

# Studies on ignition and afterburning processes of $\text{KClO}_4/\text{Mg}$ pyrotechnics heated in air

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**Abstract** Thermal behavior of  $\text{KClO}_4/\text{Mg}$  pyrotechnic mixtures heated in air was investigated by thermal analysis. Effects of oxygen balance and heating rates on the TG–DSC curves of mixtures were examined. Results showed that DSC curves of the mixtures had two exothermic processes when heated from room temperature to 700 °C, and TG curve exhibited a slight mass gain followed by a two-stage mass fall and then a significant mass increase. The exothermic peak at lower temperature and higher temperature corresponded to the ignition process and afterburning process, respectively. Under the heating rate of 10 °C  $\text{min}^{-1}$ , the peak temperatures for ignition and afterburning process of stoichiometric  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) was 543 and 615 °C, respectively. When Mg content increased to 50%, the peak ignition temperature decreased to 530 °C, but the second exothermic peak changed little. Reaction kinetics of the two exothermic processes for the stoichiometric mixture was calculated using Kissinger method. Apparent activation energies for ignition and afterburning process were 153.6 and 289.5 kJ  $\text{mol}^{-1}$ , respectively. A five-step reaction pathway was proposed for the ignition process in air, and activation energies for each step were also calculated. These results should provide reference for formula design and safety storage of  $\text{KClO}_4/\text{Mg}$ -containing pyrotechnics.

**Keywords** Thermal behavior · TG–DSC · Ignition · Afterburning · Pyrotechnic mixture

## Introduction

Pyrotechnics has been widely applied in military and civilian fields because of their ability to produce light, heat, smoke, or sound through combustion. Pyrotechnic compositions are usually composed of organic or inorganic oxidizers and fuels [1, 2]. Potassium perchlorate ( $\text{KClO}_4$ ) has long been a main oxidizer in many civil/military pyrotechnics for its mild phase transition, moderate sensibility, and fast ignitability [3–5]. Magnesium (Mg) powders are usually used as fuels to enhance the energy characteristics and improve the ignition property of pyrotechnics [6, 7]. The combination of  $\text{KClO}_4$  and Mg are typically used for flare pyrotechnics and fireworks [8, 9]. For some of these applications, the combustion of  $\text{KClO}_4/\text{Mg}$  takes place in air. In this case, the actual oxidizers participating in the combustion process include both  $\text{KClO}_4$  and the oxygen in air. Though pyrotechnic reactions do not usually depend on oxygen from the air, the combustion process can be influenced by the participation of air. Previous studies showed that the overall reactions of high explosives or pyrotechnics in air included primary reactions of artificial oxidizers with fuels and secondary reactions (afterburning) of unreacted fuels or partially oxidized products by surrounding air [10]. It was reported that for explosives such as TNT, the energy released by the afterburning reactions reached twice to four times of that released by the primary reactions [11]. Investigations on the afterburning reaction of display pyrotechnics have also been reported [12]. But there has little open literature studying the primary reactions and afterburning reactions of binary  $\text{KClO}_4/\text{Mg}$  pyrotechnics heated in air. Knowledge on this aspect should be helpful for both the formula design and safety assessment of  $\text{KClO}_4/\text{Mg}$ -containing pyrotechnics.

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In this work, we investigate the endothermic or exothermic changes of  $\text{KClO}_4/\text{Mg}$  binary pyrotechnic mixtures heated in air through TG–DSC measurement, aiming at obtaining some information on characteristic temperatures of ignition and afterburning processes. Reaction kinetics of these two processes was also studied by Kissinger method based on DSC data.

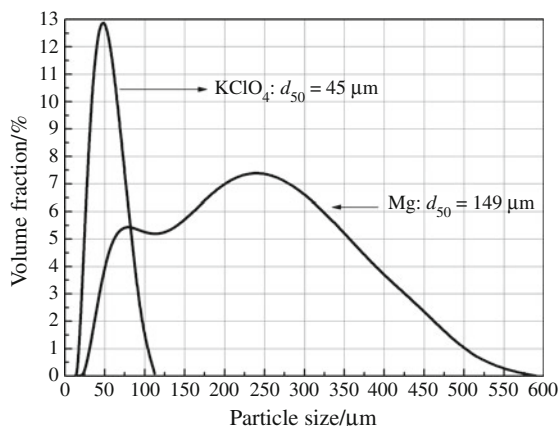
## Experimental

Analytically pure  $\text{KClO}_4$  (Kermel Chemical Co.) was firstly dried at  $60^\circ\text{C}$  and then ground in a mortar followed by passing through a mesh 200 sieve before use. Mg powders were purchased from Tangshan Weihao Magnesium powder Co. Ltd, China (Purity  $>99.9\%$ ,  $-100$  mesh). Particle size distribution of  $\text{KClO}_4$  and Mg powders was shown in Fig. 1. Mixtures of  $\text{KClO}_4/\text{Mg}$  were prepared by intimately mixing  $\text{KClO}_4$  and Mg powders in an agate mortar for 30 min. Two types of  $\text{KClO}_4/\text{Mg}$  mixtures were considered. The stoichiometric composition (zero oxygen balance) was defined as per:



where the mass ratio of  $\text{KClO}_4$  to Mg was 58.8/41.2. Another fuel-rich composition (negative oxygen balance) was  $\text{KClO}_4/\text{Mg}$  (50/50). Before testing, all samples were dried under vacuum at  $60^\circ\text{C}$  for 3 h.

