Research paper

Improvement of aluminized explosives and reaction mechanism of CL-20 with Al or Al-Mg alloy

Xiaoxiang Mao*, Longfei Jiang*, Chenguang Zhu*,
Xiaoming Wang*, and Dihua OuYang**†

*Nanjing University of Science and Technology, Nanjing, 210094, PR CHINA

**Engineering University of Chinese Armed Police Force, Xi'an 710086, PR CHINA
Phone: +86−025−84303291
†Corresponding author: oydh2013@126.com

Received: November 21, 2018 Accepted: April 9, 2019

Abstract

There is a non-ideal problem account of release of energy for aluminized explosives. In this paper, the ignition performance experiments were carried out based on three kinds of composite explosives (RDX, HMX and CL-20) with different mass percentages of aluminum (Al) powder or aluminum-magnesium (Al-Mg) alloy powder. It was found that under the decomposition temperature or ignition temperature of RDX and HMX, the metal powder not only fails to participate in the reaction, but also hinders the complete combustion of the explosives. Different to RDX and HMX, CL-20 mixed with 10% Al or Al-Mg alloy released more energy than pure CL-20, which proves the participation of the metal powder in the reaction at the CL-20 ignition temperature. Based on the analysis of thermodynamic properties of explosives, it is concluded that since CL-20 has greater explosion heat and enthalpy of formation than RDX and HMX, a localized high-temperature region of inhomogeneous composite explosive at micro-scale forms and causes the metal particles reacting.

Keywords: explosive, aluminum powder, ignition performance, TG-DTA

1. Introduction

Metalized explosives are made by adding metal powders of high calorific value to high-energy explosives. The aim is to promote significantly the power of hybrid explosives. Therefore, metalized explosives have been widely used in military and industrial fields. In general, aluminum, magnesium, barium, lithium and aluminum-magnesium alloys are additives to explosives[1), 2)]. Cook proposed a secondary reaction theory on aluminized explosive in 1956, believing that aluminum powder is inert to explosives and that detonation velocity and pressure of the aluminized explosives are depressed since aluminum powder does not participate in the reaction. Under the high temperature and pressure conditions generated by the detonation wave, secondary reactions happen between the aluminum powder and explosive product, which releases a great quantity of heat and pressure for a long time and also makes total energy of aluminized explosives higher[3)]. Furthermore, the theory of inert thermo dilution considers that aluminum powder, as an inert material, not only failed to participate in chemical reactions, but also consumes part of energy, thereby reducing the total energy of detonation waves. According to the theory of chemical thermo dilution, aluminum does participate in the detonation wave reaction, but due to the endothermic effect of Al_2O exceeding the exothermic effect of Al_2O_3, the detonation velocity and pressure of aluminized explosives decreased[4)]. Under the influence of these theories, the issue of reaction, combustion and energy release of metalized explosives has gradually become a research hotspot. It was found that under the combined effect of metal type/content/size and explosive components etc., the energy of the metalized explosive cannot be released fully and predictably, making it a typical non-ideal explosive. Current research has been carried out mainly in three aspects. The first aspect is about the mechanism of the thermal decomposition process of explosives and the combustion of metal particles. For example, in the work of Zi et al., the initial thermal decomposition pathways of the super cell structures of ε, β, γ of CL-20 at different temperatures were studied by molecular dynamics simulations, using the ReaxFF force field, the NPT and NVT ensembles and the Berendsen methods[5]. Li et al. experimentally studied the ignition performance of different types of nano aluminum powders by using CO_2 laser ignition device[6]. Gromov et al. found that the combustion process of nano aluminum powder included two stages and could achieve self-sustained combustion in the follow-up process[7]. Popenko et al. studied the combustion products of nano aluminum powder at different pressures[8]. The second aspect is to study the role of metal powders in improving the detonation performance of explosives. For example, Huang et al. studied the effect of aluminum powder particle size on the detonation performance of aluminized explosive[9]. Komarov et al. investigated the effect of nano metal powders, such as Al, Fe, Cu, Ni, Ti and Zn, on the metalized explosives[10]. Patrick et al. compared the effects of nano aluminum powders and ordinary micron-sized aluminum powders on the performance of PBX and TNT-based explosive systems[11]. The third aspect explores, from the perspective of thermal safety of hybrid explosives, the interaction mechanism between metal powders and explosives by the heat stimulation. Peng and other researchers believe that the shape, activity, and particle size of aluminum powder are important factors which can influence the ignition performance and energy level of aluminized explosives, and the shape is the most important factor[12]. Hwang et al. studied the application characteristics of nickel-coated aluminum powder in explosives. Their results show that nickel can reduce the ignition temperature of aluminum powder and increase the pressure and temperature of the explosion wave[13]. Comparatively, the experimental and theoretical studies on the participation and energy release of metal powders in the thermal decomposition and dissipative processes of metalized explosives are rare. However, this aspect is vital to understand the ignition performance and thermal safety of metalized explosives.

