

Article

The Effect of CuO on the Thermal Behavior and Combustion Features of Pyrotechnic Compositions with AN/MgAl

Tlek Ketegenov ¹, Rashid Nadirov ^{1,2} , Bagdat Teltayev ^{1,3} , Bagdatgul Milikhat ¹, Bakhyt Kalmuratova ², Hori Keiichi ⁴ and Kaster Kamunur ^{1,2,*}

¹ Institute of Combustion Problems, Almaty 050012, Kazakhstan; tlek58@mail.ru (T.K.); nadirov.rashid@gmail.com (R.N.); bagdatbt@yahoo.com (B.T.); m.bagdar@mail.ru (B.M.)

² Faculty of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty 050040, Kazakhstan; bakhyt.kalmuratova@mail.ru

³ U. Joldasbekov Institute of Mechanics and Engineering, Almaty 050040, Kazakhstan

⁴ Japan Aerospace Exploration Agency, Sagami-hara 252-5210, Japan; ko-ho@chofu.jaxa.jp

* Correspondence: kamunur.k@mail.ru; Tel.: +7-702-412-90-46

Abstract: Ammonium nitrate (AN) is of considerable interest to researchers in developing new types of energetic mixtures due to the release of environmentally benign gaseous products during burning and thermal decomposition. However, poor ignition and a low burning rate require special additives to speed up this process. The advantage of this research is the use of high-energy aluminum-based alloys as fuel to compensate for the disadvantages of AN. In addition, the effect of copper oxide (CuO) on the burning kinetics and thermodynamics of the energetic mixture based on ammonium nitrate–magnesium–aluminum alloys (AN/MgAl) is investigated. Alloys based on aluminum were created through a process of high-temperature diffusion welding, conducted in an environment of argon gas. The structure and thermal characteristics of alloys are determined by X-ray diffraction, scanning electron microscopy, and DTA-TG analyses. It has been found that CuO has significant effects on the thermal decomposition of an AN/MgAl-based energetic mixture by shifting the decomposition temperature from 269.33 °C to 261.34 °C and decreasing the activation energy from 91.41 kJ mol^{−1} to 89.26 kJ mol^{−1}. Adding CuO reduced the pressure deflagration limit from 2 MPa to 1 MPa, and the linear burning rate of the AN/MgAl energetic mixture increased approximately twice ($r_b = 6.17$ mm/s vs. $r_b = 15.44$ mm/s, at a chamber pressure of $P_0 = 5$ MPa).

Keywords: ammonium nitrate; Mg–Al alloys; copper oxide; burning rate; pyrotechnic mixtures



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1. Introduction

Pyrotechnic mixtures are a condensed composite system consisting of an oxidizer, an energetic binder, metal or metal alloy-based fuels, a burning catalyst, and other components. Perchlorates are widely used as oxidizers in pyrotechnic mixtures. However, perchlorates have several significant disadvantages due to their gaseous burning products. In particular, the formation of gaseous combustion products based on HCl, chlorine, and chlorine oxides [1–3]. Therefore, oxidizers based on ammonium nitrate (AN) have been widely studied in recent years. Despite its effective use in civil and military equipment, AN remains the object of numerous studies in creating new pyrotechnics, explosives, and propellants [4–9]. That is explained by the simplicity of the technology for its production, safety in handling, and the possibility of various types of technological processing. Even though ammonium nitrate produces clean and smokeless combustion products, its use as a component of propellants is limited by several factors: Sensitivity to initial temperatures and pressures, low burning rates, and the need to use special catalysts [10]. Therefore, to improve the energetic characteristics of ammonium nitrate-based propellants, metalized additives, mainly powdered aluminum, are introduced into their composition [11]. Aluminum provides a high calorific value for composite fuel. However, its ignition is also

tricky due to a protective oxide film on the metal surface. In addition, agglomeration of small metal particles occurs in the combustion wave, harming aluminum particles' ignition and burning time. In addition, the presence of condensed oxide Al_2O_3 , as the main product of aluminum oxidation, causes erosion of the rocket engine nozzle, which seriously affects its power [12,13].

A decrease in the protective properties of the Al_2O_3 oxide film in the AN-Al composite fuel can be achieved by alloying aluminum with various metals, for example, magnesium [14]. In recent years, Mg–Al alloys have been widely used in production due to their properties [15–19]. There is a large number of experimental works on the effect of magnesium additives on ignition characteristics and aluminum combustion [12,13,20–22].

Compared to pure Al, Mg–Al solid alloys have several advantages: Lack of aluminum agglomeration, low initial ignition temperature, and complete burning of alloy particles. Due to these advantages, it is widely used as an energetic fuel in propellants, gas generators, and pyrotechnic mixtures [23–27]. Mg–Al alloy improves the burning characteristics and thermal decomposition of AN-based energetic mixtures. Because of the initial low ignition temperature of Mg–Al alloy compared to aluminum particles [28]. It has been shown in research works that active additives based on AN reduce the pressure deflagration limit [29–31].