TG–DSC measurement was carried out using a SDT Q600 (USA) thermal analyzer. Air atmosphere (flowing rate =  $100\text{ ml min}^{-1}$ ) and a heating rate of  $10^\circ\text{C min}^{-1}$  were used to analyze the thermal events of pure components and  $\text{KClO}_4/\text{Mg}$  mixtures. Argon atmosphere was applied as a reference to interpret the experimental data of  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) in air. Varied heating rates (5, 15,  $20^\circ\text{C min}^{-1}$ ) were adopted to study the kinetic characteristics of major reactions. All the samples were heated



**Fig. 1** Particle size distribution of  $\text{KClO}_4$  and Mg powders

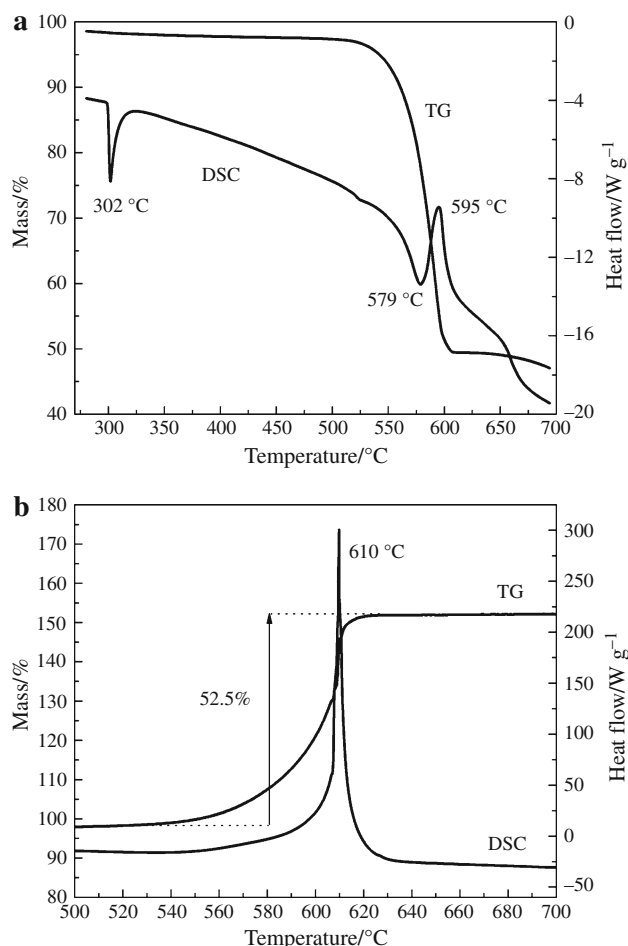
from room temperature to  $700^\circ\text{C}$ , and samples' mass was adjusted according to the violence of reactions. In detail, under the heating rate of  $10^\circ\text{C min}^{-1}$ , samples' mass was about 3.8 mg except Mg powders, which showed a significant self-heating phenomenon until the mass was reduced to 0.55 mg. Under the heating rates of 5, 15, and  $20^\circ\text{C min}^{-1}$ , samples' mass was 1.8 mg, so that the calculation of kinetic parameters was valid.

## Results and discussion

### TG–DSC curve of pure component

Thermal behavior of  $\text{KClO}_4$  powders has been previously reported [4, 13]. Temperatures for the phase change, melting, and decomposition of  $\text{KClO}_4$  used in this work were  $302$ ,  $579$ , and  $595^\circ\text{C}$ , respectively, as seen in Fig. 2a.

Figure 2b showed TG–DSC curve of pure Mg powders heated in air. No evident thermal events were detected until



**Fig. 2** TG–DSC curve for pure  $\text{KClO}_4$  (a) and Mg powders (b) ( $10^\circ\text{C min}^{-1}$ ; flowing air)

520 °C. The sharp exothermic peak at 610 °C and the 52.5% mass gain were indicative of the oxidation of Mg powders by air. Though it was possible for Mg to react with both  $\text{O}_2$  and  $\text{N}_2$  in the air during heating, causing mass increase, the predominant reaction corresponding to this exothermic peak should be represented by following equation [14, 15]:

