https://doi.org/10.18321/cpc535

Investigation of the effects of ZrO_2 on burning characteristics and thermal properties of AN/Mg-Al – composite pyrotechnic mixtures

K. Kamunur[1,2*], B. Milikhat[2], R.G. Abdulkarimova[1,2], A.I. Niyazbaeva[1], D. Sultanova[1], G. Tolen[1]

[1]Al-Farabi Kazakh National University, 71 al-Farabi ave., Almaty, Kazakhstan
[2]Institute of Combustion Problems, 172 Bogenbay batyr str., Almaty, Kazakhstan

Abstract

Ammonium nitrate (AN) is widely used as an oxidizer in propellants, explosives and pyrotechnics. Some of the disadvantages of ammonium nitrate can be reduced by using Mg-Al alloy as a fuel. The effects of zirconium oxide (ZrO_2) on the burning characteristics and thermal properties of AN/Mg-Al – based pyrotechnic mixtures have been studied. The addition of ZrO_2 increase the burning rate significantly and lowers the pressure deflagration limit (PDL) from 2 MPa to less than 1 MPa. Differential Scanning Calorimetry investigated the thermal decomposition characteristics at different heating rates, and the activation energies were evaluated. With the addition of Mg-Al alloy to pure AN, the main peak shifts lower at approximately 100 °C. At the same time, ZrO_2 does have a significant influence on the thermal properties of both of AN and AN/MgAl. The addition of MgAl alloy and ZrO_2 reduces the activation energy.

Keywords: pyrotechnic mixtures, ammonium nitrate (AN), Mg-Al alloys, zirconium oxide, burning characteristics, thermal properties, activation energy.

1. Introduction

Composite pyrotechnic mixtures are heterogeneous materials consisting of synthetic or plastic bonding matrices, metals or metal alloys, and crystalline oxidants. They are used as fuel for space launchers, tactical and strategic missiles, automobile airbag inflators, etc.

Ammonium nitrate is an oxidizer having positive oxygen (+20%) and has several disadvantages such as low burning rate, low flammability, high hygroscopic nature, and phase changes in the solid-state at temperatures below 100 °C. Despite these drawbacks, AN is widely used as an oxidizer of energetic systems because its combustion products are clean. The chemical decomposition of ammonium nitrate has been a lot studied, and the possibilities of some thermal decomposition are presented [1-6].

The use of an Mg-Al alloy as fuel for improving the burning and thermal decomposition properties of pyrotechnic mixtures based on ammonium nitrate is considered effective for improving the performance of AN-based pyrotechnic mixtures. It is known that the density, melting point, and ignition temperature of the Mg-Al alloy are lower than those of pure magnesium and aluminum [7] and this property improves the lower pressure limit of AN-based pyrotechnic mixtures [8-10]. Many studies have declared that the inclusion of metal oxides in the composition of the energetic materials is based on AN improved burning characteristics [11-15]. Although some metal oxides exert a negative effect on the burning of AN/Mg-Al composite pyrotechnic mixtures [16].

In this study, the effect of zirconium oxide (ZrO_2) on the burning characteristics in high

*Ответственный автор
E-mail: kamunur.k@mail.ru (K. Kamunur)

pressures and thermal properties of AN/Mg-Al – based pyrotechnic mixtures were investigated with a strand burner and differential scanning calorimeters at different heating rates. Further, the activation energy was evaluated by the method of Kissinger.

2. Experimental part

2.1 Materials

Ammonium nitrate was used as an oxidizer in the pyrotechnic mixtures. Diameter of AN between 212 and 350 μm. It was of ≥ 99% purity. Mg-Al alloy (50/50) is used as a fuel in the pyrotechnic mixtures with a diameter of particles between 50 to 70 μm. Zirconium oxide (ZrO_2) was used as a catalyst. The diameter of the basic metal oxide particles was 60–70μm range. The powder has a purity of at least 99.7%. Paraffin was used as an energetic binder.

2.2 Materials and propellant samples

All components of the AN/Mg-Al/ZrO_2 pyrotechnic mixtures were dried (24 h) and mixed in the ball mill (5 min). All samples were prepared by pressure pressing method. The pyrotechnic mixtures samples were prepared with and without zirconium oxide. The samples were prepared by pressing in a cylindrical shape on a hydraulic machine under a pressure of 20 MPa. The compositions of the samples are shown in Table 1.