One of the promising ways to increase the decomposition rate of ammonium nitrate and increase the burning rate of aluminum is the addition of transition metal oxides to mixed energetic compositions, which act as catalysts for these processes. Currently, the assessment of the catalytic properties of transition metal oxides CuO , Fe_2O_3 , MnO_2 , CoO , NiO_2 , TiO_2 , and Cr_2O_3 in both micro- and nano-sizes during the decomposition and burning of energetic mixtures based on AN and ammonium perchlorate is widespread in the literature [32–38]. More recently, adding CuO nanorods has increased the burning rate and improved the low-pressure flammability of an AN-based energetic mixture [39–41]. The effect of silicon oxide on the burning of aluminum powders is known [42]. Direct application of data on the catalysis of burning and decomposition of individual compounds is often impossible when applied to heterogeneous mixtures based on them [43]. As an example of such a situation, we can cite the results of A.P. Glazkova [44], who showed that the most effective catalyst for the thermal decomposition and burning of ammonium nitrate, potassium bichromate, in mixed heterogeneous compositions retains its effectiveness only in mixtures of energetic materials based on nitroether-flammable binders. It is known that the oxides of some metals interfere with the burning of the MgAl alloy in the AN/MgAl system [45].

Thus, this investigation aimed to study the effect of Al–Mg alloy on the burning efficiency of fuel systems based on ammonium nitrate, as well as to identify a catalyst that can effectively promote this process.

By investigating the role of CuO in the thermal properties and burning characteristics of pyrotechnic mixtures, our study aims to develop formulations that are more stable and safer to handle, leading to enhanced safety and reduced environmental impact. This includes promoting complete combustion, which reduces unreacted residues and environmental contamination typically associated with pyrotechnic applications. The safer handling of these materials also reduces the risk of accidental fires and explosions, contributing to a safer industry environment.

2. Materials and Methods

2.1. Materials

As a highly energetic fuel, magnesium powder (Sigma-Aldrich, St. Louis, MI, USA), known as MPF-2, was utilized. This powder has characteristics such as a particle size ranging between 200 and 250 μm , a high purity level of at least 99%, a melting point of approximately 650 $^\circ\text{C}$, and a density of 1.74 g/mL at a standard temperature of 25 $^\circ\text{C}$. Additionally, aluminum powder (Sigma-Aldrich) PA4 was employed as another fuel component. This powder features a particle size of around 65 μm , a purity level of at least

99%, a melting point near 660 °C, and a density of 2.7 g/mL at 25 °C, also referenced from Sigma-Aldrich literature. Synthesized Al–Mg alloy particles with a diameter of 70 µm are used as fuel in pyrotechnic mixtures; ammonium nitrate (AN)—purity $\geq 99\%$. According to the research of [46], to increase the stability of ammonium nitrate to moisture, it was modified with natural stearic acid mixed with paraffin in the amount of 0.2–0.4%, and particles with a diameter of 212 µm were obtained. The addition of copper oxide was investigated to improve the properties of pyrotechnic mixtures. Paraffin is widely used as a binder and fuel in solid-phase energetic compounds. The solution of paraffin in alcohol was used in this research work.

2.2. Preparation of Samples

Al–Mg-based solid solutions were synthesized by melting and diffusion bonding in different mass fractions of magnesium (30%, 35%, and 50% by weight) in argon gas flow at high temperature ($T = 750$ °C). Physical research methods in chemistry studied the phase composition and structure of the synthesized alloy, and DTA-TG-determined thermal properties.

The components of pyrotechnic mixtures are accurately measured on an electronic scale (0.001 g), mixed evenly, and hydraulically pressed with a pressure of 20 MPa.

2.3. Evaluation of Combustion Properties

The samples prepared for this study were ignited using a nichrome wire within a specially designed high-pressure chamber. Various medium pressures were applied during the experiments. The combustion process was captured using a high-speed video camera. The rate of combustion was then calculated based on the analysis of the video footage, specifically the cinegram depicting the combustion. The degree of error of the combustion speed is measured in units of 0.01 mm using the cinegram of the combustion surface. All studies were performed in triplicate at different pressures for each sample, and the burning rate was calculated using the average burning time. If 1/3 of the pyrotechnic mixture does not burn or does not burn completely, the relationship of the components is changed and the study is conducted again. Figure 1 illustrates the design of the high-pressure chamber used in these experiments.

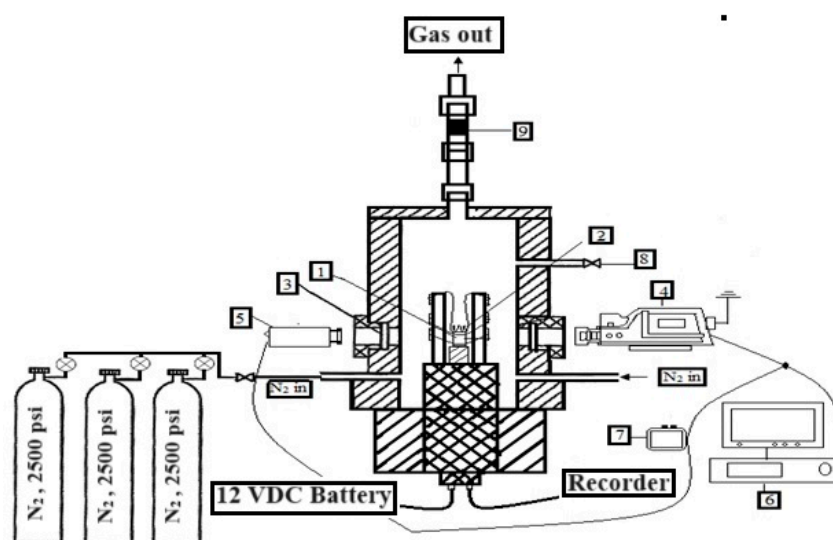


Figure 1. Schematic of the high-pressure chamber: 1—sample holder; 2—nichrome wire; 3—window for the light source; 4—high-speed video camera; 5—camera; 6—PC (monitor); 7—transformer, 8—system for pressure control; 9—filter.