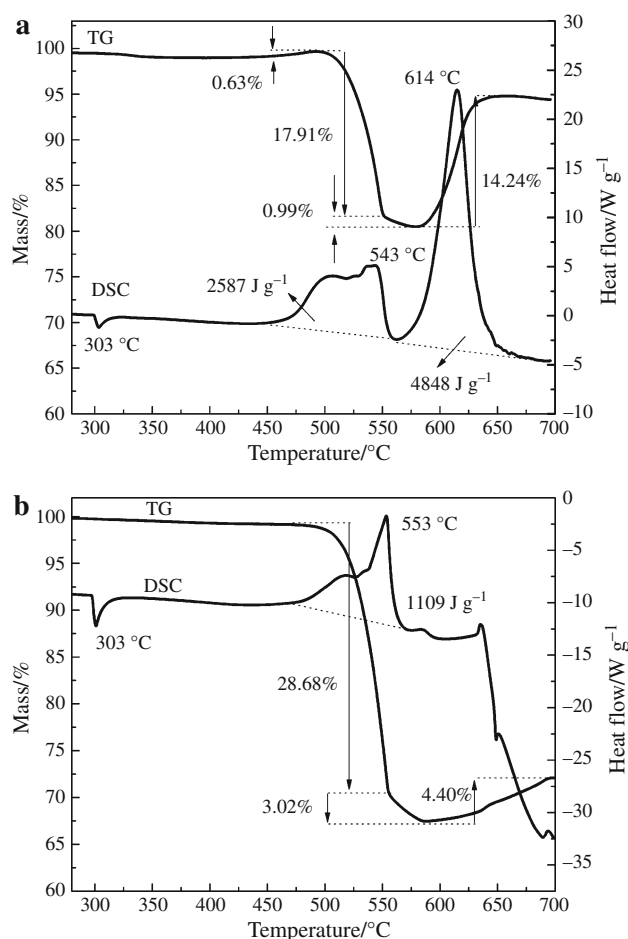


Theoretical mass increase for the above reaction is 65.7%, which was 13.7% higher than experimental data. This may be partly due to the initial MgO present on the surface of Mg particles. Alternatively, Mg powders have not been completely oxidized until 700 °C for the slow dynamic effects in the final stage. This peak temperature was lower than the previously reported ignition temperature of Mg powders of mesh 300, and the melting peak of Mg was not observed, either [16]. Reasons may be related to the fresher surface of Mg powders used in our work, because they were stored in an argon-protected glove-box until tested.

#### TG–DSC curve of $\text{KClO}_4/\text{Mg}$ (58.8/41.2) mixtures

Figure 3a showed TG–DSC curve of  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) heated in air. The TG curve was characterized by two mass increase and two mass loss stages, as labeled in Fig. 3a. The DSC trace showed a broad exothermic peak near 544 °C and a sharp exothermic peak near 614 °C except for the phase transition peak of  $\text{KClO}_4$  near 303 °C. The broad peak could be visualized to comprise several overlapping exothermic peaks, which caused the ignition of  $\text{KClO}_4/\text{Mg}$  mixtures. The sharp exothermal peak near 614 °C and the mass increase of 14% in the range of 560–650 °C revealed another oxidization process, which could be regarded as an “afterburning” reaction in the pyrotechnic system. This “afterburning” reaction was resulted from the oxidation of residual unreacted reactive Mg with air under high temperature. The total energy released by the ignition reactions was  $2587 \text{ J g}^{-1}$ , but the heat released by the afterburning reaction reached  $4848 \text{ J g}^{-1}$ , suggesting that the reaction between  $\text{KClO}_4$  and Mg in the ignition process was incomplete, which did not take place as per Eq. 1).

In order to confirm the analysis above, TG–DSC curve of  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) heated in argon atmosphere (flowing rate =  $100 \text{ mL min}^{-1}$ ) was tested, as seen in Fig. 3b. Compared with the air atmosphere, the DSC curve showed a broad exothermic peak consisting of several overlapping peaks near 553 °C, but the heat released was  $1109 \text{ J g}^{-1}$ , which reduced by over 50% than in Fig. 3a. After that point, the baseline of DSC appeared quite abnormal, so it was difficult to differentiate real exothermic events from the declined baseline. On the other hand, it was

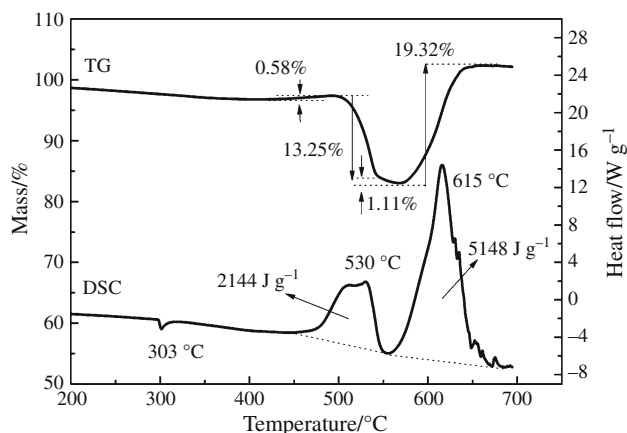


**Fig. 3** TG–DSC curve of  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) in flowing air (a) and flowing Ar (b) ( $10 \text{ }^\circ\text{C min}^{-1}$ )