2.3 Measurement of burning characteristics

The diameter of pyrotechnic mixtures strand sample is 6 mm and the length is 10 mm. The burning process was studied under nitrogen pressure in the burning chamber. Each sample was burned under a pressure of 1 to 7 MPa. The burning of pyrotechnic mixtures was recorded using high-speed camera. These videos were used to determine the burning rate of each samples.

All tests are measured 3 times at each pressure and the average burning rate is obtained. If the pyrotechnic mixture sample does not ignite or

Table 1. Sample compositions

AN	MgAl	ZrO_2
70 wt%	30 wt%	-
70 wt%	30 wt%	5 parts (without)

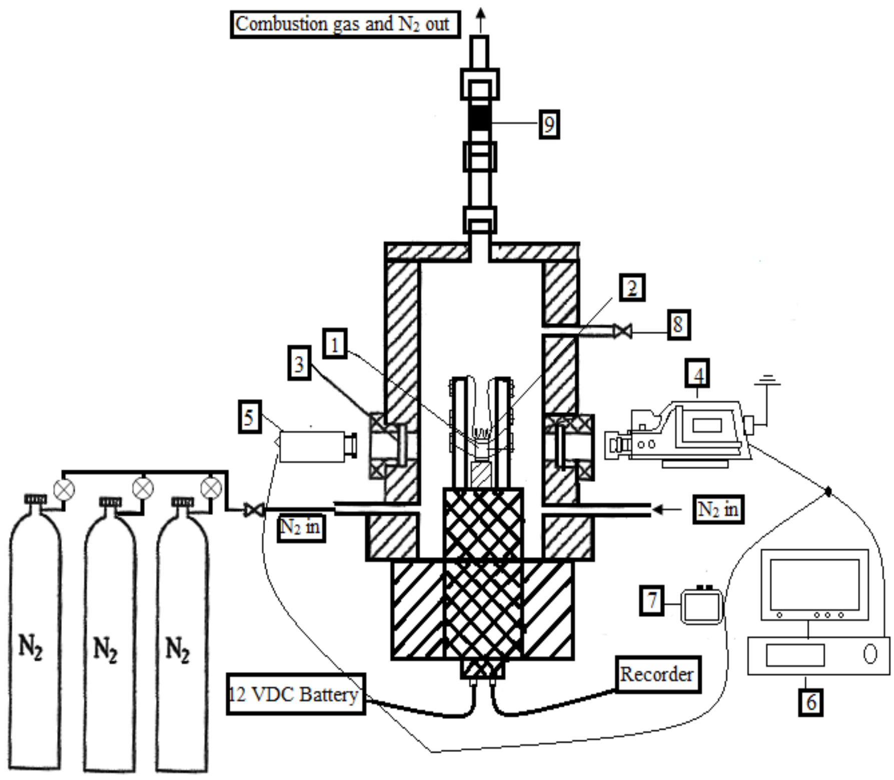


Fig. 1. Schematic of the combustion test setup: 1 – sample; 2 – nichrome wire; 3 – window; 4 – high-speed video camera; 5 – camera; 6 – PC, 7 – tranformer; 8 – system for pressure control; 9 – filter.

1/3 does not burned, the burning rate will not be determined. Figure 1 shows a scheme of a pressure burning chamber.

2.4 Measurement of thermal decomposition behavior

Thermal analysis is effective way to study thermal decomposition and ignition of pyrotechnic mixture. Thermal decomposition properties are studied by using Differential Scanning Calorimeter (DSC) in the temperature range of 60 to 400 °C. The equipment operates in atmospheric pressure in the nitrogen flow(300 cm^3/min). DSC is working with the different heating rates of (β) 2.5–20 °C min^{-1}. In DSC equipment, the DSC value was measured 3-4 times for each sample.

3. Results and discussion

3.1 Burning characteristics

Figure 2 shows the phenomena of burning of AN/MgAl – based pyrotechnic mixtures at pressures of 3 and 5MPa.

Figure 2 shows that the MgAl/AN – based pyrotechnic mixtures depending on the increase in pressure increases the in burning time in the form of a line. However, pyrotechnic mixtures do not ignite at certain reduced pressures. For example, the pyrotechnic mixtures AN/Mg-Al without ZrO_2 did not ignite when the medium pressure decreased by 2 MPa. This pressure limit required for the ignition of AN/Mg-Al – based pyrotechnic mixtures were defined as the PDL.