The combustion rate of the pyrotechnic mixtures is influenced by environmental pressure. The combustion rate for these energetic mixtures can be described using Saint Robert's law (also known as Vieille's law), which is represented by the formula:

$$r_b = a \cdot [P]^n$$

where r_b —linear combustion rate of energetic compounds, mm s^{-1} , a —combustion rate constant, and n is the pressure exponent. The values of a and n are determined through experimental means for each pyrotechnic mixture composition. These experiments focus on understanding the combustion mechanisms of the pyrotechnic mixture under constant atmospheric pressure. This expression makes it possible to determine the linear burning rate of samples using pressure values based on the scope of the application of energetic additives [47]. The accuracy of the measurement was $\pm 0.5 \text{ mm s}^{-1}$. Each measurement was replicated three times, with the mean value being utilized for subsequent analysis.

2.4. Assessment of Thermal Characteristics of Pyrotechnic Mixtures

Thermal analysis serves as an efficient method for examining the thermal decomposition and activation energy of pyrotechnic mixtures. The thermal decomposition characteristics of these mixtures are ascertained using a thermogravimetry–differential scanning calorimeter (TG-DSC) within a nitrogen atmosphere. This analysis is conducted over a temperature range of 25–600 °C, employing varying heating rates of 2.5, 5, 10, and 20 °C/min. For this purpose, 1 mg of energy additives is measured, and aluminum pans (2.5 mm in height and 5 mm in diameter) are used within the apparatus to determine their thermal properties. In the DSC equipment, each pyrotechnic mixture undergoes three separate measurements, with the average value being taken for analysis.

2.5. Determination of Composition and Structure of Materials

2.5.1. X-ray Diffraction Analysis

The X-ray phase analysis was conducted using a D8 ADVANCE diffractometer (Bruker AXS GmbH, Karlsruhe, Germany), equipped with a Cu-K α radiation source, operating at a tube voltage of 40 kV and a current of 40 mA. The analysis of the obtained diffraction patterns and the calculation of interplanar distances were performed using EVA version 4.2 software. The interpretation of the samples and the search for phases were conducted in the search/match program, utilizing the Powder Diffraction Database PDF-2 release 2020 from the International Center for Diffraction Data (ICDD), USA.

2.5.2. Methods for Studying Structure

Electron probe microanalysis was conducted on a desktop scanning electron microscope (Hitachi TM4000 Plus, Hitachi High-Tech, Tokyo, Japan). The device has a standard low vacuum mode, allowing you to examine non-conducting samples without preliminary metal deposition. Device characteristics: Magnification $\times 10 \times 100,000$; depth of field: 0.5 mm; the accelerating voltage was set at 5 kV, 10 kV, and 15 kV. The detectors used included a 4-segment highly sensitive semiconductor detector and a secondary electron detector for low vacuum mode.

3. Results

3.1. Physicochemical Characteristics of MgAl Alloy

In synthesizing a solid magnesium solution in aluminum, magnesium's degree of solubility is significant. The degree of solubility for Al–40 at.% Mg solid solution is 23%; for Al–30 at.% Mg solid solutions, the solubility of magnesium is 14.1%; and for Al–50%Mg solid solution, the solubility index of Mg in the α -Al phase is 45%, as shown in research works [48].

The Al–Mg alloy was synthesized in argon gas flows by melting the initial components at elevated temperatures. X-ray diffraction (XRD) analysis revealed the formation of a

single-phase Al–Mg alloy at a temperature of 750 °C. This indicates the feasibility of synthesizing Al–Mg alloys with varying ratios of the initial components. The phase composition of the samples synthesized in different ratios was determined using XRD (Figure 2).

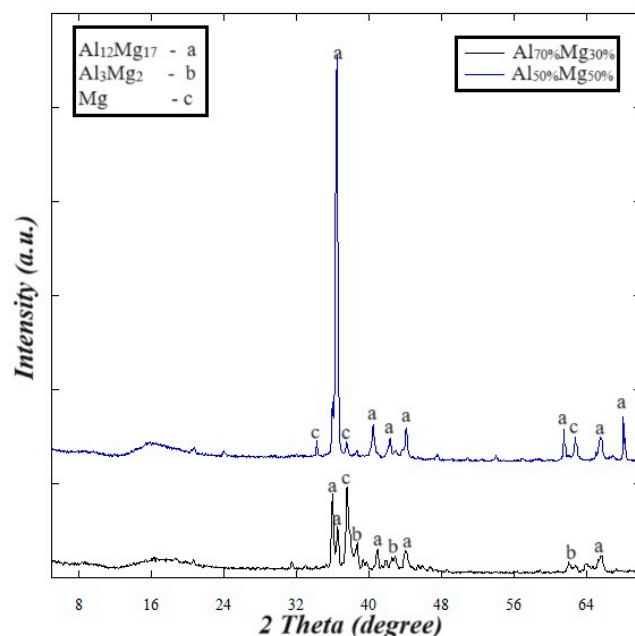


Figure 2. XRD patterns of Al–Mg alloys.

