Research paper

Characterization of a Fe_2O_3/Al/polyoxymethylene thermite composition

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Abstract

This work investigated a new thermite formulation consisting of Fe_2O_3, Al and polyoxymethylene (POM), with potential applications as a propellant in fireworks. Unmodified Fe_2O_3/Al mixtures were found to have ignition energies between approximately 30 and 40 kJ mol^{-1} while Fe_2O_3/Al/POM compositions exhibited ignition energies of about 20 kJ mol^{-1}. Fe_2O_3/Al formulations mixed in weight ratios of 4/6, 5/5, 6/4 and 7/3 all had similar minimum ignition temperatures in the range of 500 to 600 K. The addition of POM lowered the ignition temperature to between 400 and 500 K. The maximum pressure obtained from a Fe_2O_3/Al/POM (5/5/20 weight ratio) mixture during testing was 2100 kPa, exceeding the pressures obtained from CuO/Al/POM, CaO_2/Al/POM and black powder formulations. The solid combustion products resulting from this new formulation were identified as Fe and Al_2O_3,which are thought to originate from the reaction $Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$. The results of this study indicate that Fe_2O_3/Al/POM compositions show promise as energetic components of fireworks.

Keywords : composition, thermite, fire works, pressure, energy

1. Introduction

Thermite reaction of the Fe_2O_3 and Al mixture system is combustion reaction by reactions of their displacement by more activity metals will occur with a liberation of a considerable quantity of heat.[1] The Fe_2O_3/Al mixture is a classical thermite system which has been used since 1898 on the welding of railway tracks.[2] For thermite reaction, there is a report on the radical composition propagation to the sample composition and stoichiometry of Fe_2O_3/Al system.[3] This reactive system can also be used for cutting and perforation of materials, to produce alumina liners in situ for pipes, as a portable heat source, as a high-temperature igniter, as a pyrotechnic heat producer and as an additive to propellants and explosives.[2] Ignition charges have traditionally been used in various energetic devices, including airbags, electric detonators, rocket pyrotechnics and ammunition.[4] In recent years, however, fragmentation igniters have been developed which use non-explosive compositions based on thermite.[5] Thermite agents have also been studied as heat sources for the vaporization of solid materials such as lithium in sounding rocket systems.[6] These applications are possible because thermite undergoes a highly exothermic oxidation-reduction reaction which generates temperatures as high as 2500 to 3000 K.[7]

In a previous paper we reported a thermite composition augmented by the rapid decomposition of polyoxymethylene (POM), with applications in rock breaking and fireworks.[7, 8] Experimental results suggested that the performance of this material may be attributed to the high pressure gas products evolved from the rapid thermal decomposition of POM as it is accelerated by the thermite reaction between CuO or CaO_2 (added at 50 or 80 wt% of the formulation) and Al. The pressures achieved from the decomposition of this new material ranged from 700 to 1200 kPa in the case of the CuO/Al/POM mixtures and from 900 to 1200 kPa for the CaO_2/Al/POM mixtures.[8] The performance of these compositions is therefore similar to that of black powder, which generates a pressure of about 1300 kPa under the same test conditions.[9] In addition to showing similar performance to black powder, this thermite composition was found to produce primarily CO_2 and H_2O as its gaseous combustion products while the main solid products identified following combustion were Cu, $CuAl_2$ and Al_2O_3.[8),9] The presence of copper in the combustion products, however, may lead to issues with regard to environmental contamination and thus could be detrimental to the application of this thermite formulation. While there are no toxicity concerns regarding the combustion products of the CaO_2 formulation, the synthesis of CaO_2 is labor intensive.

Based on the above findings, we chose to investigate combinations of POM with a traditional thermite formulation based on the reaction of Fe_2O_3 with Al. In this paper, we report the thermal properties and pressure test results of a Fe_2O_3/Al thermite system, both with and without the addition of POM. The pressure test results obtained from Fe_2O_3/Al/POM mixtures are compared to those obtained using Cu/Al/POM, CaO_2/Al/POM and black powder.

2. Materials

Flake aluminum (Al) was obtained from the Yamato Metal powder Co., Ltd. The Al was 95% pure (by weight) and had an average particle size of 50 μm. Ferric oxide (III) (Fe_2O_3) was kindly supplied by the Titan Kogyo Co., Ltd. This material was extra pure grade (98% pure by weight) with an average particle size of 64 nm and was used as-received without further purification. Polyoxymethylene (POM) was obtained from the Kawai Lime industry Co., Ltd. Polyoxymethylene (POM) was extra pure grade with an average particle size between 200 and 800 μm and was used without further purification. Test compositions were formulated in Fe_2O_3/Al weight ratios of 4/6, 5/5, 6/4 and 7/3. Compositions were also made incorporating POM such that the POM weight ratios in the mixtures were 10, 20, 30 or 40 (as in, for example, Fe_2O_3/Al/POM=4/6/10).