Figure 3 shows the propagation of combustion wave for the AN/Mg-Al/ZrO_2 mixtures in the burning chamber at different pressures.

Figure 3 also shows increases in burning rate due to increases in pressure for AN/Mg-Al/ZrO_2. A lower PDL value is desirable for the Mg-Al/AN – based pyrotechnic mixtures to improve the ignitability at low pressure and the burning rates increased by the catalytic effect of ZrO_2.

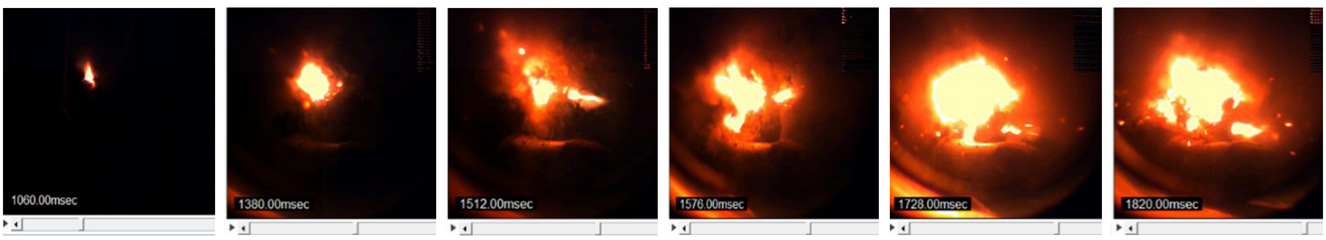
The burning Characteristics of composite pyrotechnic mixtures; AN/Mg-Al and AN/Mg-Al/ZrO_2 at different pressures are shown in Fig.4.

When addition ZrO_2, the burning rate of the pyrotechnic mixtures increases by 3 mm s^{-1} in average at each pressure. At the same time, the PDL was reduced from 2 MPa to less than 1 MPa. Pressure index of two compositions are nearly same at approximately 0.57.

3.2 Characteristics of thermal decomposition

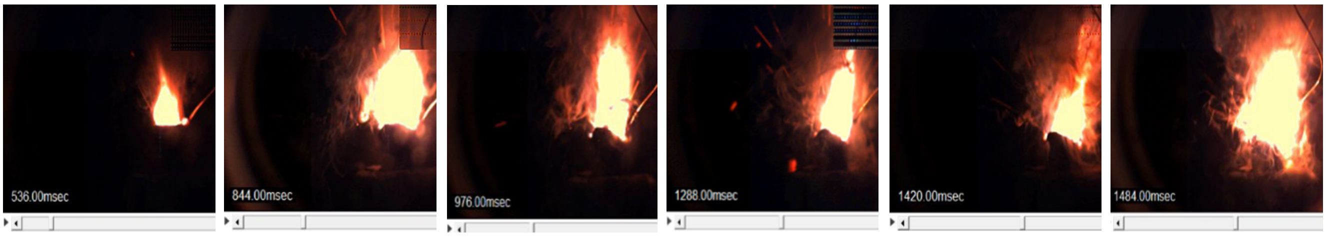
The characteristics of the thermal decomposition of pyrotechnic mixtures, prepared in different ways, were measured at different heating rates by the DSC method. Figure 5 shows two endothermic peaks at 127 and 169 °C respectively, in accordance with the DSC values of pure AN. Endothermic peaks at 127 °C are due to a phase exchange of pure ammonium nitrate and melting point at 169 °C. Wide endothermic sequences after melting with ammonium nitrate is reduced to the thermal decomposition of ammonium nitrate. At the same time, with the addition of ZrO_2, the thermal decomposition temperature decreased by 5–10 °C comparing

(AN/MgAl, 3 MPa, Burning time – 824 msec)

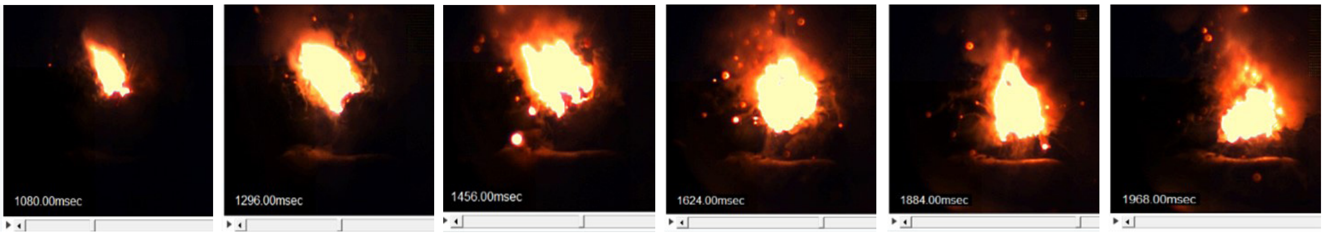


(AN/MgAl, 5 MPa, Burning time – 664 msec)

