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Effect of iron oxide on combustion and thermal decomposition of AN/MgAl-based pyrotechnic mixtures

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ABSTRACT

Ammonium nitrate (AN) is widely used as an oxidizer in energetic-burning mixtures. However, poor ignition and low burning rate require special additives to speed up this process. MgAl alloy is used as a fuel to improve the burning characteristics of AN. Mg-50%Al Alloy was synthesized by a high-temperature diffusion bonding method. In addition, the effect of iron oxide on the burning characteristics of pyrotechnic mixtures was studied. The burning characteristics of pyrotechnic mixtures were determined by ignition in a high-pressure chamber. With the addition of iron oxide, the burning rate of pyrotechnic compounds increased up to two times. Also, the pressure deflagration limit of the pyrotechnic mixture was reduced from 2 MPa to 1 MPa. In addition, the thermal characteristics of pyrotechnic mixtures were studied, and activation energies were calculated.

Keywords: ammonium nitrate, Mg-50%Al alloy, pyrotechnic mixtures, burning rate, high pressure.

1. Introduction

Pyrotechnic mixtures are the same type of heterogeneous phases, consisting of synthetic or plastic connecting matrices, metals and fuels of metal alloys and components of crystalline oxidants. They are used in space vehicles, in tactical and strategic missiles, in automobile production and in other technical branches, in propellant fuels in engines.

Ammonium nitrate (AN) with a positive oxygen bond (+ 20%) will be an oxidizing agent, AN-based composites can be widely used in the production of explosives. The thermal decomposition of ammonium nitrate has been extensively studied and several possible mechanisms of decomposition have been proposed [1-4]. In the recent years, composites based on AN were investigated for airbags, gas generators and as oxidizing for propellants. However, a low burning rate, slow flammability, high gyroscopicity and phase changes in solid states at temperatures below 100 °C are disadvantages [5]. Despite these drawbacks, ammonium nitrate is widely used as energy oxidants. Because, AN is distinguished by natural, pure burning without chlorine. To improve the quality of burning and thermal decomposition of pyrotechnic mixtures based on ammonium nitrate, the use of a MgAl alloy as a fuel is effective to improve the ignition of pyrotechnic mixtures at low temperatures. Because, the density, melting point and ignition temperature of the MgAl alloy is lower compared to pure aluminum [6]. These qualities of MgAl alloy improve the ignition limit at low pressures of pyrotechnic mixtures [7-9]. In addition, many studies have shown that the burning characteristics of AN-based pyrotechnic mixtures are improved by adding transition metal oxides and carbon-containing materials. [10-11]. However, the oxides of some metals adversely affect the ignition of the MgAl alloy in the composition of the composite [12].

In this research work, Mg-50%Al Alloy was synthesized by a high-temperature diffusion bonding method and use in pyrotechnic mixtures as a fuel. In addition, the effect of iron oxide (Fe_2O_3) on the burning characteristics and thermal decomposition of pyrotechnic mixtures on the basis of pure AN and AN/MgAl was studied using a high-pressure chamber at different pressures.

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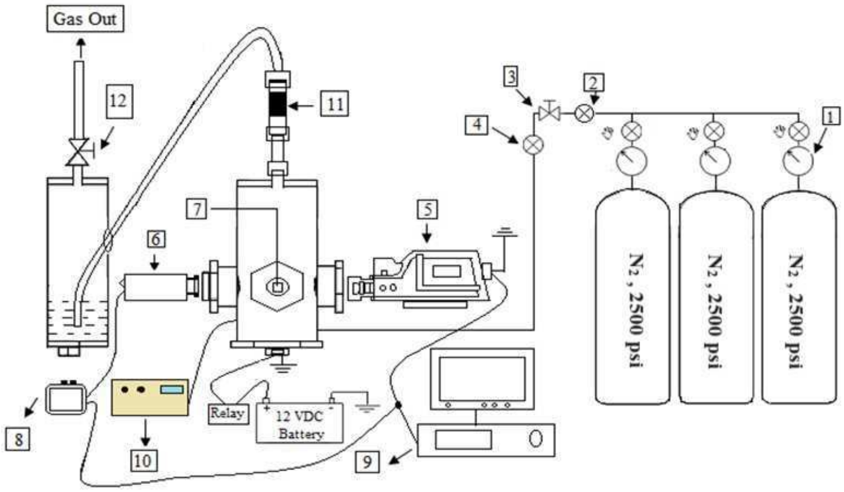


Fig. 1. Scheme of the high-pressure chamber: 1 – regulators; 2 – romote fill valve; 3 – fill flow rate control; 4 – monometer; 5 – high speed video recorder; 6 – camera; 7 – light source; 8 – screen monitor; 9 – PC; 10 – pressure control system; 11 – filter; 12 – vent flow rate control.