Previous study has found that hexanitrohexaazaiso-wurtzitane (CL-20) with 10% aluminum powder can release higher energy than pure CL-20, indicating that part of aluminum powder is affected by CL-20 to participate in combustion and release energy[14]. In order to further investigate the effect of metal powder on the non-ideal properties of metalized explosives, the ignition experiments were carried out with TG-DTA equipment on three kinds of composite explosives which were cyclotrimethylenetrinitramine (RDX), cyclotetramethylene-tetranitra- mine (HMX), and CL-20, with different mass percentages of Al powder or Al-Mg alloy powder (0, 10, 20, and 30 wt%), respectively. Magnesium is a more active metal than aluminum with a low melting point, strong volatility, and easily forms a loose structure after oxidation[15]. Aluminum particles, however, will form a dense oxide layer in the air to hinder the combustion. Therefore, by adding these two kinds of metal powders into three kinds of explosives in the current research, a effective comparative analysis could be obtained.

2. Experimental

2.1 Reagents and instruments

2.1.1 Reagent

Al powder (325 mesh, 44 μm) and Al-Mg alloy powder (325 mesh, 44 μm) provided by Tangshan Weihao Magnesium Powder Co., Ltd were selected for being mixed with explosives. The 78 wt% Al and 22 wt% Mg in the Al-Mg alloy powder is obtained by vaporize and spray method after mixing uniformly the molten state of magnesium and aluminum. RDX (80 mesh), HMX (80 mesh) and CL-20 (80 mesh) prepared by Qingyang Chemical Co., Ltd. Company are selected as the explosives.

2.1.2 Instrument

The differential thermal analyzer (DTA-50 STA449C) produced by NETZSCH Company and Hot Disk TPS 2500 S thermal conductivity meter produced by Kaigenasi company were adopted.

2.2 Sample preparation

Mix different mass percentages of Al powder or Al-Mg alloy powder (0, 10, 20, and 30 wt%, respectively), with RDX, HMX, and CL-20 uniformly. Each kind of explosives corresponds to eight samples. There are 24 samples divided into two groups in this experiment. The number and formula of samples are listed in Table 1 and Table 2.

2.3 Experimental conditions

Experimental conditions are as follows: sample weight was 0.5 mg, Al_2O_3 crucibles, and gradient heating at a constant rate of 10 K min^{-1} ranging from ambient temperature to 600 ℃. The α-Al_2O_3 was used as the reference sample to correct the reference instrument, and the crucibles were exposed during the whole process. The equipment was corrected before each test.

2.4 Calculation formula

The weights of samples were normalized to directly evaluate the effects of different mass percentages of metal powder on the energy release of explosives by Equation

Table 1 Mixed explosive formula with aluminum powder.