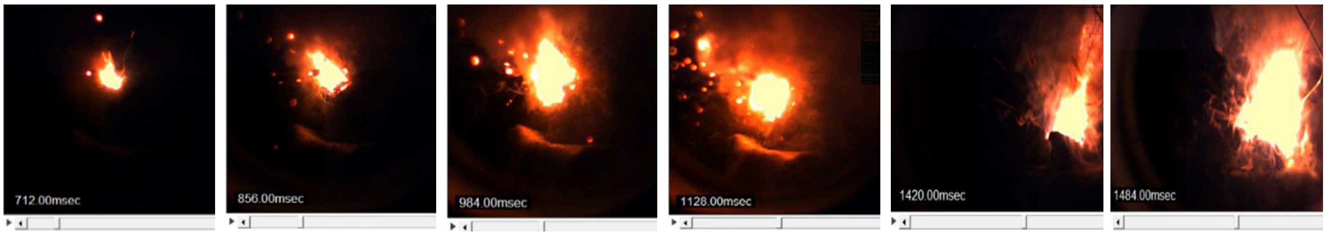
Fig. 2. Burning cinegram of AN/Mg-Al – based pyrotechnic mixtures at pressures of 3 MPa and 5 MPa.



(AN + MgAl + ZrO_2, 1 MPa, burning time – 948 msec)



(AN + MgAl + ZrO_2, 3 MPa, burning time – 906 msec)



(AN + MgAl + ZrO_2, 5 MPa, burning time – 728 msec)

Fig. 3. Burning cinegram of AN/Mg-Al/ZrO_2 – based pyrotechnic mixtures at 1 MPa, 3 MPa and 5 MPa.

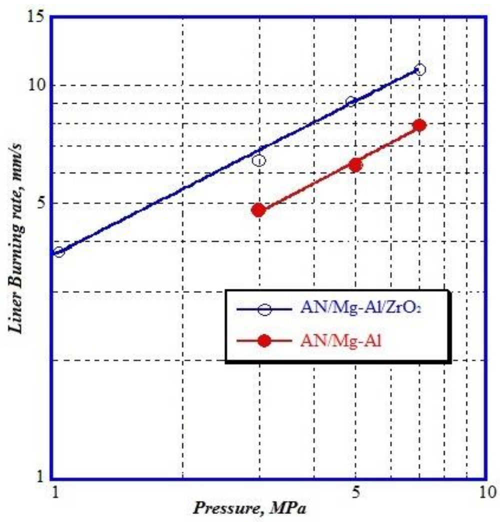


Fig. 4. Dependencies of the burning rates of AN/Mg-Al and AN/Mg-Al/ZrO_2 on the pressure.

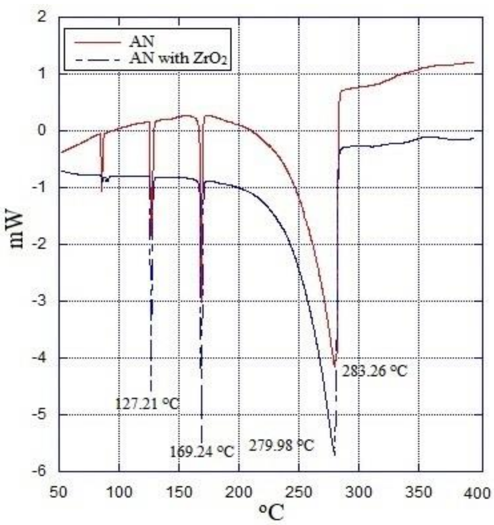


Fig. 5. DSC curves for pure AN and AN/ZrO_2.

with pure AN. The addition of zirconium oxide to ammonium nitrate may affect as a catalyst to AN.

Figure 6 shows the DSC values of the thermal decomposition of AN/Mg-Al and AN/MgAl/ZrO_2 composites.