2. Experimental part

2.1. Materials

Ammonium nitrate (purity 99%) was dried in a vacuum drying oven at 60 °C and ground in a planetary ball mill (5 min). MgAl alloy (50/50) powder synthesized by the high-temperature diffusion bonding method is used as fuel. Iron oxide and paraffin were used as a catalyst and binder, respectively.

2.2. Prepare of samples and burning

The compositional analysis of MgAl alloy powder synthesized by the high-temperature diffusion bonding method was studied using an automatic X-ray diffractometer D8 ADVANCE (Bruker AXS GmbH, Germany).

Pyrotechnic mixtures were prepared in a hydraulic press with a pressure of 4 MPa. Prepared samples were ignited with a nichrome wire in a high-pressure chamber at different medium pressures. The burning process was recorded on a high-speed video camera, and the burning rate was determined based on the cinegram of the burning. The schematic of the high-pressure chamber is shown in Fig. 1.

2.4 Measurement of thermal properties of pyrotechnic mixtures

Thermal analysis is an effective way to study a pyrotechnic mixture's thermal decomposition and activation energy. Thermal decomposition properties of pyrotechnic mixtures are determined using a thermogravimetry-differential scanning calorimeter (TG-DSC) in a nitrogen atmosphere, in the temperature range of 25–600 °C, at different heating rates (2.5, 5, 10, and 20 $Kmin^{-1}$). 1 mg of energy additives is measured, and aluminum pans (height 2.5 mm and diameter 5 mm) are placed in the device to determine their thermal properties. In DSC equipment, each pyrotechnic mixture was measured 3–4 times, and accurate values were obtained.

3. Results and Discussion

3.1 Physicochemical Characteristics of MgAl alloy

Al-Mg alloy was synthesized in the argon gas flows by melting the initial components at high temperatures. According to the results of XRD,

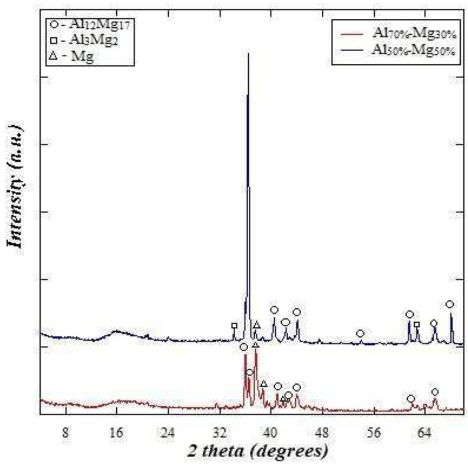
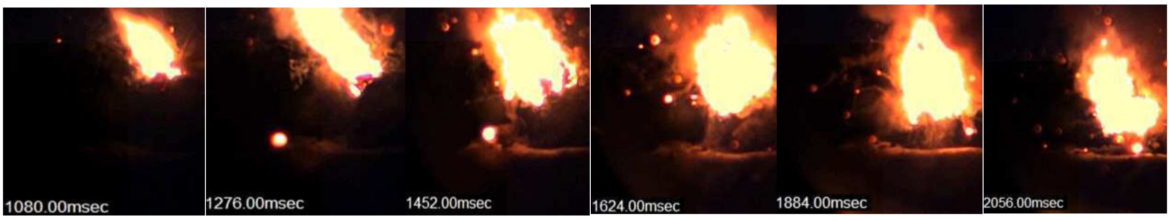
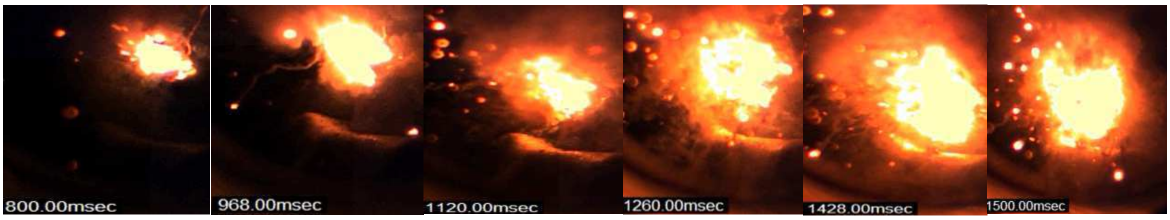


Fig. 2. XRD patterns of Al–Mg alloys.