The microstructure near the interface of the Mg–Al alloy was observed using SEM. Structural analysis and thermal properties of solid solutions based on Mg–50%Al synthesized in an inert environment at high temperatures are shown in Figure 3.

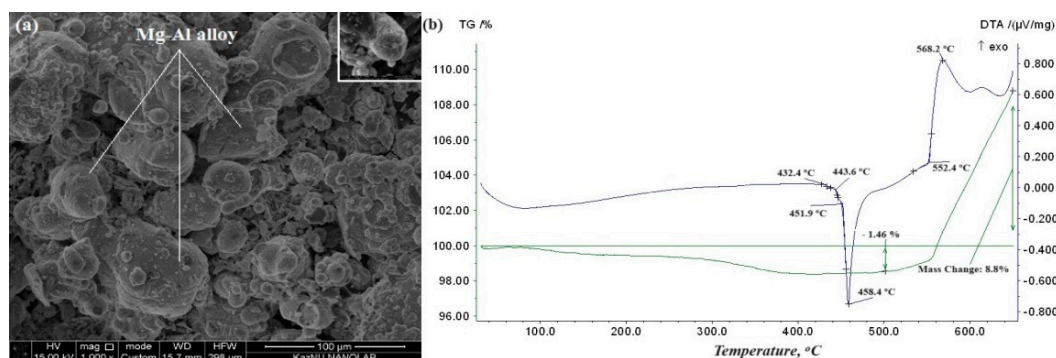


Figure 3. SEM images (a) and DSC analysis of (b) of Mg–50%Al alloy.

3.2. Thermal Properties of Pyrotechnic Mixtures

At a heating rate of $\beta = 5$ °C/min, the differential scanning calorimetry (DSC) curves for pure ammonium nitrate (AN) and the AN/CuO mixture are depicted in Figure 4. Additionally, Figure 5 illustrates the DSC curves for AN/MgAl and AN/MgAl/CuO-based pyrotechnic mixtures. Furthermore, Table 1 presents the parameters of thermal decomposition for these pyrotechnic mixtures at different heating rates. Specifically, Table 1 details the thermal decomposition results, including the maximum thermal decomposition temperature ($T_{\max}$), the initial decomposition temperature (T_{onset}), and the final decomposition temperature (T_{offset}) at the heating rate of $\beta = 5$ °C/min. The influence of CuO on the thermal decomposition of these pyrotechnic mixtures is evident in Figures 4 and 5, which display the DSC curves under an argon atmosphere at a heating rate of $\beta = 5$ °C/min.

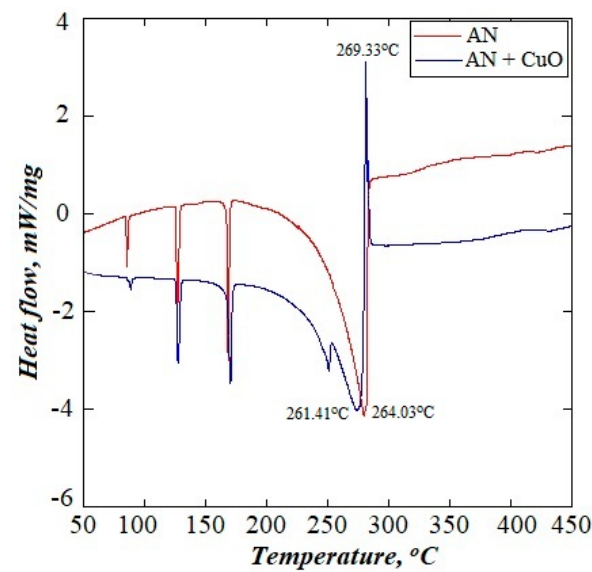


Figure 4. DSC curves for pure AN and AN/CuO.

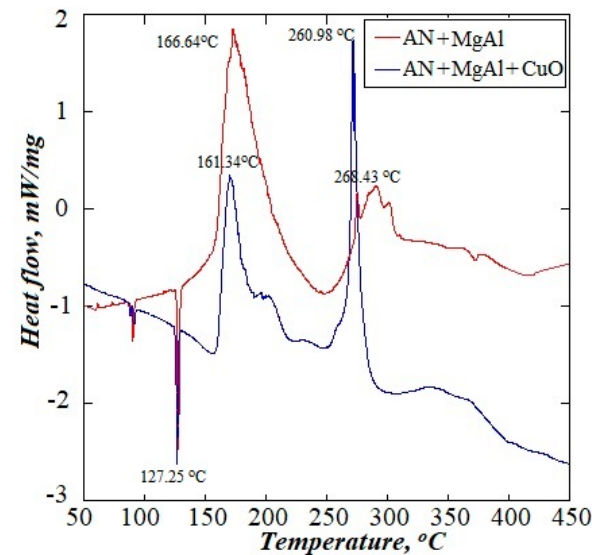


Figure 5. The DSC curves for the pure AN/MgAl and AN/MgAl/CuO pyrotechnic mixtures are provided for analysis.

Table 1. Thermal values of the DSC curve of pyrotechnic mixtures.