Number	RDX [%]	HMX [%]	CL-20 [%]	Al [%]
1#	100	–	–	0
2#	90	–	–	10
3#	80	–	–	20
4#	70	–	–	30
5#	–	100	–	0
6#	–	90	–	10
7#	–	80	–	20
8#	–	70	–	30
9#	–	–	100	0
10#	–	–	90	10
11#	–	–	80	20
12#	–	–	70	30

Table 2 Mixed explosive formula with aluminum-magnesium alloy powder.

Number	RDX [%]	HMX [%]	CL-20 [%]	Al-Mg alloy [%]
13#	100	–	–	0
14#	90	–	–	10
15#	80	–	–	20
16#	70	–	–	30
17#	–	100	–	0
18#	–	90	–	10
19#	–	80	–	20
20#	–	70	–	30
21#	–	–	100	0
22#	–	–	90	10
23#	–	–	80	20
24#	–	–	70	30

Table 3 Standard exothermic enthalpy of pure substances.

Pure substance	ΔH / kJ kg^{-1}	Ignition & melting temperature [^{o}C]
RDX	5400	~205
HMX	5673	~276
CL-20	7100	~236
Al	30222.22	660
Mg	25458.33	650
Al-Mg alloy	29174.16	463

(1) and Equation (2).

2.4.1 Mass normalization formula

$$M_s = \frac{1000}{n} \times \sum_{i=1}^{n} \frac{M_i}{M_0} \tag{1}$$

Where M_s is the normalized mass, M_0 is the original mass, M_i is the dynamic mass measured by TG-DTA device, n is the number of data points, and 1000 is reference value.

2.4.2 Theoretical exothermic enthalpy percentage of composite explosive

$$\Delta H\% = 1 + \left(\frac{\Delta H_{\text{metal}}}{\Delta H_{\text{explosive}}} - 1\right) \times p \tag{2}$$

Where ΔH_{metal} and $\Delta H_{\text{explosive}}$ are the standard exothermic enthalpy of metal (Al or Al-Mg alloy) and pure explosive respectively, as shown in Table 3, and p is the mass percentage of metal.

3. Results and discussion

3.1 Tests and results

Figure 1 and Figure 2 show the DTA curves of the two groups of samples which have been baseline-corrected. It can be shown in Figure 1(a) and (b), as the mass percentage of Al powder increases, the exothermic peaks of RDX/Al and HMX/Al gradually decrease, respectively. However, according to the DTA curves in Figure 1(c), variation trend of CL-20/Al is different. By visually observing the integral area of the curve, it can be seen that when the Al powder content is 10 wt%, the CL-20-based mixed explosive has a significantly higher heat release than the pure CL-20. As shown in Figure 2, the ignition performance of the three composite explosives has maintained a similar pattern after replacing Al with Al -Mg alloy. It is notable that there is a "bulging" in the curve of CL-20 with 10 wt% Al-Mg alloy powders, which is obviously different from other curves, as shown in Figure 2(c). We speculate that there exist some factors leading to the continuous exothermic phenomenon of mixed explosives.

On the basis of thermal analysis experiments, in order to further compare the actual influence of Al and Al-Mg alloy on the detonation performance of explosives, herein, desensitizing RDX explosives were mixed with Al and Al-Mg alloy in a mass proportion of 4:1, respectively, and the detonation tests were conducted. According to the Military standard of China (GJB772A-97), the principle of explosive detonation velocity test is to use the ionization and conductivity characteristics of wave front of the detonation. The propagation time of detonation wave in a certain length of explosive column is tested by time meter and electric probes. Therefore, the average detonation velocity of explosive can be calculated. In the process of experiment, it is required that the time measuring error of the timer should be no more than 30 ns, and there should be no visible cracks, shrinkage holes and other obvious defects in each explosive column. The standard deviation of detonation velocity test results for each explosive column should be no more than 30 m·s^{-1}. The installation diagram of explosive columns for detonation velocity test is shown in Figure 3. The specimen, timer, pulse forming network and power supply are connected as shown in Figure 4. The test results show that the average detonation velocity of RDX/Al-Mg reached 7852 m·s^{-1}, which was significantly higher than the average detonation velocity of RDX/Al (7100 m·s^{-1}). The increase ratio exceeded 10%.