(AN/MgAl/Fe_2O_3 – based pyrotechnic mixtures, 1 MPa)



(AN/MgAl/Fe_2O_3 – based pyrotechnic mixtures, 3 MPa)



(AN/MgAl/Fe_2O_3 – based pyrotechnic mixtures, 5 MPa)

Fig. 3. Burning cinegram of the AN/MgAl/Fe_2O_3 – based pyrotechnic mixtures at different pressure.

a single-phase Al-Mg alloy was synthesized at a temperature of 750 °C. Therefore, we can synthesize Al-Mg alloy in different ratios of the initial components. The phase structure of all the samples was investigated by XRD (Fig. 2).

According to XRD curves in Fig. 2, as a result of high-temperature diffusion bonding of pure Al and Mg (30%), along with β-Al_3Mg_2 and γ-$Al_{12}Mg_{17}$ mechanical alloys, Mg is clearly shown. Pure Mg particles can be explained by the diffusion of molten magnesium atoms into the layers of the crystal lattice of aluminum. Therefore, the synthesized alloys can be described as solid solutions of metastable magnesium in aluminum. The Al-50%Mg alloy XRD patterns show the formation of a single-phase alloy (γ-$Al_{12}Mg_{17}$) with an increase in the content of Mg in the initial mixture. That is, the degree of solubility of Mg in Al in the alloy is increased. The X-ray analysis also showed that with an increase in the amount of Mg, only the intermetallic phase $Al_{12}Mg_{17}$ is formed in the produced material.

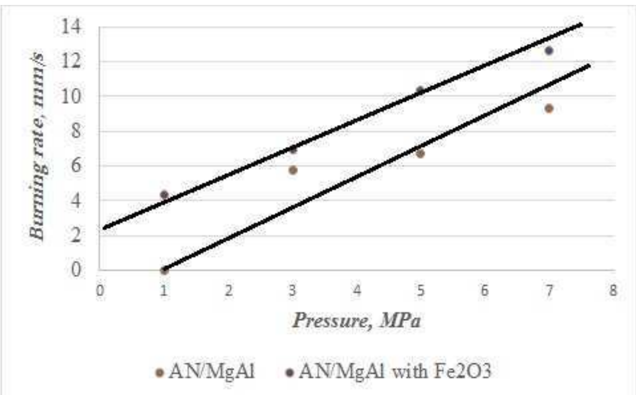


Fig. 4. Graph of the dependence of the burning rate of pyrotechnic mixtures on the medium-pressure.

3.2 Burning characteristics

A cinegram of burning of AN/MgAl-based pyrotechnic compounds at different pressures is presented in the research paper [13]. According to the results, when the pressure of the combustion medium drops below 2 MPa, pyrotechnic mixtures do not ignite. Therefore, a pressure of 2 MPa is considered the pressure deflagration limit (PDL) of the AN/MgAl mixtures. In many studies, transition metal oxides have been shown to reduce the PDL of combustible mixtures [14-15]. This study studied the effect of iron oxide on the reduction of PDL and the improvement of burning characteristics of pyrotechnic mixtures.

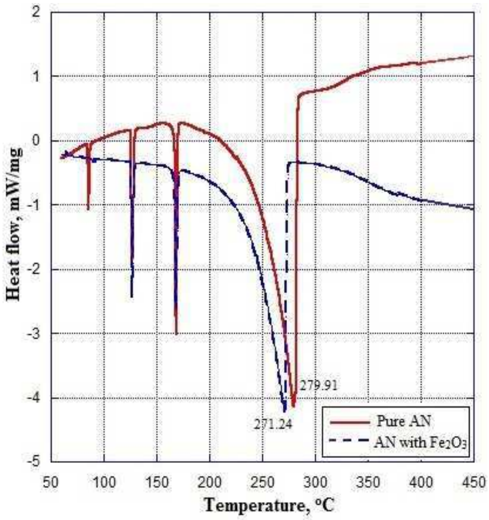


Fig. 5. DSC curves for pure AN and AN with Fe_2O_3.

