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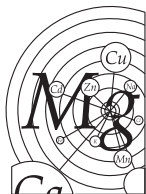
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REVIEW PAPER

APPLICATION AND PROPERTIES OF ALUMINUM IN PRIMARY AND SECONDARY EXPLOSIVES

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ABSTRACT

Aluminum is an easily available and cheap material, which is widely used in military and civil industries, e.g. in space technology, explosion welding, mining, production of oil and natural gas, manufacture of airbags. Primary and secondary explosives containing aluminum are described in this part of the work. Aluminum is added to high explosives of different shapes and sizes. These parameters influence *inter alia* detonation velocity (D), explosion heat, detonation pressure, pressure impulse and thermal stability. Detonation parameters of high explosive (HE) containing aluminum have been determined for binary systems consisting of high explosive or oxidizer and aluminum, plastic bonded explosives (PBX), melt cast explosives, thermobaric explosives (TBX), ammonium nitrate fuel oil (ANFO). Aluminum causes different effects on detonation velocity and explosion heat depending on the type of high explosive in binary systems. The dependence of the aluminum content in a mixture with ammonium nitrate with detonation velocity increased for an aluminum range from 0 to 10%, changed little between 10 and 16% of aluminum added and decreased from 16 to 40% of the aluminum content. For an aluminum content higher than 40%, the detonation process was not observed. The performance of explosives can be determined by the shock wave intensity. An increase in the pressure impulse made Al particle react with gaseous products and the air behind the front of detonation wave. The addition of aluminum also influences the thermal stability of high explosive materials.

Keywords: aluminum, primary explosives, secondary explosives, detonation parameters.

INTRODUCTION

Materials which release large quantities of heat and gaseous decomposition products by violent exothermic chemical reactions are known as high explosive materials (HE). This transformation is called detonation. HE are divided into primary explosives (PE) and secondary explosives (SE). Formulations of HE are usually compositions of explosive materials and additives that facilitate technological processes and improve properties of final products. Formulations of HE are widely used in military and civil industry. Civil applications of HE materials are in space technology (LONG et al. 2015), explosion welding (GÜLENC et al. 2016), the mining industry, where HE are used to crush hard rocks (ROLLINS et al. 1973). In addition, cumulative charges are used to drill new bore holes in the extraction of petroleum and natural gas (LIU 2008), while pyrotechnic charges are used to open airbags (JANG 2015).

The main threat during the storage of HE is the risk of uncontrolled explosion caused by external stimuli, for example heat, friction, strike and electric spark. Thermal stability is determined by such parameters as decomposition temperature, the quantity of generated heat flow or weight loss (GOŁOŃFIT, ZYŚK 2015). The calorimetric analysis is used widely to determine these parameters (SHAN et al. 2016, WANG et al. 2016).

Detonation is the basic process proceeding in HE. Detonation occurs at a speed greater than the speed of sound propagation in the material. A detonation wave is a complex system consisting of the shock wave front (10^{-5} cm) and the following zone of chemical reaction (0.1-1.0 cm). HE are stimulated to detonate by an intense shock wave or by deflagration to detonation transition (DDT). A jump of pressure occurs at the forehead of the shock wave, which causes an increase in temperature. High temperature evokes a chemical reaction in the material. The released energy of the chemical reaction sustains the whole process. The speed at which the detonation wave moves is called the velocity of detonation (D). Gaseous products move in the same direction as the detonation wave, which is determined as the mass velocity of gaseous products – W . Figure 1 shows the structure of the detonation pressure peak marked with a pressure step (p_c) at the front of the shock wave.