found from the TG curve that the slight mass gain at low temperatures disappeared, and the two successive mass loss processes also presented. This indicated that the ignition process in argon may not involve the reaction of the air with Mg. Note that the TG curve still showed a small mass gain after the ignition, revealing a second oxidation process of Mg under high temperature. This mass gain was only 4.4%, so it was probably resulted from the oxidation of unreacted Mg by a small amount of air taken into the system by flowing Ar. These results suggested that the reaction between  $\text{KClO}_4$  and Mg with stoichiometric ratio was not complete during the ignition process, neither in argon nor in air. The unreacted reactive Mg would be secondly oxidized by air under high temperatures.

#### Effect of oxygen balance on the thermal behavior of $\text{KClO}_4/\text{Mg}$ mixtures

Oxygen balance is an important consideration in designing pyrotechnics. Negative oxygen balance, that is, fuel-rich formula was usually employed in practice. Figure 4 showed



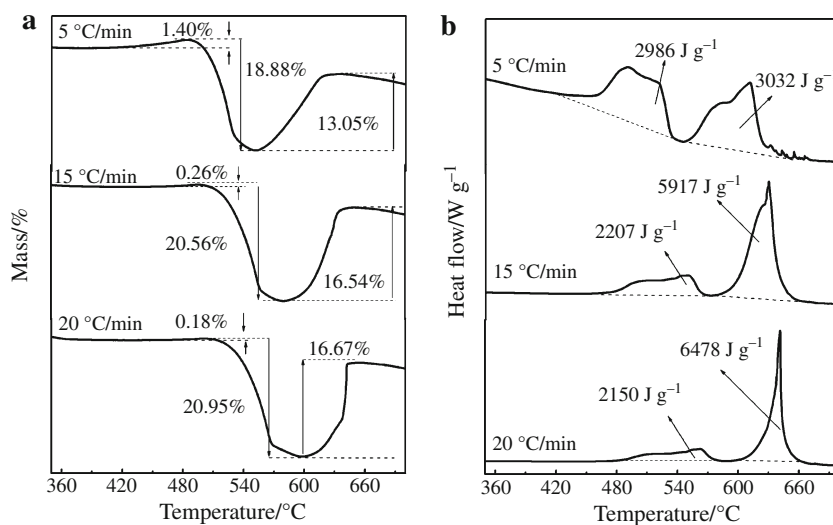
**Fig. 4** TG–DSC curve of  $\text{KClO}_4/\text{Mg}$  (50/50) ( $10\text{ }^\circ\text{C min}^{-1}$ ; flowing air)

TG–DSC curve of  $\text{KClO}_4/\text{Mg}$  (50/50) (fuel-rich) heated in flowing air. For this fuel-excessive composition, the peak temperature corresponding to the afterburning reaction also presented near  $615\text{ }^\circ\text{C}$ , but the exothermic peak for the ignition process decreased to  $530\text{ }^\circ\text{C}$ . The fall in peak ignition temperature should be ascribed to the better heat transfer between reactants when the amount of metal Mg increased, which promoted ignition reactions. On the other hand, the heat released by the ignition reactions decreased to  $2144\text{ J g}^{-1}$ , but the heat released by afterburning reactions increased to  $5148\text{ J g}^{-1}$ . This indicated that in the case of combusting in air, the reaction heat of fuel-rich composition depended more on the afterburning reaction, though the fuel-rich formula could have a better ignition performance.

#### Effect of heating rates

Figure 5 showed TG–DSC curves of  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) obtained under different heating rates (5, 15, and

**Fig. 5** TG curves (a) and DSC curves (b) for  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) under different heating rates (flowing air)



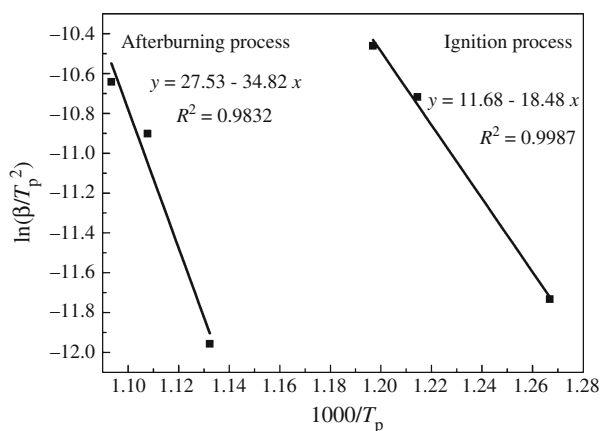
$20\text{ }^\circ\text{C min}^{-1}$ ) in air. As the heating rates were increased, the exothermic peaks for both ignition and afterburning process shifted to higher temperatures, the reaction heat of the ignition process decreased while that of the afterburning process increased. As for TG curves, the initial mass increase became less evident, but the mass loss and secondary mass gain became more when heating rates increased. Combining with TG and DSC results, it was inferred that the reaction between  $\text{KClO}_4$  and Mg became more incomplete with increasing heating rates.