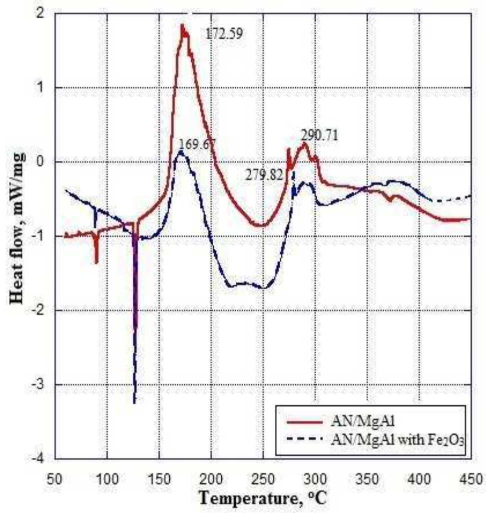


Fig. 6. DSC curves for AN/MgAl and AN/MgAl with Fe_2O_3 pyrotechnic mixtures.

Figure 3 shows burning cinegrams of AN/MgAl/Fe_2O_3–based pyrotechnic mixtures at different pressure. Figure 3 shows a linear decrease in the burning time with a linear increase in pressure in pyrotechnic mixtures based on AN/MgAl with the addition of Fe_2O_3. In addition, compared to the initial pyrotechnic compositions, the PDL value decreased to 1 MPa pressure, and the burning rate increased to 2 times. As a result, Fe_2O_3 played a catalytic role in the initial pyrotechnic mixtures.

Figure 4 shown the burning characteristics of AN/MgAl and AN/MgAl/Fe_2O_3–based pyrotechnic mixtures at different pressures.

Figure 4 shows that with the addition of iron oxide, the burning rate of pyrotechnic mixtures increased to 2-4 mm/s on average for each pressure value.

3.3 Thermal decomposition of AN and AN/MgAl with and without Fe_2O_3

Figure 5 shows thermal curves of thermal decomposition of AN with Fe_2O_3. Many scientific studies have been conducted on the thermal decomposition of AN.

According to the DSC curves in Fig. 5, 127 °C corresponds to the phase change of AN and 169 °C to the melting of ammonium nitrate. Compared to AN, adding Fe_2O_3 reduced the thermal decomposition temperature to 9–10 °C. The decomposition temperature dropped to about 209.31 from 248.03 at 10 °C min^{-1} when 5% Fe_2O_3 was added. The peak temperature changes and exothermic reactions showed an intense response between AN and Fe_2O_3.

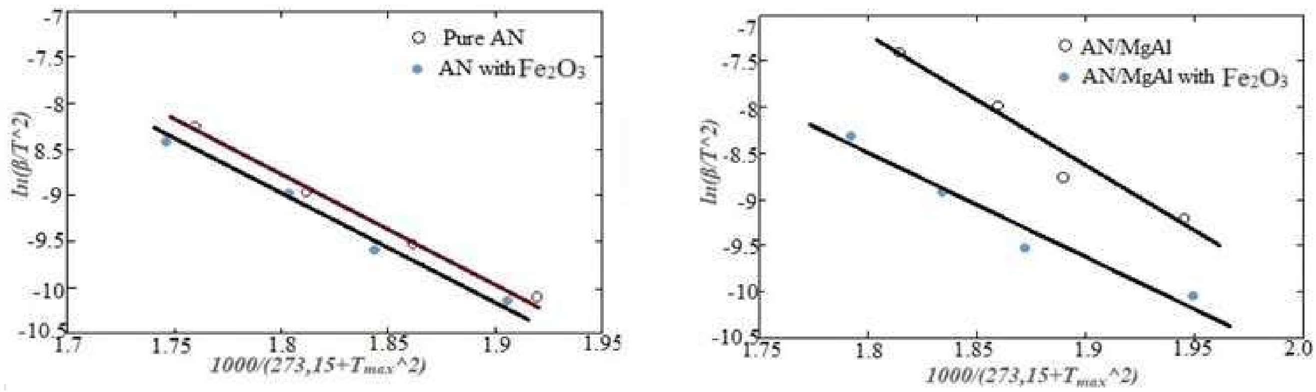


Fig. 7. Kissinger plot of pure AN and AN/MgAl with Fe_2O_3.

Figure 6 shows the effect of Fe_2O_3 on the thermal decomposition of AN/MgAl-based pyrotechnic mixtures.

As shown in Fig. 6, a notable change happened when Fe_2O_3 was added to the AN/MgAl alloy. Adding Fe_2O_3 to AN/MgAl-based additives reduced the thermal decomposition temperature by 12±2 °C and is shown to have a catalytic effect for pyrotechnic mixtures.