A reduction in pressure occurs behind the shock wave. At the end of the chemical reaction zone lies the Chapman-Jouguet point, which determines the conditions of stable detonation. Further reduction of pressure occurs outside the chemical reaction zone due to the propagation of gaseous detonation products. Reactions which are occurring to the Chapman-Jouguet point sustain the shock wave. Dependence of the shock wave time with pressure for conventional HE and thermobaric explosives (TBX) is shown in Figure 2 (XING et al. 2014, MOHAMED et al. 2016). Hypertension and hypotension phases occur for HE. Depending on the type of material, hypertension and hypotension phases develop differently. For TBX, the peak pressure is smaller

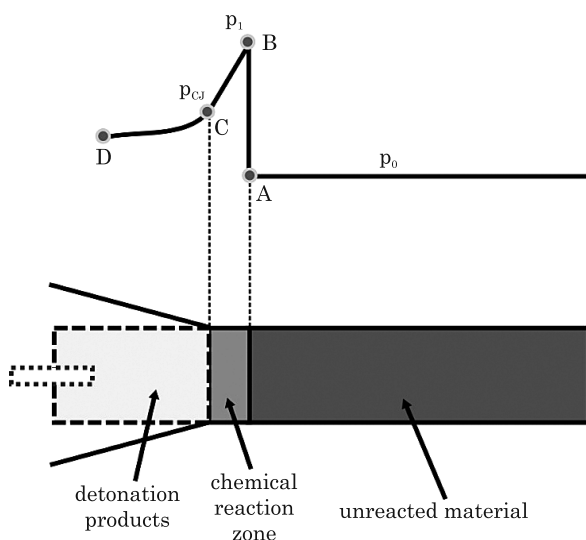


Fig. 1. The structure of a detonation wave: AB – the front of shock wave, BC – chemical reaction zone, CD – Taylor wave, p_0 – initial pressure, p_1 – overpressure peak, p_{CJ} – pressure at the Chapman-Jouguet point

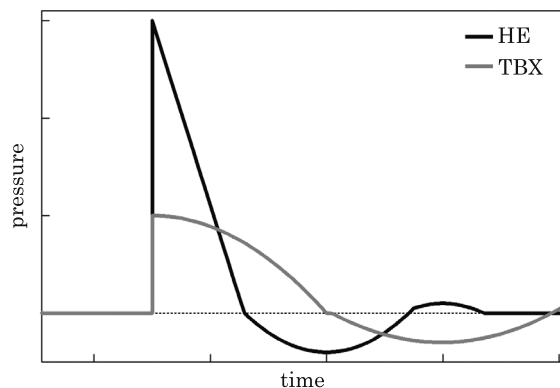


Fig. 2. The dependence of time on pressure for conventional high-energetic materials – HE and thermobaric explosives – TBX (XING et al. 2014, MOHAMED et al. 2016)

but lasts longer and consequently the surface area of the pressure in hypertension is higher than for conventional HE. This explains why TBX have very good demolition properties (TRZCIŃSKI, MAIZ 2015).

Detonation velocity is described by equation (1) according to the hydrodynamic theory of detonation:

$$D = \frac{k+1}{k} \sqrt{\frac{8310kT_2}{M_2}} \quad (1)$$

where: D – detonation velocity, k – the ratio of heat capacity at constant pressure to heat capacity at constant volume, T_2 – temperature of detona-

tion/decomposition products, M_2 – average molecular weight of decomposition products. The highest temperature and the lowest average molecular weight of degradation products must be obtained to receive the highest value of detonation velocity. The highest temperature is achieved in materials which contain a sufficient amount of oxygen for oxidizing decomposition products to the highest oxidation state. The lowest molecular weight is obtained for products received in incomplete oxidation, such as hydrogen (H_2) or carbon monoxide (CO). A typical approach in the development of new mixtures of HE is to obtain the maximum velocity of detonation, which is a compromise between the highest temperature and the lowest average molecular weight. A higher detonation velocity can be achieved when an additional substance which increases the temperature and reduces the average molecular weight of degradation products is added to the formulation. These materials can be metals such as aluminum, magnesium and their alloys (YEN, WANG 2012, ZYGMUNT et al. 2014). In the literature, there are a number of publications which describe the effect of aluminum addition on the functional parameters of HE. These parameters are detonation velocity, detonation temperature, pressure and explosion heat.

The aim of this work is to present the use of aluminum in explosives (primary and secondary) and its effect on the performance characteristics of these mixtures.