#### Reaction kinetics of the ignition and afterburning process

As analyzed above, ignition and afterburning processes are two separate stages in the combustion processes for  $\text{KClO}_4/\text{Mg}$  pyrotechnics under air atmosphere, and the overall combustion rate can be connected with the kinetics of these two processes. Knowledge of the kinetic parameters of respective process is of practical meaning for the application of  $\text{KClO}_4/\text{Mg}$ -containing pyrotechnics. Therefore, we calculated apparent activation energies  $E_a$  and pre-exponential factors  $\ln A$  of two exothermic processes for  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) in order to find some clues on predicting the rate-controlling process under combustion conditions. In this work, kinetic parameters ( $E_a$  and  $\ln A$ ) were determined using Kissinger method [17] based on the DSC data of different heating rates (5, 15, and  $20\text{ }^\circ\text{C min}^{-1}$ ). Kissinger method was one of the commonly used and reliable model-free methods to evaluate the activation energy without considering any implicit reaction model [18–20]. Even though  $E_a$  determined by Kissinger method was a special case corresponding to a fixed conversion, and it may not display the overall trend of  $E_a$ , we could interpret the obtained activation energies as an overall value

including all steps of complex reactions occurred during each process [21, 22]. Another reason for us to choose Kissinger method instead of other isoconversional methods such as Ozawa [23] and Flynn and Wall [24] method was as follows. When using Ozawa and Flynn and Wall methods, the calculation of activation energies was based on the precise determination of the conversion fraction with changing temperature. However, in the present work, due to the unknown quantity of air participated in the ignition and afterburning process, it was impossible to obtain meaningful conversion fraction values representing either the overall reaction or a certain intermediate reaction. According to Kissinger method, by plotting  $\ln(\frac{\beta}{T_p^2})$  versus the reciprocal temperatures  $1/T_p$ , where  $T_p$  is the peak temperature of the DSC curve,  $\beta$ , the heating rate, apparent active energy  $E_a$  corresponding to each peak could be obtained from the slopes of straight lines, and pre-exponential factors  $\ln A$  could be obtained from the intercept of straight lines.

Figure 6 showed the linear regression of  $\ln(\frac{\beta}{T_p^2})$  versus  $1/T_p$ . The values of  $E_a$  and  $\ln A$  for the ignition process and afterburning process were  $153.6 \text{ kJ mol}^{-1}$ ,  $21.50 \text{ s}^{-1}$ , and  $289.5 \text{ kJ mol}^{-1}$ ,  $37.99 \text{ s}^{-1}$ , respectively. The higher activation energy of the latter process revealed that afterburning process was probably the rate-controlling step in the whole combustion process of  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) mixtures, as could also be interpreted in terms of the physical picture. As analyzed above, the afterburning process occurred after the ignition process, so the reactivity of residual Mg was lower than in the former process, because the residual Mg was usually coated by primary products like MgO even KCl. In this case, the secondary oxidation of Mg was performed through its melting and erupting out of the fractured coating [25], which was a more difficult process than the direct oxidation of fresh Mg.



**Fig. 6** Plot of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  for  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) (flowing air)

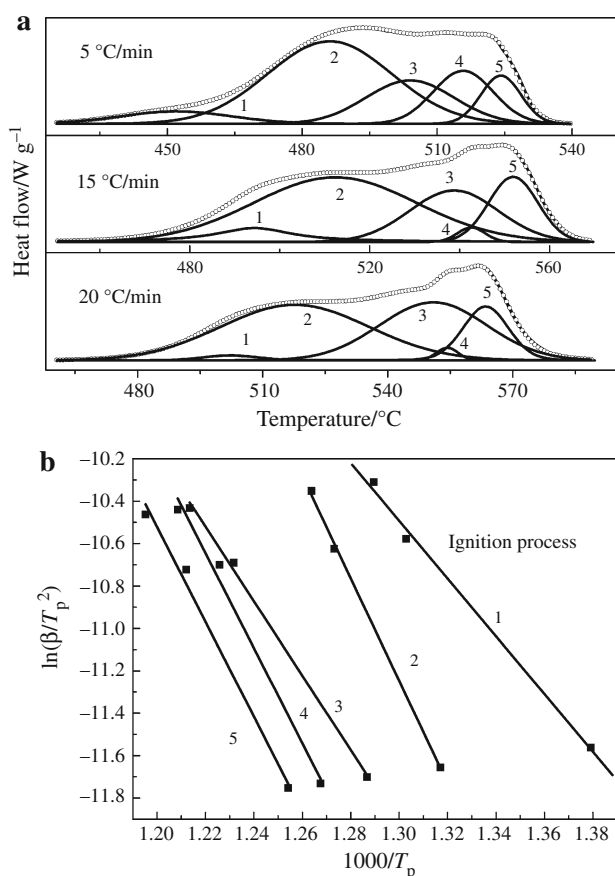
In a word, the experimental results in Figs. 3a, 4, and 5 as well as the apparent activation energies indicated that, when heating stoichiometric  $\text{KClO}_4/\text{Mg}$  in air, the oxidation of Mg by  $\text{KClO}_4$  was dominant, though the air participated in the oxidation of Mg. From the practical application point of view, when pursuing a faster burning rate for this composition, one of the useful methods was to improve the completeness of the first process, so that the amount of unreacted Mg decreased. Before searching some operable ways, a further understanding of the ignition process was necessary and helpful, as would be discussed in the next section.