Sample	β , °C/min	Thermal Decomposition					
		1st Step			2nd Step		
		T_{onset}	T_{offset}	T_{max}	T_{onset}	T_{offset}	T_{max}
AN/CuO		(200–300 °C)			(250–310 °C)		
	2.5	207.63	250.77	245.38	251.24	252.24	251.67
	5	224.09	267.89	261.41	268.51	271.29	269.33
	10	239.26	279.96	274.25	280.16	284.42	281.36
	20	243.59	297.99	291.01	297.75	302.53	299.52
AN/MgAl		(140–220 °C)			(230–310 °C)		
	2.5	146.70	164.64	153.22	230.89	246.23	239.20
	5	153.39	174.41	166.64	245.62	278.75	260.98
	10	159.11	205.76	172.59	269.17	292.78	282.34
	20	169.05	216.34	184.44	281.36	303.54	298.62

Table 1. Cont.

Sample	β , °C/min	Thermal Decomposition					
		1st Step			2nd Step		
		T_{onset}	T_{offset}	T_{max}	T_{onset}	T_{offset}	T_{max}
			(130–180 °C)			(230–300 °C)	
AN/MgAl/CuO	2.5	130.30	169.35	152.21	235.31	245.83	239.75
	5	153.60	172.96	161.34	256.79	267.89	268.43
	10	160.03	182.91	170.68	268.09	277.90	271.94
	20	163.71	197.25	177.75	280.61	291.74	284.73

Figure 6 shows the DSC curves of the thermal decomposition of AN/MgAl/CuO-based pyrotechnical mixtures in an inert environment at different heating rates.

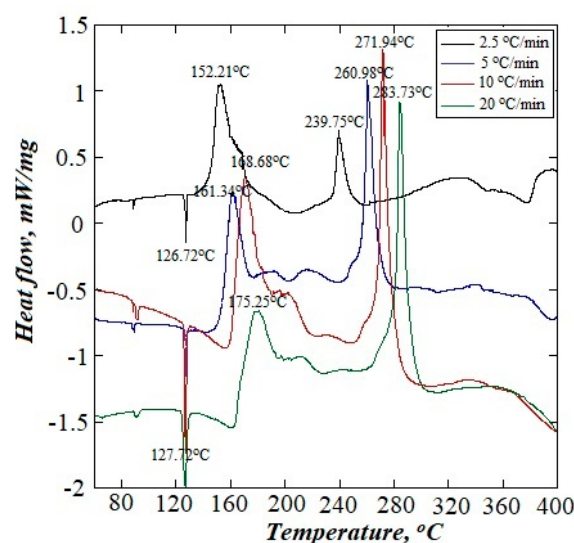


Figure 6. DSC curve of AN/MgAl/CuO mixture at different heating rates.

Figure 7 shows the mass loss curve obtained by the DSC-TG results of AN/MgAl-based pyrotechnic mixtures. The thermogravimetric analysis curve was obtained from 50 °C to 350 °C. All mass losses measured by TG were AN/CuO, AN/MgAl, and AN/MgAl/CuO.

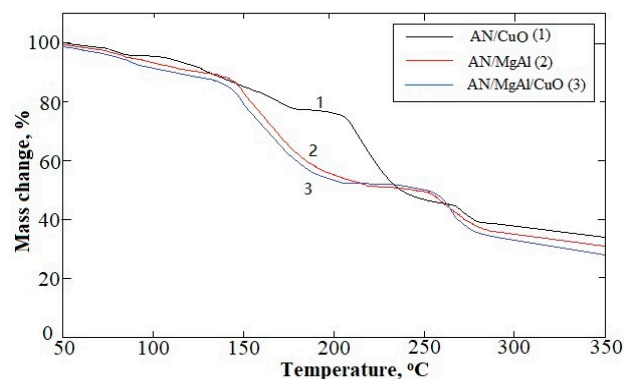


Figure 7. Thermogravimetric analysis of AN/MgAl/CuO mixture under nitrogen atmosphere (heating rate $\beta = 5$ °C/min).

3.3. Thermal Decomposition Kinetics

Figure 8 shows various plots of AN with CuO, AN/MgAl, and AN/MgAl/CuO pyrotechnic mixtures. Figure 8 shows the activation energy parameters of AN/MgAl/CuO-based pyrotechnic mixtures by the Kissinger method according to the values of $\ln(\beta/T_p^2)$.

and $1/T_p$. In calculating the activation energy of energetic mixtures, Kissinger proposed the following equation [35]:

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

where T_p is the highest temperature of the thermal decomposition peak of the DSC curve. E_a can be calculated based on the plotted lines of $\ln(\beta T_p^{-2})$ versus T_p^{-1} [39]. E_a of pyrotechnic additives depends on the change of the T_p value in the DSC curve. Therefore, the possibility of changing the E_a values of the mixture when CuO is added was investigated.

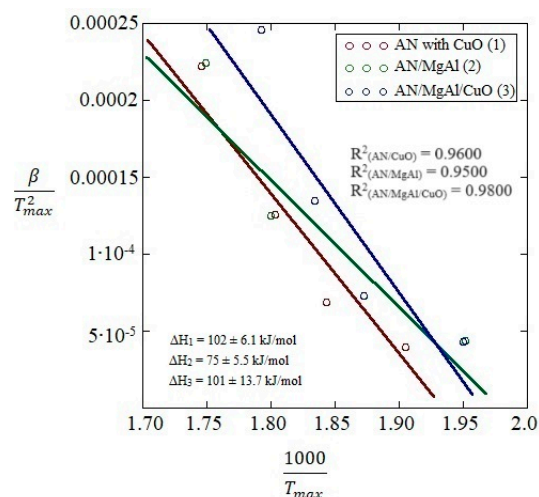


Figure 8. Kissinger plot of AN with CuO, AN/MgAl, and AN/MgAl with CuO.