Figure 6 shows that typical DSC values for AN/Mg-Al and AN/Mg-Al with ZrO_2 pyrotechnic composites. According to DSC values, the endothermic peak of 127 °C is due to the phase exchange of ammonium nitrate. Large exothermic peaks are registered between 166.41 and 172.59 °C. This is due to the thermal decomposition associated with the melting of ammonium nitrate at the temperature of about 169 °C under the action of a MgAl alloy [17].

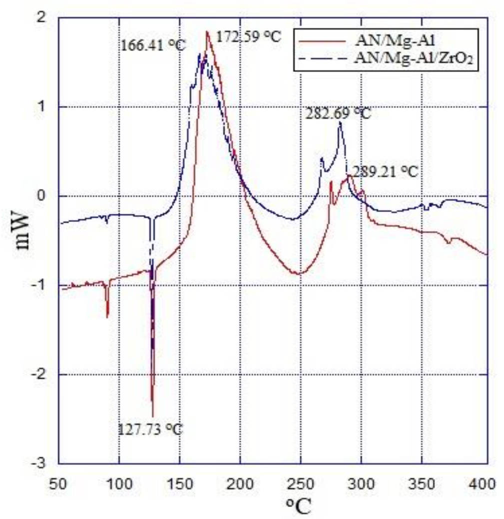


Fig. 6. DSC curves for AN/Mg-Al and AN/Mg-Al with ZrO_2.

$NH_4NO_3 \leftrightarrow NH_3 + HNO_3$ H = 176 kJ mol^{-1} (1)

From 282.69 to 289.21 °C there are small exothermic peaks. AN is decomposed into water and N_2O [18].

$NH_4NO_3 \rightarrow N_2O + 2H_2O$ ΔH = −59 kJ mol^{-1} (2)

Figure 6 shows the effect of ZrO_2 on AN/Mg-Al – based pyrotechnic mixtures. The first large exothermic peak from 140 to 240 °C coincide with the thermal decomposition of the MgAl alloy, which accompanies the melt of ammonium nitrate. Ammonium nitrate in small exothermic peaks at a temperature between 250 and 300 °C appears from the separation of water and nitrogen oxide (N_2O) by dissolving gaseous products. Therefore, the principle of Fig. 6 is the same with Fig. 5, which indicates that the ZrO_2 compound do significantly affect the thermal decomposition characteristics of AN/MgAl pyrotechnic mixtures. The addition of Mg-Al alloy as a fuel and ZrO_2 as a catalyst increased the thermal decomposition temperature of ammonium nitrate and increases the ignition of pyrotechnic composites.

3.3 Kinetics of thermal decomposition

The activation energy is important in the kinetics of thermal decomposition properties of pyrotechnic mixtures and is evaluated using the Kissinger method based on the DSC analysis [15-16].

According to the Kissinger method, E_a is expressed by the following equation:

$$\frac{E_a}{R} = \frac{dln(\beta T_p^{-2})}{dT_p^{-1}}$$

where T_p is the temperature of the thermal decomposition.

Where T_p is the peak temperature of the DSC curve. β is heating rate of DSC. It can be assumed that E_a changes from the change in T_p values of the DSC curve under the influence of the catalyst.

As noted in Section 3.2, the thermal peaks of thermal decomposition of AN/Mg-Al pyrotechnic mixtures are less than 100 °C compared to pure ammonium nitrate. The values of these pyrotechnic mixtures can be determined by the DSC values measured at each heating rate in determining the activation (E_a) of gas generators with β = 2.5, 5, 10 and 20 K min^{-1}. Table 2 shows the values of T_p for ammonia nitrate and AN/Mg-Al – based pyrotechnic mixtures.

Figure 7 shows the relationships between ln (βT_p^{-2}) and T_p^{-1} for AN and AN/Mg-Al pyrotechnic mixtures. The E_a values were determined as 99.0 and 91.5 kJ/mol for pure AN and AN/Mg-Al, respectively. The activation energy decreased with the addition of Mg-Al alloy, and this result shows that the thermal decomposition of AN is activated by the exothermic reaction with Mg-Al alloy in the condensed phase.