3.2 Non-ideal performance analysis of mixed explosives

For comparison, the relative exothermic enthalpy percentage of the two groups of samples, as listed in Table 4 and Table 5, is calculated based on the exothermic enthalpy of pure explosives. The data in parentheses are theoretical exothermic enthalpy percentages of composite explosives. It can be seen that as the mass percentage of Al or Al-Mg alloy increases, the exothermic enthalpies of RDX and HMX-based composite explosives decrease gradually, indicating that rather than participating in the ignition and combustion, the metal powder actually affect the complete reaction of composite explosives. Unlike RDX and HMX, the mass percentage of energy released by the CL-20-based composite explosives with 10 wt% Al or Al-Mg alloy reaches 105.2% and 104.5% respectively, which surpasses the theoretical value of the energy released from pure explosive. It is a strong proof that a part of the metal powder participates in the combustion

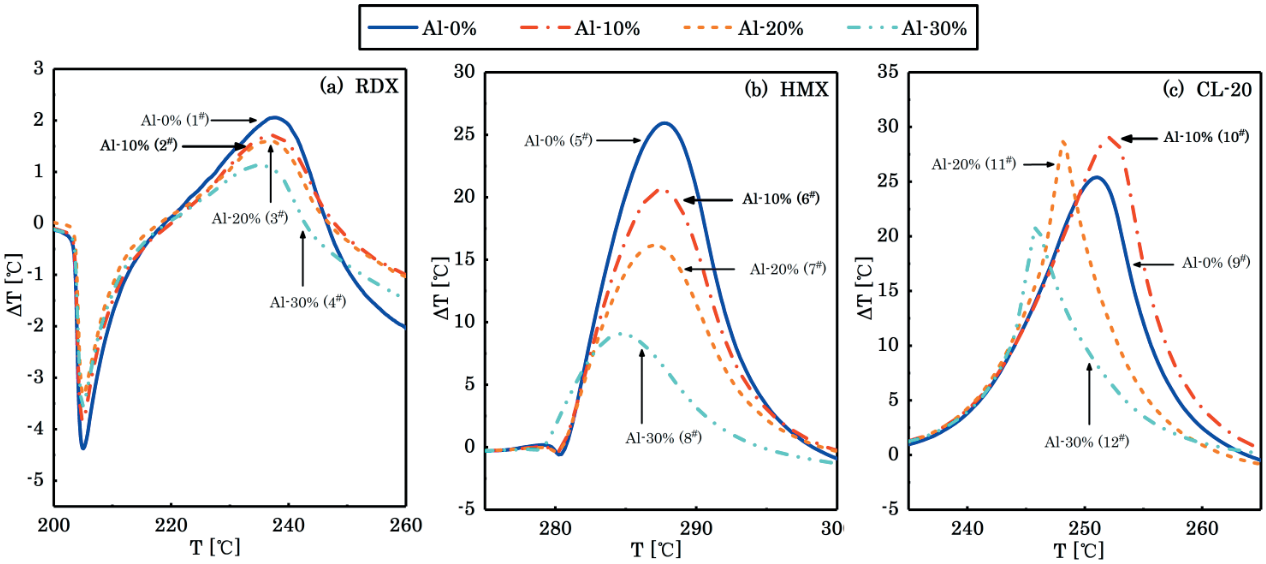

Figure 1 DTA curves of three kinds of explosives with different mass percentages of Al powder.