Possible reaction pathways of the ignition process for  $\text{KClO}_4/\text{Mg}$  (58.8/41.2)

From TG results in Figs. 3a, 4, and 5, we could see that the ignition process for  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) in air was initiated from the pre-oxidation of Mg powders by air and dominated by the subsequent decomposition reaction between  $\text{KClO}_4$  and Mg. One important question we want to know about the decomposition reaction was that if it was a pure solid–solid reaction or a reaction between decomposition-deduced  $\text{O}_2$  by  $\text{KClO}_4$  and Mg or combinations of them.

In fact, previous investigation by Tribelhorn [26] showed that the overall reaction between an oxidant and a fuel in the pyrotechnics may include some combinations of the following processes: a solid–solid reaction, a solid–liquid reaction involving either a molten oxidant, or a molten fuel, a reaction between fuel and gaseous oxygen (or some other gaseous species) formed by the prior thermal decomposition of the oxidant. The nature of oxidant and fuel as well as their ratios influenced the specific reaction paths. Studies on  $\text{KClO}_4/\text{Al}$  mixtures indicated that  $\text{KClO}_4$  melted before the reaction between  $\text{KClO}_4$  and Al [13]. Lee et al. [27] found that when  $\text{Zr}/\text{KClO}_4$  mixtures were fired under ambient conditions, the Zr could initially react with the interstitial air in the voids of mixture. In the present work, no melting peaks of  $\text{KClO}_4$  or Mg were observed before the exothermic events, and the broad exothermic peak in DSC traces corresponding to the ignition process showed more than two overlapping peaks, revealing that the decomposition process involved reactions of multiple steps. Therefore, it was inferred that the ignition reactions of  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) in air were combinations of following reactions: (i) solid–gas reaction between reactive Mg powders with  $\text{O}_2$  in air; (ii) solid–solid reaction between  $\text{KClO}_4$  and Mg; (iii) solid–gas reaction between the  $\text{O}_2$  produced by decomposition of  $\text{KClO}_4$  and Mg.

Based on these knowledge and inference, the overlapping exothermic peaks in DSC curves representing ignition



**Fig. 7** Separation of overlapping exothermic peaks (*solid lines* for experimental data; *dash lines* for individual peaks; *symbols* for sum of the individual peaks) (**a**) and plot of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  for individual simulated peaks (**b**) in ignition process of  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) (flowing air)

processes were resolved by virtue of Peak Fit program. Firstly, the experimental data were simulated according to a four-step reaction model, which assumed that the solid–gas reaction (iii) included two separate steps: decomposition of  $\text{KClO}_4$  and the oxidation of Mg by the released  $\text{O}_2$ , as was similar with the decomposition of  $\text{Zr}/\text{KClO}_4/\text{NC}$  pyrotechnics [28]. However, the calculated results did not match well with the experimental data. Therefore, we inferred that the intermediate reaction of Eq. 3:

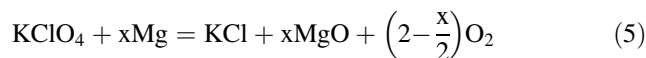


probably existed with a significant extent in the present work, though it was pointed that the intermediate reaction involving the formation of  $\text{KClO}_3$  did not take place in a significant extent in the presence of Zr [28]. Then, a set of calculations with five reaction steps were performed, in which various combinations of interdependent reactions were considered. During calculations, it was found that the calculated curves were very sensitive to the shapes and interactions of different peaks. The shapes and interactions of individual peaks could be associated with the reaction mechanisms and frequency factors of specific reaction steps. However, it was difficult to know the interdependence of these five steps. So it was further assumed that the reaction mechanisms for five steps under different heating rates were similar. Finally, five individual peaks with a similar change trend under different heating rates were found to allow an adequate match of the experimental DSC curve, as seen in Fig. 7a.