3. Experimental

3.1 Thermal analysis

Differential thermal analysis (DTA) and Thermogravimetry (TG) of Fe_2O_3/Al and Fe_2O_3/Al/POM samples was performed using a Seiko Electric Co., Ltd. TG-DTA 6400 instrument. Measurements were conducted over the temperature range of 20 to 1200 K at a rate of 10 K min^{-1} under air.

3.2 Scanning electron microscopy

Fe_2O_3 and Al sample surfaces were observed via scanning electron microscopy (SEM) using a Jeol Co., Ltd. JSM-6400. Sample surfaces were coated with Au prior to observations.

3.4 Ignition temperature measurements

Ignition temperature measurement specimens were obtained by forming thermite samples of approximately 30 mg total weight into pellets. These molded pellets were placed in a heated electric furnace and the time until ignition was recorded at various temperatures.

3.5 X-Ray diffraction measurements

Following both ignition delay and pressure tests, solid reaction products were identified by X-Ray diffraction measurements using a Rigaku RINT 2400.

3.6 Combustion tests

Figure 1 shows the combustion test apparatus (Matsuki Science Ltd.), in which samples weighing approximately 500 mg were placed on a coiled Ni-Cr wire (0.4 mm in diameter and 6 cm long). The wire was subsequently heated with a 20 V power source. Evolved gases pressures were subjected to analysis by Extra Taff software, to capture digital recorder (DR-3M) on a TEAC Co., Ltd.

4. Results and Discussion

4.1 TG-DTA

Figure 2 shows the TG-DTA curves obtained from samples composed of Fe_2O_3/Al (5/5), POM and Fe_2O_3/Al/POM (5/5/20) under atmospheric pressure in air. The Fe_2O_3/Al plots in Figure 2-(1) exhibit an exothermic peak due to surface oxidation at approximately 610K and another peak due to endothermic melting around 670K. The exothermic peak at about 910K is due to complete oxidation of the Al. The weight gain evident from the TG plot up to the maximum temperature of 1200K is about 32.0%. The TG-DTA results in Figure 2-(1) confirm the reaction of Al but do not prove that an oxidation-reduction reaction occurs between Fe_2O_3 and Al.

Figure 2-(2) shows the TG-DTA curves of a POM. From DTA curve, endothermic peak 170K is the melting of POM, and endothermic peak at approximately 260K is the decomposition of POM. From TG curve along with the decomposition of POM is a weight loss of 100%.

Figure 2-(3) shows the TG-DTA curves of the Fe_2O_3/Al /POM (5/5/20) mixture. In these plots, an endothermic peak due to melting of the POM is observed around 170K as well as an endothermic peak at approximately 260K, which results from decomposition of the POM accompanied by gas evolution.[5] The weight loss between 170 and 260K is about 15%. An exothermic peak due to surface oxidation is seen at 610K and another endothermic melting peak appears at 670K. The exothermic peak at around 920K results from oxidation of the Al. The weight gain calculated from the TG data from the lowest point at 260K up to 1200K is about 30%. The results of TG-DTA therefore show the thermal decomposition of POM and oxidation reaction of Al; although, as with Figure 2-(1), reactions between the components of the Fe_2O_3/Al/POM mixture cannot be proven. The thermal reaction of Al during the thermite reaction produces a thermal load resulting from surface oxidation of the metal by rapid heat load from the outside and this is considered pivotal to the