3.4 Calculation of activation energy

The activation energy (Ea) is the minimum energy for chemical reactions and is estimated by the Kissinger method based on the values of the DSC curve. This method is widely used and does not require a detailed reaction model. In recent years, many researchers have calculated the activation energy of composite rocket fuel and solid high-energy materials using the Kissinger method [16].

According to the values in the DSC curve, the activation energy of pure AN and Fe_2O_3–added AN, calculated by the Kissinger method, is 99.03 $kJmol^{-1}$ and 95.47 $kJmol^{-1}$, respectively. In addition, the activation energy of AN/MgAl and AN/MgAl/Fe_2O_3–based pyrotechnic mixtures is 91.41 $kJmol^{-1}$ and 89.26 $kJmol^{-1}$, respectively. Adding Fe_2O_3 to pyrotechnic mixtures based on ammonium nitrate and AN/ MgAl improves burning characteristics and reduces activation energy to about 3–5 $kJmol^{-1}$.

It can be concluded that adding Fe_2O_3 to pure AN and AN/MgAl–based energy mixtures reduces the kinetic barriers of thermal decomposition and lowers the activation energy to low-temperature regions, significantly improving thermal properties.

4. Conclusion

The production of a single-phase Mg-50%Al alloy by the high-temperature diffusion bonding method was determined at a temperature of 750 °C, and the PDL value was reduced from 2 MPa to 1 MPa compared to the original AN/MgAl-based pyrotechnic mixtures. In addition, the burning rate was increased to 2–4 mm/sec for each pressure value. Also, Adding Fe_2O_3 to pyrotechnic mixtures based on ammonium nitrate and AN/MgAl improves burning characteristics and reduces activation energy to about 3–5 kJ mol^{-1}.

Acknowledgment

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Темір оксидінің AN/MgAl негізіндегі пиротехникалық қоспалардың жануы мен термиялық ыдрауына әсері

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АННОТАЦИЯ

Тотықтырғыш ретінде аммоний нитраты (AN) Қатты зымыран отындарында, жарылғыш заттарда және пиротехникалық композиттерде кеңінен қолданылады. Дегенмен, бірнеше маңызды кемшіліктер оны қолдану аясын азайтады. Композиттер құрамындағы АН-ның осы кемшіліктерін жақсарту үшін энергетикалық отын ретінде MgAl қорытпасы қолданылады. Mg-50%Al қорытпасы жоғары температуралы диффузиялық байланыс әдісімен синтезделді. Сонымен қатар, темір оксидінің пиротехникалық қоспалардың жану сипаттамаларына әсері зерттелді. Пиротехникалық қоспалардың жану сипаттамалары жоғары қысымды камерада жандыру арқылы анықталды. Темір оксиді қосылғанда пиротехникалық қосылыстардың жану жылдамдығы екі есеге дейін өсті. Сондай-ақ, пиротехникалық қоспаның қысымдық тұтану шегі 2 МПа-дан 1 МПа-ға дейін төмендетілді. Сонымен қатар, пиротехникалық қоспалардың теримялық сипаттамалары зерттелініп, активтену энергиялары есептелінді.

Түйін сөздер: аммоний нитраты, Mg-50%Al қорытпасы, пиротехникалық қосылыстар, жану жылдамдығы, жоғары қысым.

Влияние оксида железа на горение и термическое разложение пиротехнических смесей на основе AN/MgAl

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АННОТАЦИЯ

В качестве окислителя нитрат аммония (НА) широко используется в порохе, взрывчатых веществах и пиротехнических составах. Однако ряд существенных недостатков сузили сферу его применения. Для устранения этих недостатков НА в составе композитов в качестве энергетического топлива используют сплав MgAl. Сплав Mg-50%Al синтезирован методом высокотемпературной диффузионной связи. Кроме того, изучено влияние оксида железа на характеристики горения пиротехнических смесей. Характеристики горения пиротехнических смесей определялись методом воспламенения в камере высокого давления. При добавлении оксида железа скорость горения пиротехнических составов увеличивалась до двух раз. Также снижен предел горения пиротехнической смеси по давлению с 2 МПа до 1 МПа. Кроме того, были изучены термические характеристики пиротехнических смесей и рассчитаны энергии активации.

Ключевые слова: нитрат аммония, Mg-50%Al сплав, пиротехнические смеси, скорость горения, высокое давление.