ALUMINUM IN PRIMARY EXPLOSIVES

Primary explosives (PE) are used to stimulate secondary explosives, propellants and pyrotechnics. These compounds are characterized by particularly high sensitivity to external stimuli such as impact, friction, flame and electric spark. For these reasons, work with these materials is very dangerous and requires extra caution. High flammability and susceptibility to electric charge characterize primary explosives. The combustion of primary explosives quickly proceeds to detonation, thus they can be used in very small quantities. PE are divided into detonators and primers (igniters). The shockwave is created by detonators. They are used for explosive munitions or demolition charges. Primers provide flame or molten slag generating output. They are used for small arms ammunition. Detonators and primers can be initiated by electric or non-electric charges. Mixtures containing mercury fulminate, lead azide, lead 2,4,6-trinitroresorcinate, tetrazene or diazodinitrophenol are used as primary explosives. Primers containing 52% lead 2,4,6-trinitroresorcinate, 22% barium nitrate, 5% tetrazene, 10% antimony trisulfide and 10% Al powder have an impact sensitivity equal 11 ± 2 cm (OYLER et al. 2015). For comparison, the impact sensitivity of PE containing 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) is in the range between 20 and 25 cm achieved in the same test (BROWN et al. 2015). The first patented PE mixtu-

res at the end of the twentieth century did not contain heavy metal salts. These mixtures contain potassium dinitrobenzofuroxanate, zirconium peroxide and fuels like aluminum, boron, titanium, zirconium, magnesium (HAGEL, REDECKER 1999). Other mixtures contain Al or Al alloy with Mg as a fuel (ERICKSON et al. 2012, JOHNSON, HIGA 2014, PILE, JOHN 2014), bismuth oxide (ERICKSON et al. 2012, PILE, JOHN 2014) or iodates (JOHNSON, HIGA 2014) as an oxidant. The mixture of an oxidizer and fuel can be applied in exploding bridgewire (EBW) devices. The authors of a US Patent (COLBURN et al. 1964) proposed a mixture which had 74% of molybdenum trioxide and 26% Al for use in EBW devices. The advantages of this mixture are resistance to shock, friction and high temperature. The mixture of MoO_3 and Al could be heated to 866 K without spontaneous ignition. This mixture could be heated for one hour to 755 K without affecting the reliability of EBW devices. The mixture of MoO_3 and Al created sparks and did not lead to explosion in 33% of the tests of dropping 6 kg of weight from 50 cm of high. The mixture of potassium perchlorate-aluminum led to explosion in 75% of the same test.

ALUMINUM IN SECONDARY EXPLOSIVES

Aluminum powder in HE mixtures influences their detonation parameters such as detonation velocity, shock wave intensity during detonation, explosion heat, pressure impulse and stability. Testing new materials is very expensive, hence it is important to carry out theoretical calculations (CHINNAYYA et al. 2004, MASSONI et al. 2006, PETITPAS et al. 2009, SMIRNOV et al. 2014) which allow determination of the effect of Al on detonation parameters of HE. Detonation parameters of HE containing aluminum are described in many papers, for instance dealing with a binary system consisting of HE or oxidizer and Al, plastic bonded explosive (PBX), melt cast explosives, TBX, ammonium nitrate fuel oil (ANFO) (KEICHER et al. 1999, WHARTON, ROYLE 2000, PASZULA et al. 2004).

The basic parameter of detonation is detonation velocity (D). The addition of aluminum to HE changes detonation velocity. This metal can result in increasing (MARANDA et al. 2011) or decreasing values to less than 1000 m s^{-1} (MARANDA, CUDZIŁO 2001). Binary systems of HE+Al were chosen in order to demonstrate the influence of the Al content on detonation velocity. The selected HE were nitroguanidine (NQ), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), bis(2,2,2-trinitroethyl)nitramine (BTNEN), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (CL-20), 2-methyl-1,3,5-trinitrobenzene (TNT), nitroglycerin (NG), nitromethane. The structural formulas of the selected HE are shown in Figure 3.