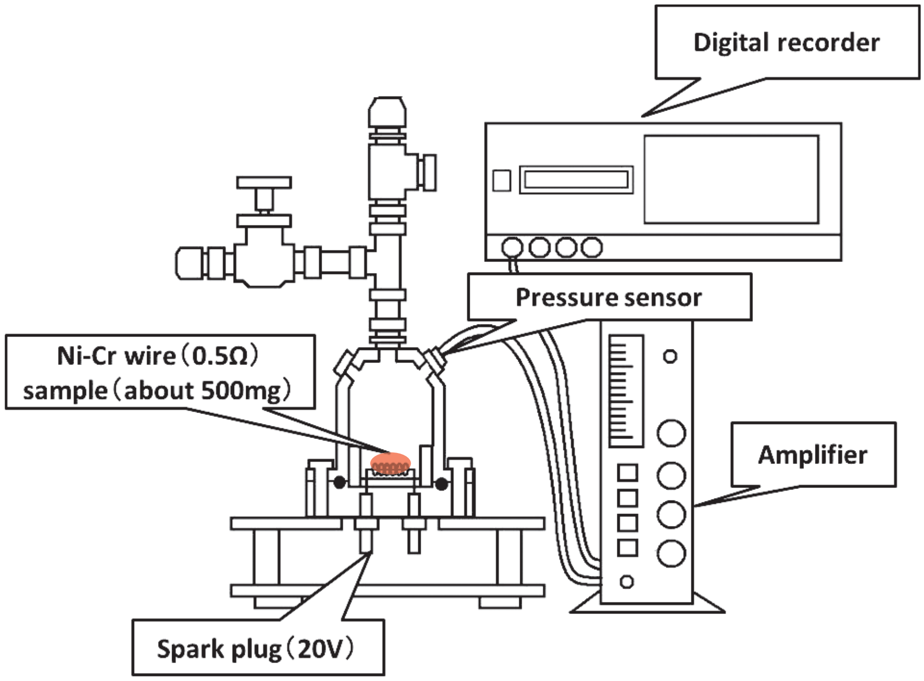

Figure 1 Pressure test apparatus.

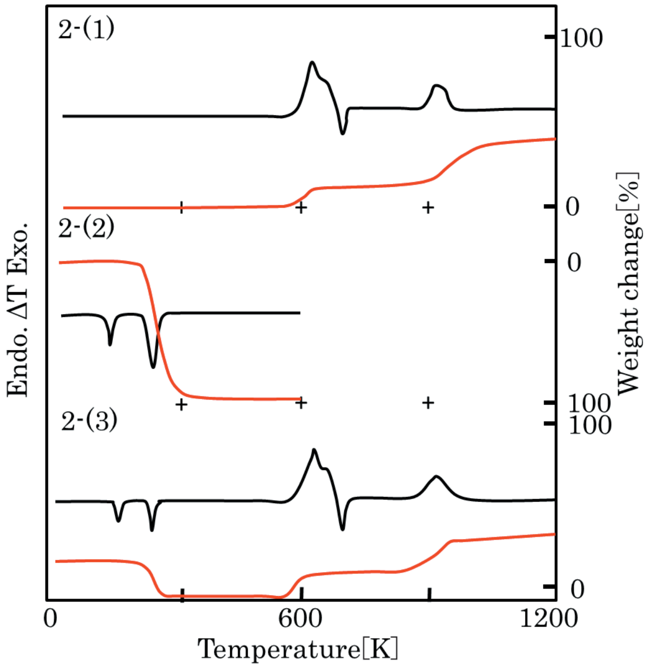

Figure 2 TG-DTA curves obtained for Fe_2O_3/Al (5/5), POM and Fe_2O_3/Al/POM (5/5/20) mixtures.

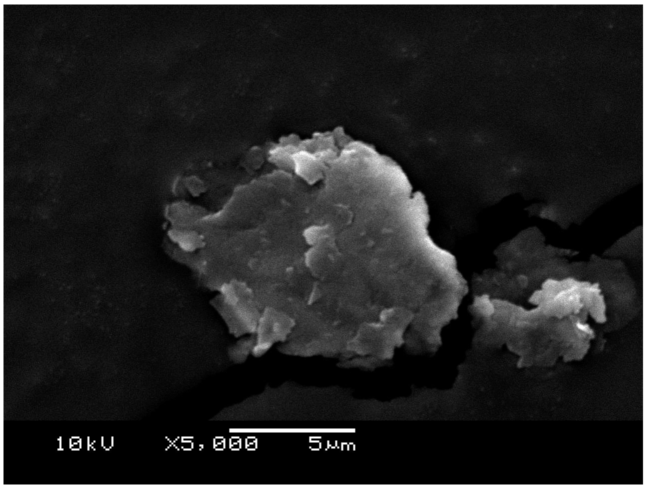

Figure 3-(1) SEM photograph of the Al used in this study.