3.4. Burning Characteristics of AN/MgAl/CuO Pyrotechnic Mixtures

Initial ignition temperature, constant burning rate, and pressure index are essential when using energy materials in propellants. The value of the pressure indicator should be less than 0.6 for gas generators and more than 1.0 for solid propellants. The effect of various transition metal oxides (CuO, Fe_2O_3 , ZrO_2 , TiO_2 , and Cr_2O_3) on the combustion characteristics of AN/MgAl-based mixtures was studied. As a result, the combustion rate of energetic mixtures with copper oxide was 2–3 mm/sec higher than that of other oxides.

Figure 9 shows the cinegrams of the combustion of AN-based pyrotechnic mixtures without added copper oxide at different pressures.

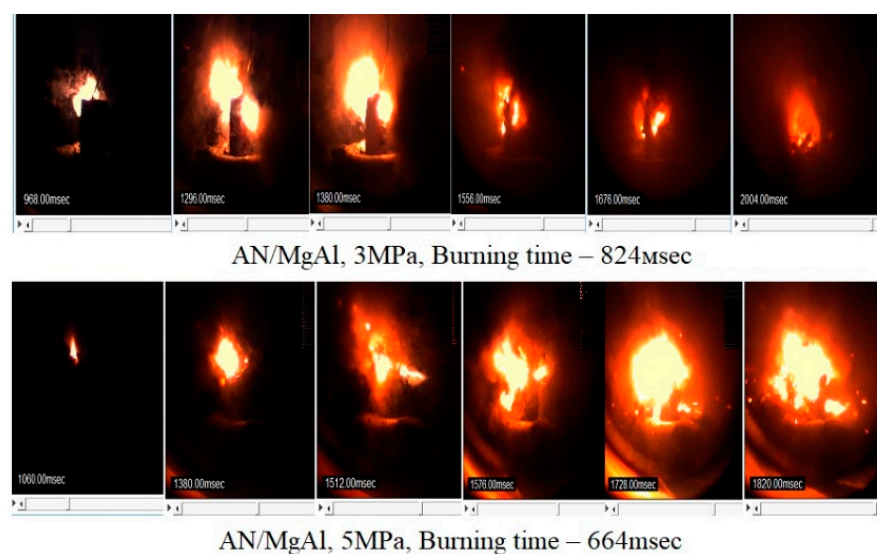


Figure 9. Burning cinegram of the AN-based pyrotechnic mixtures (without CuO) at a different pressure.

Figure 10 shows the combustion fronts of pyrotechnic mixtures of AN/Mg–Al with CuO at different pressures in a pressurized combustion chamber.

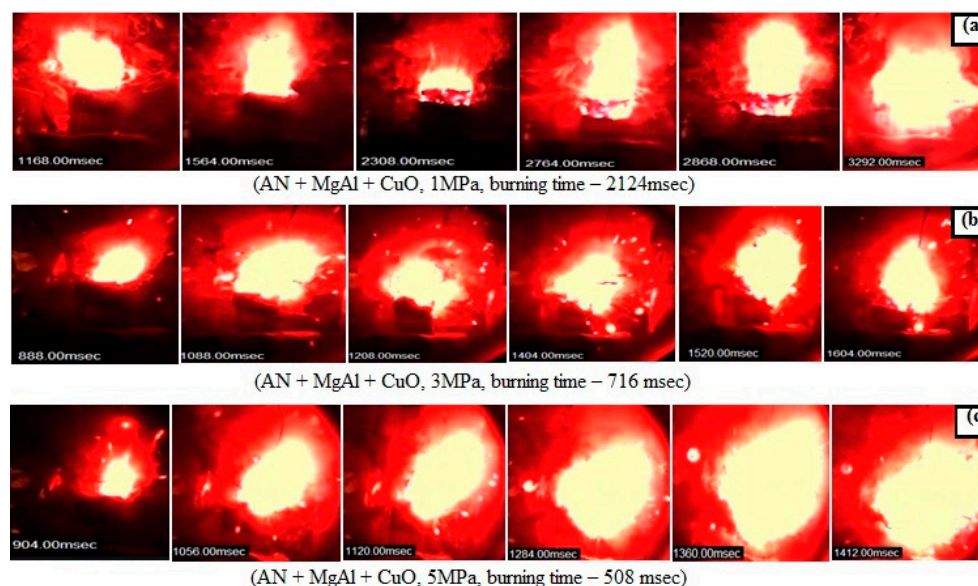


Figure 10. Burning cinegrams of AN/MgAl with CuO-based pyrotechnic mixtures at different pressures ((a)—1 MPa, (b)—3 MPa, (c)—5 MPa).

Figure 11 illustrates the relative burning rates at different pressures for the AN/MgAl and AN/MgAl with CuO-based pyrotechnic mixtures. It was observed that the addition of CuO to the AN/MgAl-based pyrotechnic mixture approximately doubled the burning rate across all pressure values. The maximum burning rate achieved with CuO addition was 15.44 mm/s at an initial pressure of $P_0 = 5$ MPa.

