water boundary for different concentrations of diluent are shown in figures 2–5. For neat TNM the structure of the velocity profiles has a shape that is typical of condensed high explosives—the velocity behind the shock jump decreases, and the von Neumann spike is formed in the reaction zone (figure 2, curve 1). The parameters of Von Neumann spike were found by analysis of shock waves interactions in the pressure P-particle velocity u plane [8]: $u_N = 2.52 \pm 0.06$ km/s, $P_N = 26.5 \pm 0.6$ GPa. The reaction time for TNM was determined experimentally earlier [6]. It is equal to 175 ± 25 ns, which agrees well with the data of [9]. The obtained values of velocity and pressure at the Chapman–Jouguet (CJ) point are 1.55 ± 0.03 km/s and 16.4 ± 0.3 GPa, respectively, which is approximately 1.6 times less than that of Von Neumann spike. The measured state at the CJ point agrees well with the maximum reaction rate is realized immediately behind the shock jump, where the maximum value of velocity is observed, and the amplitude of Von Neumann spike decreases twice for approximately 15 ns. The evaluation of the initial velocity behind the shock jump shows that its value exceeds 10^7 s^{-1} . This is typical for powerful high explosives.



Figure 2. Particle velocity profiles on the TNM–M—water boundary for different concentration of M: 100:0(1), 90:10(2) and 85:15(3).

The results obtained for TNM–M mixture are qualitatively different from the results for the neat TNM—the addition of M results in the decrease of amplitude of Von Neumann spike, whereas detonation parameters increase (figures 2 and 3). It is likely that the decrease in the amplitude of Von Neumann spike is due to an increase in the initial reaction rate, as a result of which the explosive begins to react directly in the front of the shock wave. An indirect confirmation of this is the blurring of the shock front near the velocity maximum by almost ten nanoseconds, which is observed on all velocity profiles in the range of methanol concentrations from 10 to 40% (figures 2 and 3). The assumption of a reaction in the front in homogeneous high explosives is substantiated in [11] and makes it possible to explain the sharp decrease in the amplitude of Von Neumann spike and the reaction rate behind the front.

When the methanol concentration does not exceed 40%, the recorded velocity profiles are smooth, without any oscillations (figures 2 and 3). This means that detonation waves in pure TNM and its mixtures with methanol are stable with respect to disturbances, which leading to the formation of a cellular structure. A further increase in methanol concentration leads to the appearance of oscillations on the velocity profiles (figure 4), which indicates the instability of the detonation front. Dependence 1 in figure 4 was obtained for the mixture of TNM-M (50:50) in experiments using 7 μ m Al foil to reflect laser radiation. Reliable recording of speed for a sufficiently long time means that the amplitude of perturbations of the detonation front is much less than 7 μ m. Otherwise, a noticeable deformation of the foil would be observed, which would lead to a drastic change in the intensity of the reflected laser radiation and the impossibility of detecting the velocity of HE boundary with water window. For this reason, an increase in the methanol concentration up to 60% does not allow the registration of wave profiles in this formulation. Increasing the foil thickness to 400 μ m smoothes the oscillations, as can be seen in figure 4 in dependence 2 for 50% methanol. But even in this case, the velocity profile for the mixture of TNM-M (40:60) remains oscillating (dependence 3 in figure 4). This means that the amplitude of the disturbances is in the order of 100 μ m. The sharp rise in speed after



Figure 3. Particle velocity profiles on the TNM–M—water boundary for different concentration of M: 74: 26(1), 65: 35(2) and 60: 40(3).

100 ns after the shock wave reaches the boundary with water in dependences 2 and 3 is due to the circulation of compression and rarefaction waves along the foil. The critical concentration of methanol $C_{\rm cr}$, above which the detonation in TNM–M mixture does not propagate, is 62%.