Table 3 shows the values of T_p for pure AN with ZrO_2 and AN/Mg-Al with ZrO_2 pyrotechnic mixtures with ZrO_2, and Fig. 8 shows the Kissinger plot for pure AN with ZrO_2 and AN/Mg-Al with ZrO_2. The E_a of AN with ZrO_2 and AN/Mg-Al with ZrO_2 was 90.0 and 89.0 kJ mol^{-1}, respectively. The E_a of AN

Table 2. The values of T_p for AN and AN/Mg-Al – based pyrotechnic mixtures

[β/ °C min^{-1}]	T_p/°C	
	AN	AN/MgAl
2.5	221.99, 235.29, 250.51, 252.10	146.70, 150.21, 153.22, 164.64
5	224.05, 239.35, 262.26, 264.03	153.39, 159.22, 166.64, 174.41
10	248.03, 261.25, 280.06, 283.47	159.11, 167.11, 172.59, 205.76
20	257.65, 272.32, 292.98, 297.37	169.05, 175.25, 184.44, 215.34

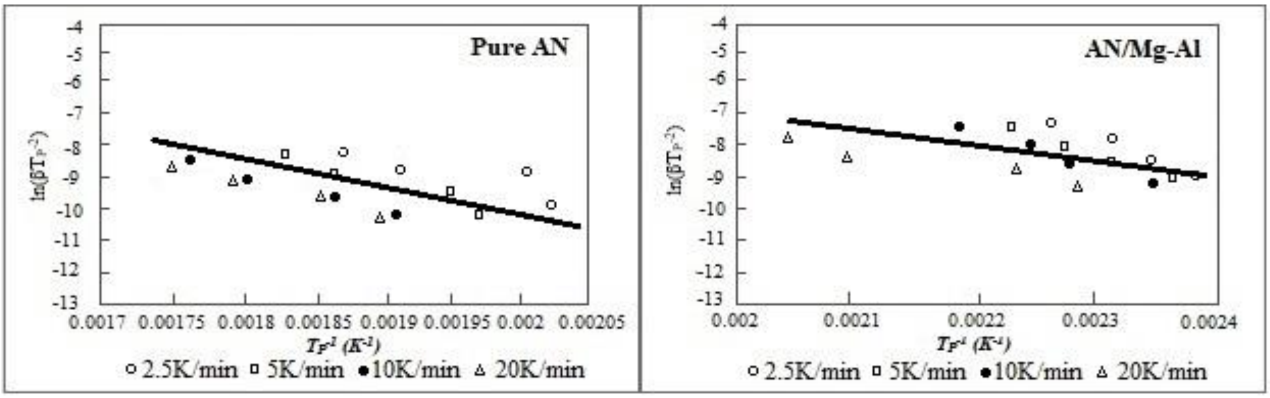


Fig. 7. Kissinger plots of AN and AN/Mg-Al – based pyrotechnic mixtures.

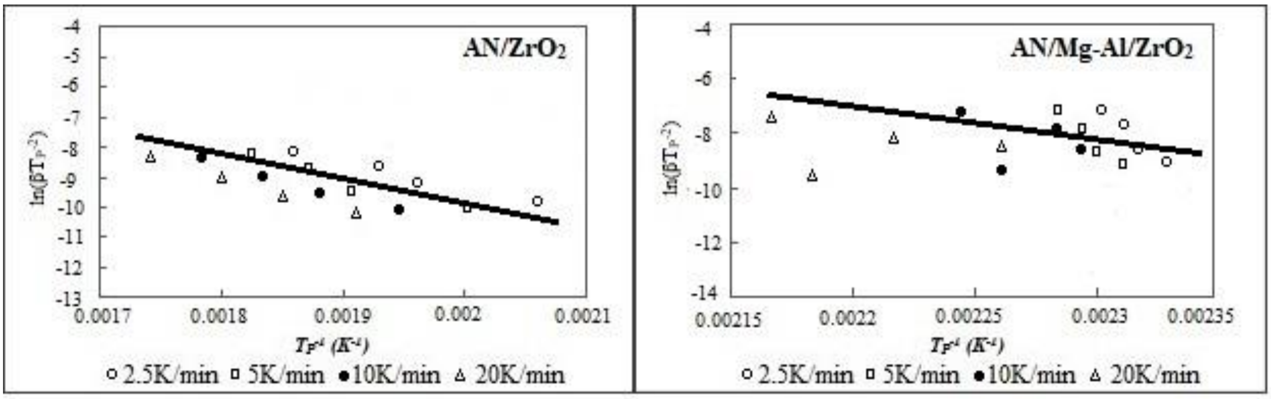


Fig. 8. Kissinger plot of pure AN with ZrO_2 and AN/Mg-Al with ZrO_2.