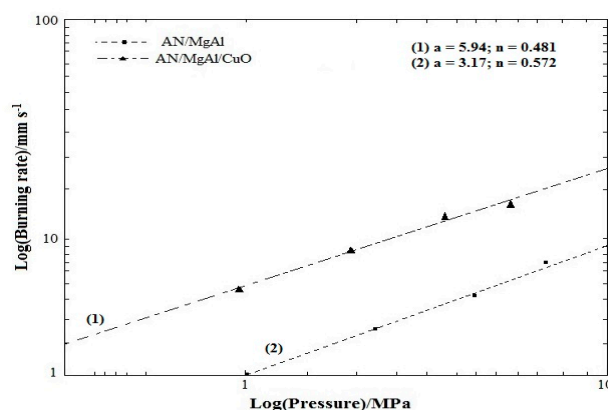


Figure 11. Change in the burning rate of AN/MgAl and AN/MgAl with CuO-based pyrotechnic compounds depending on the pressure value.

Figure 11 shows the change in the burning rate of AN/MgAl and AN/MgAl with CuO-based pyrotechnic compounds depending on the pressure value.

4. Discussion

4.1. Physicochemical Characteristics of MgAl Alloy

Figure 2 shows the formation of Al_3Mg_2 and $Al_{12}Mg_{17}$ in the phase composition of the Al-30%Mg solid solution. Also, along with peaks of Al-30%Mg solid solution, peaks of pure Mg are visible. However, there is a reduction and shift of the Al peaks, which allows Mg particles dissolved in aluminum to settle into the crystal lattice layers of the solid solution. The solid solution of Mg in Al, synthesized at high temperatures, was identified

as a metastable composite material. The X-ray diffraction (XRD) patterns of the Al–50%Mg alloy indicated the formation of a single-phase solid solution (γ -Al₁₂Mg₁₇), correlating with an increase in the Mg content in the initial compounds. This suggests an enhanced solubility of Mg in Al within the alloy. X-ray analysis also revealed that with an increased Mg amount, only the intermetallic phase Al₁₂Mg₁₇ is formed in the produced material.

Figure 3a shows the surface morphology of the Mg–50%Al alloy. The morphology of the Mg–Al alloy appears to be more comprehensively coated and structured with a magnesium coating compared to pure aluminum. Therefore, it allows the use of the solid solution synthesized at high temperatures as fuel in pyrotechnic mixtures.

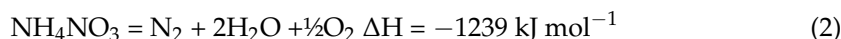
Figure 3b shows the DTA curve of the Mg–50%Al solid solution synthesized at high temperature. The endothermic peak at 458.4 °C corresponds to the melting point of the Mg–50%Al solid solution. In addition, the exothermic peaks corresponding to 568.2 and 616.9 °C may result from the oxidation of pure magnesium and pure aluminum in a solid solution.

The DTA curve of the Al–50 at.% solid solution synthesized at high temperature corresponds to the thermal analysis values of the alloy in some research works [46]. Therefore, it can be assumed that the Al–50%Mg solid solution synthesized at high temperature is a single-phase alloy.

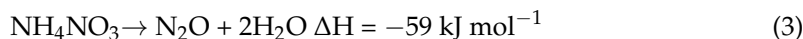
4.2. Characteristics of Thermal Decomposition

Figure 4 presents the DSC curve for both pure AN and AN mixed with copper oxide. The DSC curves indicate an endothermic phase at 127 °C, which aligns with the phase transition of AN, as referenced in the literature [49]. Additionally, an endothermic peak at 169 °C is observed on the DSC curve, corresponding to the melting point of AN. The range of 220 °C to 270 °C corresponds to a large area of endothermic decomposition of AN. Compared to pure AN, the DSC curve of AN/CuO showed an exothermic interval from 270 °C to 280 °C. The exothermic peak in the DSC curve of the AN with CuO system may be an intermediate product formed from AN's thermal decomposition under CuO's influence because $[\text{Cu}(\text{NH}_3)_2](\text{NO}_3)_2$ is described as an intermediate product at about 270 °C in the literature [41].

Figure 5 shows the DSC curves of AN/MgAl and AN/MgAl with CuO pyrotechnic mixtures ($\beta = 5 \text{ K min}^{-1}$). According to the DSC curves, a two-stage exothermic decomposition is shown. The first exothermic peak is shown between 140 °C and 180 °C. According to the following equation, this exothermic phenomenon corresponds to the thermal decomposition of ammonium nitrate under the influence of the MgAl alloy [50].



In the decomposition of AN under the influence of the MgAl alloy, a secondary exothermic phase was observed between 250 °C and 280 °C. This can be explained by the thermal decomposition of AN into nitrogen oxide due to the increase in temperature [51]:



The incorporation of CuO into AN/MgAl-based additives has been shown to decrease the thermal decomposition temperature by approximately 5 ± 2 °C, demonstrating its significant impact on the thermal behavior of pyrotechnic mixtures. Furthermore, as indicated by the DSC curve in Figure 4, the addition of the MgAl alloy as a fuel to AN results in the primary thermal decomposition of AN occurring around its melting point. A decrease in exothermic peak maximum temperature compared to that of the basic mixture is approximately 100 °C (from 269.33 °C to 161.34 °C).