Based on the probable reaction mechanisms, the physical meanings of each peak were identified as follows. Peak 1 represented the exothermic reaction:



Peak 2 represented the solid–solid reaction between  $\text{KClO}_4$  and Mg, which proceeded as per



as caused the first drastic mass loss in DSC traces. The reaction temperature for Eq. 5 was lower than both the decomposition temperature for pure  $\text{KClO}_4$  and the oxidation temperature for pure magnesium. This phenomenon can be illustrated by referring to the mechanism of solid state reaction and migration of more reactive components through the product layer to the oxidation interface [29]. Besides, the first exothermic reaction should also promote this solid–solid reaction. Peak 3 correspond to the decomposition of  $\text{KClO}_4$  as per Eq. 3, followed by the continuing decomposition of  $\text{KClO}_3$  into  $\text{KCl}$  and  $\text{O}_2$  (peak

**Table 1** Kinetic parameters and suggested reactions of multiple steps in ignition process of  $\text{KClO}_4/\text{Mg}$  (58.8/41.2)

Exothermic peaks	$E_a/\text{kJ mol}^{-1}$	$\ln A/\text{s}^{-1}$	Linear regression coefficient	Reaction
Peak 1	113.24 ( $\pm 6.59\%$ )	9.82	0.9978	$2\text{Mg} + \text{O}_2(\text{air}) = 2\text{MgO}$
Peak 2	200.86 ( $\pm 3.35\%$ )	25.46	0.9994	$\text{KClO}_4 + x\text{Mg} = \text{KCl} + x\text{MgO} + \left(2 - \frac{x}{2}\right)\text{O}_2$
Peak 3	145.96 ( $\pm 4.67\%$ )	15.88	0.9989	$\text{KClO}_4 = \text{KClO}_3 + \frac{1}{2}\text{O}_2$
Peak 4	186.31 ( $\pm 9.95\%$ )	21.92	0.9951	$\text{KClO}_3 = \text{KCl} + \frac{3}{2}\text{O}_2$
Peak 5	185.99 ( $\pm 8.84\%$ )	21.55	0.9961	$2\text{Mg} + \text{O}_2(\text{KClO}_4) = 2\text{MgO}$

4). Peak 5 represented the oxidation reaction of Mg by the released  $\text{O}_2$ , which led to the slowdown of mass loss rate.

Afterward, the activation energies of five reactions were calculated using Kissinger method, and results were given in Fig. 7b and Table 1. It was found that  $E_a$  changed in the range of 113.24–200.86  $\text{kJ mol}^{-1}$  during the ignition process, and the incomplete solid–solid state reaction between  $\text{KClO}_4$  and Mg had the highest activation energy, which was probably the rate-controlling step of overall ignition process.

## Conclusions

Thermal behavior of  $\text{KClO}_4/\text{Mg}$  binary pyrotechnic mixtures heated in air was investigated by simultaneous TG–DSC in this work. Results showed that  $\text{KClO}_4/\text{Mg}$  had two separate exothermic processes, which corresponded to ignition and afterburning reactions, respectively. Exothermic peaks were influenced by both heating rates and the  $\text{KClO}_4/\text{Mg}$  ratios. When heating rates were increased, exothermic peaks of these two processes all shifted to higher temperatures. Compared with the stoichiometric composition  $\text{KClO}_4/\text{Mg}$  (58.8/41.2), the fuel-rich mixture  $\text{KClO}_4/\text{Mg}$  (50/50) had a lower peak ignition temperature, but the exothermic peak of afterburning reactions changed little. The ignition process was suggested to comprise five-step overlapping reactions. The initial mass increase of samples heated in air revealed that the first step reaction was the oxidation of Mg by air. Reactions of four other steps were inferred based on published knowledge on similar pyrotechnic systems, that is, the incomplete solid–solid reaction between  $\text{KClO}_4$  and Mg, the two-step decomposition of  $\text{KClO}_4$ , and the reaction of decomposition-induced  $\text{O}_2$  with Mg. Apparent activation energies of the overall ignition process, afterburning process and individual reactions belonging to ignition process indicated that the whole combustion rate of  $\text{KClO}_4/\text{Mg}$  (58.8/41.2) in air was controlled by the afterburning process, and the solid–solid reaction of  $\text{KClO}_4$  with Mg was the controlling step in the ignition process. Fuel-rich  $\text{KClO}_4/\text{Mg}$  compositions were expected to obtain a better performance in practical applications in case of combusting in air.