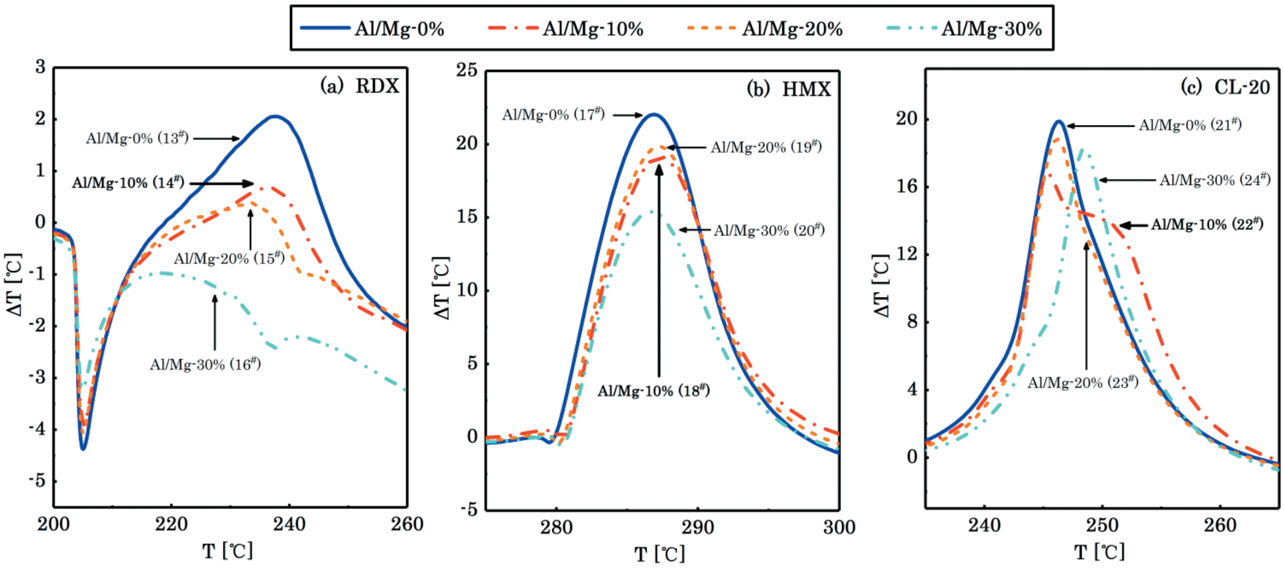

Figure 2 DTA curves of three kinds of explosives with different mass percentages of Al-Mg alloy powder.

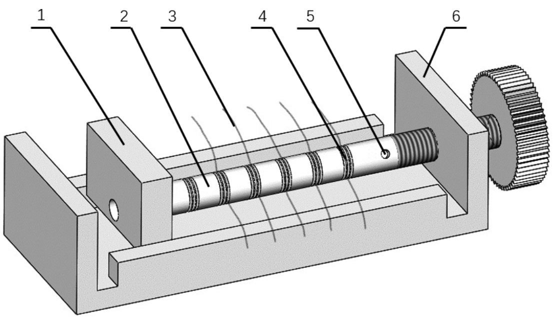

Figure 3 Installation of explosive columns in the wooden trough (1-Wooden trough; 2-Explosive column; 3-Probe; 4-Sponge cushion; 5-Timber column; 6-Top pressure device).

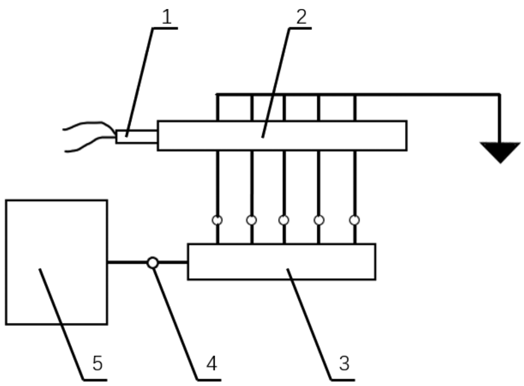

Figure 4 Connection between specimen and instrument (1-Detonator; 2-Specimen; 3-Pulse forming network; 4-Wire; 5-Timer).

reaction and releases energy. It can be concluded that, different to RDX and HMX, CL-20 can enable the metal powder participating in combustion under the decomposition temperatures when they are at a certain mass proportion.