Table 3. The values of T_p for AN and AN/MgAl with ZrO_2

[β/ °C min⁻¹]	T_p/K	
	AN with ZrO_2	AN/MgAl with ZrO_2
2.5	212.25, 226.13, 240.65, 249.50	156.08, 159.21, 160.99, 164.52
5	236.27, 251.17, 258.56, 267.49	159.21, 161.34, 162.44, 169.21
10	245.07, 260.84, 271.90, 282.69	159.33, 162.64, 164.41, 177.99
20	264.67, 274.63, 283.00, 300.14	160.87, 164.52, 170.09, 188.35

with ZrO_2 is reduced by 9.0 kJ mol^{-1} comparing with that of AN itself, suggesting that ZrO_2 accelerate the thermal decomposition reaction of AN pyrotechnic mixtures slightly in the condensed phase.

The activation energy of AN thermal decomposition is reduced by addition Mg-Al alloy and zirconium oxide (ZrO_2). These results show that the thermal decomposition of pure AN and AN/Mg-Al – based pyrotechnic mixtures can be improved by ZrO_2. The rate determining steps of AN/Mg-Al pyrotechnic mixtures may begin in the gas-phase reaction zone. Addition of ZrO_2 can be assumed to improve the gas-decomposition reactions of composites or combustion reaction in the gas-phase reaction zone as a catalyst and increases the burning rate. The same pressure index of burning rate for AN/Mg-Al and AN/Mg-Al/ ZrO_2 may support this idea ZrO_2 acts as a catalyst.

4. Conclusion

The use of the Mg-Al alloy as a fuel for the AN-based pyrotechnic mixtures increases the burning rate. Addition of ZrO_2 to AN/Mg-Al reduces the PDL from 2 MPa to less than 1 MPa and increases the burning rate significantly. ZrO_2 additive reduces the activation energy of the pure AN from 99.0 to 90.0 kJ/mol and improves the gas decomposition reactions in the condensed phase. However, it can be assumed that the addition of ZrO_2 to AN/Mg-Al-based pyrotechnic mixtures affected the transitioned the from condensed phase zone to gas phase zone. ZrO_2 can be the catalyst for our AN – based pyrotechnic mixtures system.

References

[1]. Kajiyama K, Izato Y, Miyake A (2013) J Therm Anal Calorim 113:1475-1480. DOI:10.1007/s10973-013-3201-5

[2]. Yang M, Chen X, Wang Y, Yuan B, Niu Y, Zhang Y, Liao R, Zhang Z (2017) Journal of Hazardous Materials 337:10-19. DOI:10.1016/j.jhazmat.2017.04.063

[3]. Atamanov MK, Noboru I, Shotaro T, Amrousse R, Tulepov MY, Kerimkulova AR, Hobosyan MA, Hori K, Martirosyan KS, Mansurov ZA (2016) Combustion science and technology 188:2003-2011. DOI:10.1080/00102202.2016.1220143

[4]. Oommen C, Jain SR (1999) J Hazard Mater. 67:253-281. DOI:10.1016/S0304-3894(99)00039-4

[5]. Kamunur K, Jandosov JM, Abdulkarimova RG, Hori K, Yelemessova ZhK (2017) Eurasian Chemico-Technological Journal 19:34-346. DOI:10.18321/ectj682

[6]. Sinditskii VP, Egorshev VY, Levshenkov AI, Serushkin VV (2005) Propellants Explos Pyrotech. 30:269-280. DOI:10.1002/prep.200500017

[7]. Yasmine A, Schoenitz M, Dreizin EL, (2013) Journal Combustion and Flame 160:835-842. DOI:10.1016/j.combustflame.2012.12.011

[8]. Murata H, Azuma Y, Tohara T et al. (2000) Science and Technologyof Energetic Materials, 61(2):58-66.

[9]. Shoshin YL, Mudryy RS, Dreizin EL (2002) Combustion and Flame 128(3)259-269. DOI:10.1016/S0010-2180(01)00351-0

[10]. Habu H, Hori K (2006) Journal Science and Technology of Energetic Materials 67(6):187-192.

[11]. Kohga M, Nishino S (2009) Propellants, Explosives, Pyrotechnics 34(4):340-346. DOI:10.1002/prep.200800060

[12]. Rodić V (2012) Scientific Technical Review, 62(3-4):21-27.