Detonation velocity depends on the aluminum content in mixtures with the HE in different ways. Detonation velocity increases up to the Al content $x_{wAl} = 0.1$ ($D = 3580 \text{ m s}^{-1}$), then decreases for a higher Al content in the mix-

NG-Al (GOGULYA et al. 2004). The values for systems with lithium fluoride (LiF) as inert additive were additionally compiled. The decreasing of the detonation velocity with a decreasing Al size was observed for such systems as HMX-Al and BTNEN-Al. It is worth noting that using nano-Al with TNT caused an opposite behavior, that is an increasing detonation velocity compared with mixtures containing micro-Al (BROUSSEAU et al. 2002). lower values of detonation velocity (about 170-350 m s⁻¹) were observed in HMX+Al systems (Al size below 0.5 μm) than in HMX-LiF (GOGULYA et al. 2004). The authors admitted that they were unable to verify whether Al reacts in the reaction zone or it is the ballast. Similar values were observed in BTNEN-Al and BTNEN-LiF systems. The authors claimed that all Al reacted in the reaction zone. The values of detonation velocity obtained in the NG-Al system were similar to those in the NG system.

In the mixture of ammonium nitrate (AN) with aluminum, the dependence of detonation velocity on the Al content was divided into three sections (MARANDA et al. 1989):

- 1) an increase in detonation velocity to $x_{wAl} = 0.10$, which was the result of increasing temperature and explosion heat which supported the shock wave;
- 2) small change in detonation velocity for $x_{wAl} = 0.10-0.16$, in this section maximum detonation velocity was observed $D_{max} = 3460$ m s⁻¹ for $x_{wAl} = 0.14$;
- 3) a decrease in detonation velocity above $x_{wAl} = 0.16$.

Detonation was not observed above $x_{wAl} = 0.4$ for this mixture (PASZULA et al. 2008). Detonation parameters of ANFO with Al addition are greater (by about 7.7%) than those of traditional ANFO (MARANDA et al. 2003). ANFO with 3 and 5% of Al have similar detonation parameters.

The influence of the Al content on detonation velocity was also researched in PBX. The selected composition was based on hydroxyl terminated polybutadiene (HTPB)-dioctyl adipate (DOA)-RDX-Al, HTPB-DOA-HMX-Al, glycidyl azide polymer (GAP)-triethylene glycol dinitrate (TEGDN)-[2-methyl-3-nitrooxy-2-(nitrooxymethyl)propyl] nitrate (TMETN)-RDX-Al. The detonation velocity for selected PBX ($x_{wAl} = 0.10$ and 0.20) is shown in Figure 5. The size of Al equal to 100-200 nm was marked as nAl. The detonation velocity in PBX based on HTPB decreased with a higher amount of Al. The replacement of micro-Al with nano-Al did not cause a significant change in detonation velocity. In PBX based on GAP, detonation velocity was observed to decrease significantly for nano-Al compared to micro-Al (BROUSSEAU et al. 2002, PRAKASH et al. 2004).

Other significant parameters which characterize the process of detonation were detonation pressure and pressure impulse. Detonation pressure of RDX+Al mixtures is comparable or lower than that of RDX. The pressure impulse increased from 368 to 1031 Pa s, also for TBX (TRZCIŃSKI et al. 2012). This means that Al particles react with gaseous products and the air behind