3.3 Analysis of reaction mechanism of CL-20 with Al or Al-Mg alloy

As shown in Figure 5, the external functional groups of the three explosives are dominated by nitro groups. Also, it is well worth of exploring why only CL-20 can promote the participation of metal powder in the reaction at the

Table 4 Exothermic enthalpies (*ΔH*) percentage of three groups' explosives with Al powder.

Sample	ΔH%			
	Al-0%	Al-10 wt%	Al-20 wt%	Al-30 wt%
RDX/Al	100 (100)	74.4 (145.97)	61.5 (191.93)	40.8 (237.9)
HMX/Al	100 (100)	80.3 (143.27)	64.8 (186.55)	36.1 (229.82)
CL-20/Al	100 (100)	**105.2 (132.57)**	79.4 (165.13)	55.1 (197.7)

Table 5 Exothermic enthalpies (*ΔH*) percentage of three groups' explosives with Al-Mg alloy powder.

Sample	ΔH%			
	Al-Mg 0%	Al-Mg 10 wt%	Al-Mg 20 wt%	Al-Mg 30 wt%
RDX/Al-Mg	100 (100)	45.9 (144.03)	51.4 (188.05)	25.1 (232.08)
HMX/Al-Mg	100 (100)	85 (141.43)	88.1 (182.85)	73.9 (224.28)
CL-20/Al-Mg	100 (100)	**104.5 (131.09)**	89.4 (162.18)	82.9 (193.27)

428

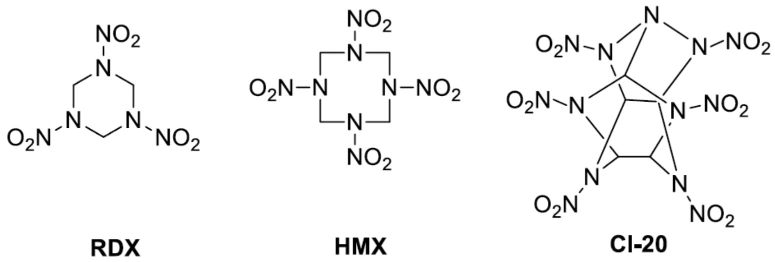

Figure 5 External functional groups of three explosives.

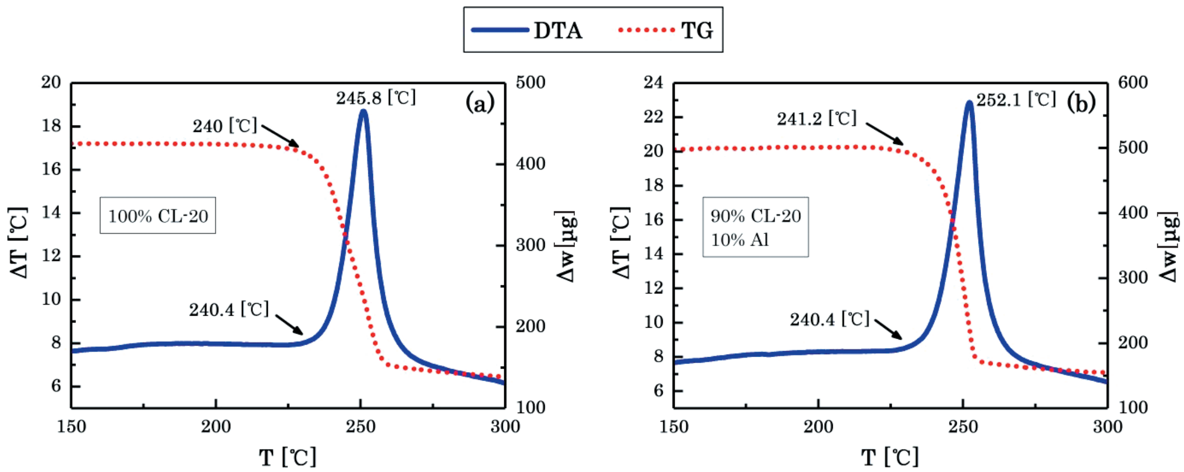

Figure 6 TG-DTA curves of CL-20 before and after addition of aluminum powder (a: Pure CL-20; b: CL-20 90 wt% and Al 10 wt%).