Figure 6 shows the DSC curves of the AN/MgAl/CuO pyrotechnic mixture at different heating rates. Temperature changes with increasing heating rates show the thermal decomposition of pyrotechnic mixtures. Table 1 shows the change in values of thermal decomposition temperatures corresponding to each heating rate.

Figure 7 shows the mass loss curve obtained by the DSC-TG results of AN/MgAl-based pyrotechnic mixtures. All mass losses measured by TG were pure AN, AN/CuO, AN/MgAl, and AN/MgAl/CuO. The mass losses of the four samples were 99.8%, 91.3%, 78.2%, and 79.5%, respectively. With the addition of metal alloys and metal oxides to the pyrotechnic mixture, the mass loss rate of the cross is increased.

4.3. Thermal Decomposition Kinetics

Figure 8 reveals the activation energies (E_a) for AN and AN with MgAl, as determined from DSC data, to be about 102 kJ/mol and 75 kJ/mol, respectively. The E_a values for AN/MgAl and AN/MgAl with CuO mixtures are found to be 75 kJ/mol and 101 kJ/mol, respectively. Adding CuO to pure ammonium nitrate and pyrotechnic mixtures reduced activation energy values.

Adding MgAl alloy and copper oxide to pure AN reduces E_a and increases thermal decomposition. It can also be concluded that adding CuO to the AN/MgAl pyrotechnic mixture reduces the kinetic barriers of thermal decomposition, and lowering the initial thermal decomposition temperature significantly increases the rate of chemical reactions.

4.4. Burning Behaviour of AN/MgAl Pyrotechnic Mixtures with and without CuO

Figure 9 shows changes in the burning front of AN/MgAl-based pyrotechnic mixtures at different pressures. At a pressure of 5 MPa, the value of the burning rate increases by $r_b = 6.17 \text{ mm.s}^{-1}$. The study findings indicate that pyrotechnic mixtures fail to ignite when the pressure of the combustion medium falls below 2 MPa. Consequently, a pressure of 2 MPa is identified as the pressure deflagration limit (PDL) for the AN/MgAl mixtures. Previous research has demonstrated that transition metal oxides, such as copper oxide, can reduce the PDL of combustible mixtures [47]. Therefore, this study also explores the role of copper oxide in lowering the PDL and enhancing the burning characteristics of pyrotechnic mixtures.

An increase in the pressure of the external environment and the addition of CuO contribute to the rise in the burning rate of pyrotechnic mixtures and a decrease in PDL. For example, when the medium pressure is 1 MPa, the combustion front of pyrotechnic mixtures spreads evenly and ignites relatively slowly ($r_b = 6.07 \text{ mm s}^{-1}$). With an increase in pressure, the burning rate increased up to 2–3 times ($r_b = 11.48$ and $r_b = 15.44 \text{ mm s}^{-1}$). In addition, the PDL value decreased to 1 MPa.

Figure 11 shows the relative values of the burning speed of AN/MgAl and AN/MgAl with CuO mixtures in a nitrogen atmosphere at different pressure values. Compared to the AN/MgAl pyrotechnic mixture, the burning rate of the AN/MgAl/CuO mixture at all pressure values increased about two times. Adding CuO achieved the maximum result of the combustion rate ($r_b = 15.44 \text{ mm/s}$ at pressure $P_0 = 5 \text{ MPa}$).

The burning characteristics of AN-based pyrotechnic mixtures were improved under the influence of copper oxide. As shown in Figure 11, the burning rate increased due to the increase in pressure value. The flame pressure index is calculated using the combustion characteristics at different pressure values. However, the n value of the pyrotechnic mixtures with CuO is more significant than that of the blank pyrotechnic mixtures.

In summary, using high-temperature synthesized MgAl solid solution as a fuel in AN-based energetic mixtures can improve some of the main disadvantages of AN. Adding CuO to AN/MgAl pyrotechnic mixtures can be assumed to improve the burning characteristics. Catalysts play an essential role in the thermal decomposition characteristics of reagents (oxidizing agent and binder), pressure ignition limit, and increased burning rate.

5. Conclusions

The synthesis of the Mg–50%Al alloy through high-temperature diffusion bonding has been found to significantly enhance the combustion characteristics and thermal properties of energy mixtures based on ammonium nitrate. In addition, based on the catalytic effect of CuO on energy additives, the PDL value decreased from 2 MPa to 1 MPa, and the burning

rate increased to 4–6 mm/s for each pressure value ($r_b = 6.17$ mm/s vs. $r_b = 15.44$ mm/s, at chamber pressure $P_0 = 5$ MPa). Also, the kinetics of thermal decomposition of AN-based energy mixtures in the CuO condensed phase were improved, and the activation energy values were significantly reduced compared to the original AN ($E_a = 102$ kJ mol^{−1} to 75 kJ mol^{−1}). Ammonium nitrate as an oxidizer in pyrotechnic compounds has been considered environmentally and economically viable. In addition, adding MgAl alloy and copper oxide compensated for some of the disadvantages of AN.

Thus, this research provides a scientific foundation for future innovations in sustainable pyrotechnics. By detailing the thermal properties and burning characteristics of AN/MgAl mixtures with CuO, we are setting the stage for further research and development in this area, potentially leading to new materials, technologies, and methods that continue to improve the sustainability and safety of pyrotechnic applications.

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