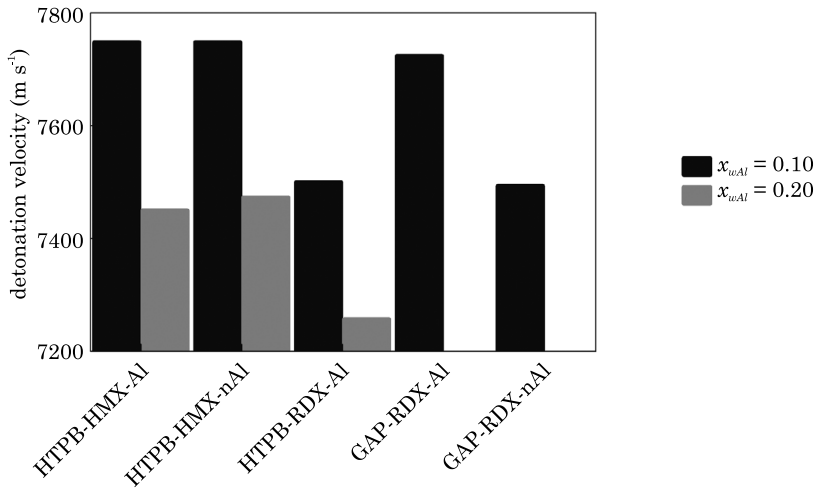


Fig. 5. The detonation velocity for HTPB-HMX-Al, HTPB-RDX-Al and GAP-RDX-Al PBX (BROUSSEAU et al. 2002, PRAKASH et al. 2004)

the front of detonation wave (TRZCIŃSKI et al. 2007b). The authors of this study did not determine the influence of Al particles on pressure impulse due to the large value of standard deviation of Al. Opposite effects of Al on detonation pressure and pressure impulse were observed in the mixtures of nitromethane with PAM (TRZCIŃSKI et al. 2007a), AN+Al, to $x_{wAl} = 0.05$ (ZYGUNT 2009, HADZIK et al. 2012). Figure 6 shows the dependence of detonation velocity on the Al content in PBX based on HTPB/DOA/RDX/Al (PRAKASH et al. 2004). Detonation pressure decreases with the content of Al increasing to 10%, then there was a local maximum at 15%, and afterwards decreasing detonation pressure was noted for values above 25%. PBX with the 15% Al content in HTPB/DOA/RDX/Al provides optimal values of detonation pressure and impulse.

The performance of explosives can be determined by the shock wave intensity. The dependence of the shock wave intensity of the Al content in the

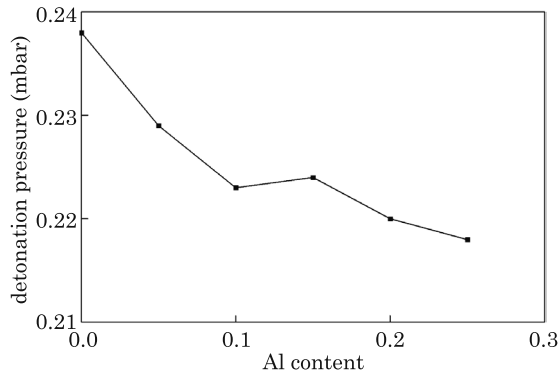


Fig. 6. The dependence of aluminum content on the detonation velocity for HTPB-RDX-Al PBX (PRAKASH et al. 2004)

mixtures NQ+Al (MARANDA et al. 2011) and TBX (TRZCIŃSKI et al. 2012, YAN et al. 2016) is shown. For NQ+Al mixtures, the estimated shock wave intensity parameters increased with the increasing Al content (Table 1).

Table 1
Parameters of shock wave at the distance of 1.5 m from the charge (MARANDA et al. 2011)

Content of mixture NQ/Al	Amplitude P_s (kPa)	Specific impulse I_s (Pa s)
95/5	46	18.1
90/10	66	17.0
85/15	93	18.0

Al powder and Al foils were used to prepare TBX charge for the shock wave intensity measurements. The charges were designed as follows: the core – phlegmatized RDX (RDX_{ph}), the external layer – mixtures of ammonium perchlorate (AP) and Al powder (TRZCIŃSKI et al. 2012) or Al foil, Al powder (YAN et al. 2016). Table 2 shows the parameters of shock wave intensity for various charges. The increasing Al content caused an increase in the shock wave intensity parameters. For charges with Al foil, a decrease in these parameters was observed.