decomposition temperature. As shown in Figure 6, we can conclude that there is no endothermic peak or exothermic peak appeared before the decomposition temperature of CL-20, and there was no decomposition temperature drift. Meanwhile, the decomposition temperature of explosives was at 200–300 °C which is far lower than the melting point of aluminum (660 ℃). Accordingly, it can be judged that, since neither pre-reaction nor catalytic reaction happened, it is meaningless to analyze the reaction between CL-20 and Al or Al-Mg alloy from the perspective of the reaction kinetics.

Previous study has indicated that the CL-20/Al composite explosive with 10 wt% Al powder can release more energy than that of pure CL-20 under ignition temperature. As Al-Mg alloy is a more active metal than aluminum, our aim is to tackle the problem of non-ideal performance of the aluminized explosives by replacing aluminum with Al-Mg alloy. Although the detonation tests show that the average detonation velocity of RDX/Al-Mg was significantly 10% higher than the RDX/Al, the DTA experiments still fail to achieve the expected goal. This experimental study reproduced the results of the aluminized explosives based on DTA, as shown in Table 4 and Table 5. However, one question emerges – why Al or Al-Mg alloy can take part in chemical reactions under the CL-20 ignition temperature (236 °C), as shown in Table 3, while the actual melting point of Al-Mg alloy and Al is 463 °C and 660 °C respectively. Another question is why Al or Al-Mg alloy in RDX and HMX cannot react under their ignition temperature.

Detonation temperature, explosion heat, combustion heat and enthalpy of formation are main thermodynamic properties of explosive. Theoretically, detonation temperature is related to the calorific value generated by the reaction and the calculation of detonation temperature has adiabatic conditions, so there is a time cumulative effect. Explosion heat is the heat released instantaneously during the explosion and is almost unaffected by the time. It is known that the explosion heat of CL-20 is 2764.76 $kJ\cdot mol^{-1}$, almost twice as much as that of RDX (−1254.1 $kJ\cdot mol^{-1}$) and HMX (1829.12 $kJ\cdot mol^{-1}$), and as long as the explosive decomposed, part of the heat released instantaneously. However, the explosion heat should be limited to constraints of isovolumetric or isobaric. The combustion heat is the value of the heat released by substance completely burned. Each property mentioned above describes the performance of explosive in the state of detonation or combustion and can be classified as macroscopic value.

In the view of micro-scale and the open transient environment of the DTA test ignition, we believe that enthalpy of formation is more reasonable to explain the above-mentioned question. The enthalpy of formation of RDX is 92.6 $kJ\cdot mol^{-1}$, HMX is 104.8 $kJ\cdot mol^{-1}$, and CL-20 is 460 $kJ\cdot mol^{-1}$. In terms of calories per gram, RDX is 0.28 $kJ\cdot g^{-1}$, HMX is 0.35 $kJ\cdot g^{-1}$, and CL-20 is 1.05 $kJ\cdot g^{1}$. The reason why Al or Al-Mg alloy mixed with RDX and HMX, unlike CL-20, did not react at the decomposition temperature may be that the heat instantaneously released by CL-20 enables the metal particles react at that temperature. Similar to the ecological “niche effect”, high-temperature zone at micro scale is formed with explosive particles as the core. The temperature at which the metal particles liquefy and participate in the chemical reaction is reached, thus the partial combustion of the Al powder or the Al-Mg alloy powder can be promoted.

It is generally known that hot-spot initiation theory described an early stage of initiation mechanism of explosives. Correspondingly, in the niche effect assumption, certain amount of high-temperature zones forms after the ignition in some of energetic materials. In those high-temperature zones, there exists a relative ideal and self-sustained reaction.