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## References

1. Conkling JA. Chemistry of pyrotechnics: basic principles and theory. New York: Marcel Dekker Inc.; 1985.
2. Hosseini SG, Eslami A. Thermoanalytical investigation of relative reactivity of some nitrate oxidants in tin-fueled pyrotechnic systems. *J Therm Anal Calorim.* 2010;101:1111–9.
3. Hosseini SG, Pourmortazavi SM, Hajimirsadeghi SS. Thermal decomposition of pyrotechnic mixtures containing sucrose with either potassium chlorate or potassium perchlorate. *Combust Flame.* 2005;141:322–6.
4. Lee JS, Hsu CK. The DSC studies on the phase transition, decomposition and melting of potassium perchlorate with additives. *Thermochim Acta.* 2001;367–368:367–70.
5. Barišič D, Haberle IB. Aging of pyrotechnic compositions. The investigation of chemical changes by IR spectroscopy and x-ray diffraction. *Propellant Explos Pyrotech.* 1989;14:162–9.
6. Tuukkanen IM, Charsley EL, Laye PG, Rooney JJ, Griffiths TT, Lemmetyinen H. Pyrotechnic and thermal studies on the magnesium-strontium nitrate pyrotechnic system. *Propellant Explos Pyrotech.* 2006;31:110–5.
7. Tuukkanen IM, Brown SD, Charsley EL, Goodall SJ, Rooney JJ, Griffiths TT, Lemmetyinen H. Studies on the ageing of a magnesium-strontium nitrate pyrotechnic composition using isothermal microcalorimetry and thermal analysis techniques. *Thermochim Acta.* 2004;417:223–9.
8. Knowlton GD, Ludwig CP. Low temperature autoignition composition. US Patent, 6479702, 2004.
9. Krone U. Pyrotechnical mixture for producing a smoke screen. US Patent, 4968365, 1990.
10. Salzano E, Basco A, Cammarota F. Confined after-burning of display pyrotechnics and explosives. In: 32nd Combustion meeting, Napoli (IT), 2009.
11. Donhaue L, Pegg MJ, Zhang F. Afterburning of TNT detonation products in air. In: Seventh international symposium on hazards, prevention, and mitigation of industrial explosives (7th ISGHP-MIE). St. Petersburg, Russia, 2008.
12. Basco A, Salzano E. The risk of storage plant of pyrotechnics. *Chem Eng Trans.* 2010;19:231–6.
13. Pourmortazavi SM, Fathollahi M, Hajimirsadeghi SS, Hosseini SG. Thermal behavior of aluminum powder and potassium perchlorate mixtures by DTA and TG. *Thermochim Acta.* 2006;443:129–31.
14. Sharma TP, Varshney VS, Kumar S. Products of combustion of the metal powders. *Fire Sci Technol.* 1992;12:29–38.
15. Ravindran N, Chattopadhyay DK, Zakula A, Battocchi D, Webster DC, Bierwagen GP. Thermal stability of magnesium-rich primers based on glycidyl carbamate resins. *Polym Degrad Stab.* 2010;95:1160–6.
16. Pourmortazavi SM, Hajimirsadeghi SS, Kohsari I, Fathollahi M, Hosseini SG. Thermal decomposition of pyrotechnic mixtures containing either aluminum or magnesium powder as fuel. *Fuel.* 2008;87:244–51.
17. Kissinger HE. Reaction kinetics in differential thermal analysis. *Anal Chem.* 1957;29:1702–6.
18. Barral L, Cano J, Lopez J, Lopez-Bueno I, Nogueira P, Ramirez C, et al. Thermogravimetric study of tetrafunctional/phenol novolac epoxy mixtures cured with a diamine. *J Therm Anal Calorim.* 1998;51:489–501.
19. Chrissafis K. Kinetics of thermal degradation of polymers—Complementary use of isoconversional and model-fitting methods. *J Therm Anal Calorim.* 2009;95:273–83.
20. Gao M, Wu W, Yan Y. Thermal degradation and flame retardancy of epoxy resins containing intumescent flame retardant. *J Therm Anal Calorim.* 2009;95:605–8.
21. Tiptipakorn S, Damrongsakkul S, Ando S, Hemvichian K, Rimdusit S. Thermal degradation behaviors of polybenzoxazine and silicon-containing polyimide blends. *Polym Degrad Stab.* 2007;92:1265–78.
22. Boey FYC, Qiang W. Experimental modeling of the cure kinetics of an epoxy-hexaanhydro-4-methylphthalicanhydride (MHPA) system. *Polymer.* 2000;41:2081–94.

23. Ozawa T. Kinetic analysis of derivative curves in thermal analysis. *J Therm Anal Calorim.* 1970;2:301–24.
24. Flynn JH, Wall LA. A quick, direct method for the determination of activation energy from thermogravimetric data. *J Appl Polym Sci B.* 1966;4–5:323–8.
25. Shih TS, Wang JH, Chong KZ. Combustion of magnesium alloys in air. *Mater Chem Phys.* 2004;2–3:302–9.
26. Tribelhorn MJ, Venables DS, Brown ME. Combustion of some zinc-fuelled binary pyrotechnic systems. *Thermochim Acta.* 1995;256:309–24.
27. Lee JS, Hsu CK. The effect of different zirconium on thermal behaviors for Zr/KClO<sub>4</sub> priming composition. *Thermochim Acta.* 2001;367–368:375–9.
28. Solymosi F. Structure and stability of salts of halogen oxyacids in the solid phase. New York: Wiley; 1977.
29. Mclain JH. Pyrotechnics from the viewpoint of solid state chemistry. Philadelphia: Franklin Institute; 1980, p. 20.