Simultaneously with the particle velocity in the experiments, the detonation velocity D was recorded, whose dependence on the methanol concentration is shown in figure 5. In the neat tetranitromethane, the detonation velocity is approximately 6.48 km/s. When methanol is added, it increases to 6.76 km/s at a methanol concentration of 10% and remains almost constant until the stoichiometric concentration of TNM–M mixture is 75.4 : 24.6. In the vicinity of stoichiometry, D reaches a maximum value of 6.9 km/s and decreases with further dilution. The dependence obtained agrees well with the well-known literature data [1,8,12]. The same character of dependence of detonation velocity on the diluent concentration was observed for a mixtures of TNM–nitrobenzene [13], TNM–propylene oxide and TNM–hexane [14].

It was also found that in TNM–M mixtures there was some discrepancy between particle velocity profiles for the same concentration compound of the mixture, which were obtained in different experiments. Figure 6 shows four particle velocity profiles for the mixture of TNM–M (85 : 15). In all experiments, the parameters of experimental assemblies and ambient condition were the same. The shell from PMMA with the internal diameter of 36 mm, wall thickness of 2 mm and the length of 150 mm was used in each experiment. Detonation wave in the mixture was initiated by the charge of TNT–RDX with diameter of 40 mm. The ambient temperature was 20 °C. The mixture was investigated in 2 h after preparation. It can be seen that the discrepancy between profiles is about 350 m/s, what exceeds the experimental error. It is noteworthy that detonation velocity is the same in all experiments (6.79 \pm 0.03 km/s).

The varying of material, diameter and length of the shell in a wide range, initiating charge, ambient condition and time after mixture preparation did not lead to better reproducibility of results. Such discrepancy in experimental results was mentioned in the works of [2] and [3]. According to the author of [3], this phenomenon can be explained by the multi-stage chemical



Figure 4. Particle velocity profiles on the TNM–M—water boundary for different concentration of M and the Al-foil thickness: $50:50, 7 \ \mu m \ (1); 50:50, 400 \ \mu m \ (2); 40:60, 400 \ \mu m \ (3).$



Figure 5. The dependence of detonation velocity on the methanol concentration of TNM–M mixture.

reactions in the detonation waves of a mixtures of liquid HE with not detonating additives. And as result, the rate of energy release is affected by a number of factors, the effect of which for each particular mixture is often difficult to identify. In other words, such a pattern of propagation of detonation waves is undoubtedly due to the kinetics of a chemical reaction and is



Figure 6. Particle velocity profiles for the TNM–M mixtures of 85:15 in the same experiments, where the amplitude of particle velocity on the boundary with water is different: 2660 (1), 2530 (2), 2430 (3) and 2320 m/s (4).

a manifestation of one-dimensional longitudinal instability [15]. Moreover, this instability begins at 10% methanol and lasts up to 40%.

4. Conclusion

As a result of an experimental study of TNM–M mixture, it was found out that the detonation parameters, the structure of the reaction zone, and the stability of detonation waves substantially depend on the diluent concentration. The addition of 10-15% methanol leads to an increase in the detonation velocity and Chapman–Jouguet pressure by 5 and 10%, respectively. Especially significantly changes the nature of the flow in the reaction zone. When the concentration of methanol changes in the interval of 10-40%, the amplitude of Von Neumann spike does not exceed 100 m/s, whereas for the neat TNM it is in the order of 1 km/s. It can be explained by increase of the initial rate of reaction in the mixture and consequently chemical reaction directly in the shock front [16].

In the same concentration range, smooth velocity profiles are recorded, without oscillations, which inevitably arise when the cellular structure of the detonation front. However, detonation waves in TNM–M mixture are unstable with respect to longitudinal perturbations, in which the disturbed flow, like the original, remains one-dimensional with a planar detonation front. The result is poor reproducibility of the wave profiles, which is observed in the performed experiments. In [17], it is noted that the criterion for the stability of a detonation wave with respect to longitudinal perturbations depends not only on the activation energy, but also the heat of reaction. Detailed studies [17, 18] generally confirm this conclusion, but in quantitative terms, the criterion for the stability of detonation waves is much more complex.

At concentrations above 40%, instability with respect to the curvature of the front becomes prevalent, leading to the formation of the cellular structure of the detonation front, which persists until the critical concentration of methanol.

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