4. Conclusions

(1) The results of detonation velocity test of RDX mixed with Al or Al-Mg alloy show that Al-Mg alloy plays a positive role in the increase of detonation velocity. The detonation velocity can increase about 10% if Al-Mg alloy is used to replace Al mixed with the explosive.

(2) At the decomposition temperatures of RDX and HMX, Al does not combust, but hinders the reaction of explosive, resulting in incomplete energy release of composite explosives. Although Al-Mg alloy has lower reaction temperatures and more active chemical properties than Al, this situation has not improved significantly by replacing Al with Al-Mg alloy in composite explosive.

(3) Different to RDX and HMX, the composite explosive of CL-20 mixed with 10 wt% Al or Al-Mg alloy releases a higher energy value than the theoretical value of pure CL-20. It can be determined that the metal powder participates in the reaction and releases energy.

(4) The TG-DTA curves of the composite explosive of CL-20 mixed with 10 wt% Al or Al /Mg show that no endothermic peak or exothermic peak appeared before the decomposition temperature of CL-20, and no decomposition temperature drift occurs.

(5) Beyond the analysis of thermodynamic properties of three kinds of explosives, we speculate that a localized high-temperature region formed in the inhomogeneous composite explosive of CL-20/Al, since CL-20 has a higher ability of instantaneous heat release (high explosive heat value and formation enthalpy). As the surface reaction temperature of the metal particles is reached, the CL-20 mixed with a certain percentage of metal powders happens to a “niche effect” of the chemical reaction.

Acknowledgements

This work was supported by the National Science Foundation of China under Grant 51676100; 51506222; 51076066.

References

1) R. A. Schaefer and S. M. Nicolich, 36th International Annual Conference of ICT, Karlsruhe, Germany (2005).
2) H. X. Xu, X. W. Li, F. Q. Zhao, W. Q. Pang, S. L. Jia, and H. J. Mo, Chin. J. Ener. Mater., 19, 232−239 (2011).
3) L. Chen and X. P. Long, “Detonation of aluminized explosive”, National Defense Industry Press, Beijing (2004). (in Chinese).
4) Y. B. Sun, J. M. Hui, and X. M. Cao, “Military hybrid explosive”, 389, The Publishing House of Ordnance Industry, Beijing (1995). (in Chinese).
5) L. Zhang, L. Chen, C. Wang, and J. Y. Wu, Explosion & Shock Waves, 76, 825−830 (2014).
6) X. Li, F. Q. Zhao, H. X. Hao, Y. Luo, S. Y. Xu, E. G. Yao, and N. Li, Acta Armamentarii, 35, 640−647 (2014).
7) A. Gromov and V. Vereshchagin, J. European Ceramic Society, 24, 2879−2884 (2004).
8) E. M. Popenko, A. A. Gromov, Y. I. Pautova, E. A. Chaplina, and H. J. Ritzhaupt-Kleissl, Applied Surface Science 257, 3641−3644 (2011).
9) H. Huang, Y. Huang, and S. B. Li, Chin. J. Explos. Propellants, 25, 1−3 (2002). (in Chinese).
10) V. F. Komarov, G. V. Sakovich, and A. B. Vorozhtsov, 40th International Annual Conference of ICT, Karlsruhe, Germany (2009).
11) B. Patrick, E. D. Helen, and D. C. Matthew, 12th International Detonation Symposium, California (2002).
12) J. H. Peng, W. H. Chen, H. Su, T. Wu, and R. H. Liu, J. Safety and Environment, 4, 177−179 (2004).
13) J. S. Hwang, C. K. Kim, and J. R. Cho, 38th International Annual Conference of ICT, Karlsruhe, Germany (2007).
14) X. X. Mao, L. F. Jiang, C. G. Zhu, and X. M. Wang, Adv. Mater. Sci. and Eng., 4, 1−8 (2018).
15) C.G. Zhu, H. Z. Wang, and L. Min, J. Energ. Mater., 32, 219−226 (2014).