Table 2
Parameters of shock wave in the bunker at the distance of 2 m from the charge
(Al1 – powder with diameter of particles to 325 Mesh, Al2 – powder with diameter of particles from 100 to 325 Mesh) (TRZCIŃSKI et al. 2012, YAN et al. 2016)

Charge symbol	Amplitude P_s (kPa)	Specific impulse I_s (Pa s)
RDX _{ph}	56	25
RDX _{ph} +Al foil (10 μm)	60	35
RDX _{ph} +Al powder	89	43
RDX _{ph} +Al foil (100 μm)	27	22
RDX _{ph} +AP/Al1 50/50	66	34
RDX _{ph} +AP/Al1 25/75	65	39
RDX _{ph} +Al1	89	43
RDX _{ph} +AP/Al2 50/50	73	42
RDX _{ph} +AP/Al2 25/75	60	32
RDX _{ph} +Al2	71	45

Another parameter specifying the detonation process is explosion heat. The higher the value of explosion heat achieved by HE, the more work potentially performed by this HE. Mixtures of RDX_{ph}+Al are characterized by higher values of explosion heat than mixtures with a content of inert additive, e.g. aluminum oxide or LiF (KICIŃSKI, TRZCIŃSKI 2008, TRZCIŃSKI et al. 2007b). Explosion heat increases with an increasing Al content to $x_{wAl} = 0.30$,

after which it decreases to $x_{wAl} = 0.60$ (KICIŃSKI, TRZCIŃSKI 2008, TRZCIŃSKI et al. 2007b). Explosion heat intensifies with an increasing Al content in AN+Al mixtures (PASZULA et al. 2008). Nano-Al in ANFO, TNT (BROUSSEAU et al. 2002), RDX (KICIŃSKI, TRZCIŃSKI 2008) increases explosion heat in comparison with micro-Al. Nano-Al causes higher values of explosion heat because it has a larger surface area and reacts more easily with oxygen. In the CL-20-Al mixture, a significant increase of explosion heat (23-40%) was observed compared with CL-20 (MAKHOV 2014). This mixture was an exception because the mole number of gaseous products of decomposition decreases with the increasing explosion heat in this system. This is caused by a large part of condensed products. Al reacts with carbon dioxide and water and produces products with lower molecular weights: carbon oxide and hydrogen. In addition, it was observed that the use of nano- and micro-Al did not significantly affect the value of explosion heat in the mixture of CL-20-Al. Values of explosion heat are higher in the RDX+Al mixture (TRZCIŃSKI et al. 2007b) in atmospheric air or oxygen-argon mixture in comparison with nitrogen or argon. If the content of oxygen is around 20% in the atmosphere, an afterburning of detonation products and Al can be observed. Al and Al-Mg alloys oxidize to aluminium oxide and magnesium oxide when the explosion temperature of these substances is higher than 2200-2300 K (KOZAK et al. 2012).

Thermal stability is an important parameter which characterizes HE. This parameter is determined by using different techniques of thermal analysis of compound decomposition, e.g. Differential Scanning Calorimetry (DSC). Al in the mixture with CL-20 and 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (BTATz) causes a visible change in the DSC curve (XING et al. 2015). The first exothermic transition (CL-20 decomposition) takes place at higher temperatures and the second exothermic transition (BTATz decomposition) takes place at lower temperatures with the addition of Al. Kinetic and thermodynamic parameters were calculated and a positive value of free energy of the activation was obtained. This means that the decomposition reaction does not occur when adequate heating is provided. The critical temperature of thermal explosion and the initial decomposition temperature are higher in the mixture CL-20+BTATz+Al in comparison with the mixture without Al.

CONCLUSION

The aluminum content and particle size in a binary HE+Al system produced different effects on detonation velocity and explosion heat. These parameters depend on the type of used HE. In an AN+Al mixture, the dependence of detonation velocity (D) on Al was complex. It was divided into three sections: increase in D to 10% of Al content, low change of D to 16% of Al content and decrease in D above 16% of Al content. The detonation process was not observed above 40% of Al content for this mixture.

The pressure and pressure impulse are characteristic parameters of a detonation process. These parameters depend on the composition and particle size of Al. The increase in the pressure impulse induced Al particles to react with gaseous products and the air behind the front of a detonation wave. A decrease in the pressure impulse was observed in PBX based on HTPB. The Al content also effects an increase in the intensity of the shock wave which is generated during detonation.

Aluminum is widely used in military and civil materials. An appropriate composition and particle size of Al can ensure production of formulations with desired parameters.

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