[13]. Naya T, Kohga M (2013) Propellants explosive, pyrothec. 38:87-94. DOI:10.1002/prep.201200060

[14]. Naya T, Kohga M (2013) Propellants explosive, pyrothec. 38:547-554. DOI:10.1002/prep.201200159

[15]. Naya T, Kohga M (2015) Journal of Energetic Materials 33(4):288-304. DOI:10.1080/07370652.2014.988775

[16]. Lee J-K, Kim ShK (2011) Materials Transactions, 52(7):1483-1488. DOI:10.2320/matertrans.M2010397

[17]. Chaturvedi S, Dave PN (2013) J. Energ. Mater. 31:1-26. DOI:10.1080/07370652.2011.573523

[18]. Vyazovkin S, Clawson JS, Wight CA (2001) Chem. Mater. 13:960-966. DOI:10.1021/cm000708c

Исследование влияния ZrO_2 на характеристики горения и термические свойства АС/Mg-Al – композитных пиротехнических смесей

К. Камунур[1,2*], Б. Милихат[2], Р.Г. Абдулкаримова[1,2], А.И. Ниязбаева[1], Д. Султанова[1], Г. Толен[1]

[1]КазНУ имени аль-Фараби, пр. Аль-Фараби, 71, Алматы, Казахстан
[2]Институт проблем горения, ул. Богенбай батыра, 172, Алматы, Казахстан

Аннотация

Аммиачная селитра (АС) широко используется в качестве окислителя в ракетном топливе, взрывчатых веществах и пиротехнике. Некоторые недостатки нитрата аммония можно уменьшить, используя сплав Mg-Al в качестве топлива. Изучено влияние оксида циркония (ZrO_2) на характеристики горения и термические свойства пиротехнических смесей на основе АС/Mg-Al. Добавление ZrO_2 значительно увеличивает скорость горения и снижает предел дефлаграции под давлением с 2 МПа до менее 1 МПа. Дифференциальная сканирующая калориметрия исследовала характеристики термического разложения при различных скоростях нагрева и оценила энергии активации. При добавлении сплава Mg-Al к чистой АС основной пик смещается ниже примерно при 100 °С. В то же время ZrO_2 действительно оказывает значительное влияние на термические свойства как АС, так и АС/MgAl. Добавление сплава MgAl и ZrO_2 снижает энергию активации.

Ключевые слова: пиротехнические смеси, нитрат аммония (НА), сплавы Mg-Al, оксид циркония, характеристики горения, тепловые свойства, энергия активации.

АС/Mg-Al – композиттік пиротехникалық қоспалардың жану сипаттамалары мен жылу қасиеттеріне ZrO_2 әсерін зерттеу

К. Камунур[1,2*], Б. Милихат[2], Р.Г. Абдулкаримова[1,2], А.И. Ниязбаева[1], Д. Султанова[1], Г. Толен[1]

[1]Әл-Фараби атындағы ҚазҰУ, әл-Фараби даңғ., 71, Алматы, Қазақстан
[2]Жану проблемалары институты, Бөгенбай батыр к-сі, 172, Алматы, Қазақстан

Аңдатпа

Аммоний нитраты (АН) зымыран отындарында, жарылғыш заттарда және пиротехникада тотықтырғыш ретінде кеңінен қолданылады. Аммоний нитратының кейбір кемшіліктерін отын ретінде Mg-Al қорытпасын пайдалану арқылы азайтуға болады. Цирконий оксидінің (ZrO_2) АН/Mg-Al негізіндегі пиротехникалық қоспалардың жану сипаттамалары мен жылулық қасиеттеріне әсері зерттелді. ZrO_2 қосу жану жылдамдығын айтарлықтай арттырады және қысымның дефлаграциясы шегін 2 МПа-дан 1 МПа-дан төменге дейін төмендетеді. Дифференциалды сканерлеу калориметриясы әртүрлі қыздыру жылдамдықтарында термиялық ыдырау сипаттамаларын зерттеді және белсендіру энергияларын бағалады. Таза айнымалы тоққа Mg-Al қорытпасын қосқанда, негізгі шыңы шамамен 100 °С төмен ығысады. Сонымен қатар ZrO_2 АН және АН/MgAl екеуінің де жылулық қасиеттеріне айтарлықтай әсер етеді. MgAl және ZrO_2 қорытпасын қосу активтену энергиясын төмендетеді.

Кілт сөздер: пиротехникалық қоспалар, аммоний селитрасы (АН), Mg-Al қорытпалары, цирконий оксиді, жану сипаттамалары, жылу қасиеттері, активтену энергиясы.