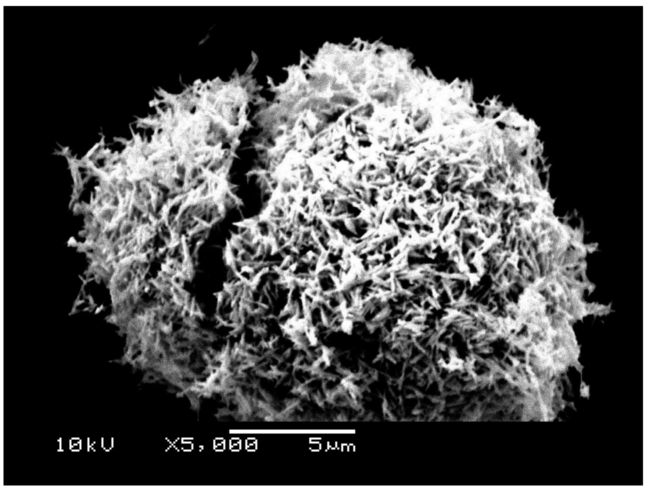

Figure 3-(2) SEM photograph of the Fe_2O_3 used in this study.

performance of thermite.[6)]

4.2 Surface observations with SEM

Figure 3 presents SEM images of the surfaces of Fe_2O_3, Al and a Fe_2O_3/Al mixture. Figures 3-(1) and 3-(2) show that the Al particles used in this study have a scale-like appearance while the Fe_2O_3 is composed of needle-like crystals. In the image of the Fe_2O_3/Al mixture in Figure 3-(3), Fe_2O_3 crystals can be seen adhering to the Al surfaces.

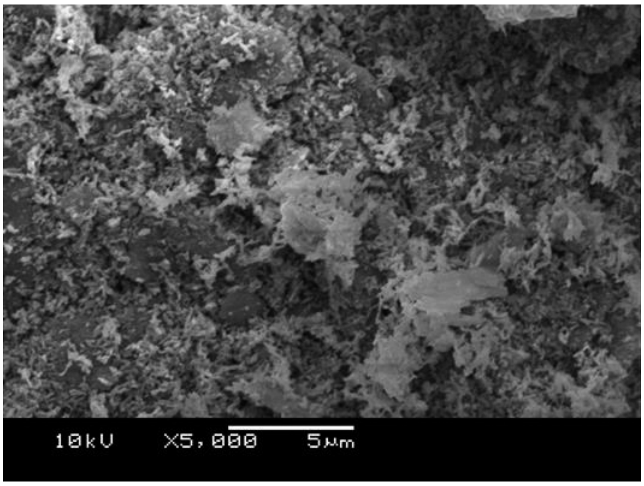

Figure 3-(3) SEM photograph of a Fe_2O_3/Al mixture.

Table 1 Ignition energy and minimum ignition temperature data.

Samples	Ignition energy [kJ mol^{-1}]	Minimum ignition temperature [K]
Fe_2O_3/Al (4/6)	46.4	590
Fe_2O_3/Al/POM (4/6/20)	23.1	440
Fe_2O_3/Al (5/5)	32.6	560
Fe_2O_3/Al/POM (5/5/20)	23.8	420
Fe_2O_3/Al (6/4)	43.8	600
Fe_2O_3/Al/POM (6/4/20)	22.7	500
Fe_2O_3/Al (7/3)	44.6	600
Fe_2O_3/Al/POM (7/3/20)	23.3	560

4.3 Ignition temperature measurements of Fe_2O_3/Al and Fe_2O_3/Al/POM mixtures

Using ignition point data obtained from Fe_2O_3/Al and Fe_2O_3/Al/POM mixtures, the relationships between ln (1/sec) and reciprocal of the absolute temperature (1/T) for both mixtures are plotted in Figure 4-(1). The activation energies obtained from the slopes of these plots are 32.6 kJ mol^{-1} for Fe_2O_3/Al (5/5) and 23.8 kJ mol^{-1} for Fe_2O_3/Al/POM (5/5/20).

The minimum ignition point temperatures were found to be 560K for Fe_2O_3/Al (5/5) and 420K for Fe_2O_3/Al/POM (5/5/20) and so the addition of POM reduces the minimum ignition temperature by about 100K. The activation energy and minimum ignition results for the other Fe_2O_3/Al mixtures (4/6, 5/5, 6/4 and 7/3)and Fe_2O_3/Al/POM mixtures (4/6/20, 5/5/20, 6/4/20 and 7/3/20) are presented in Table 1. The activation energies of the Fe_2O_3/Al mixtures ranged from 30 to 40kJ mol^{-1} while the Fe_2O_3/Al/POM mixtures had activation energy values of approximately 20kJ mol^{-1}. The minimum ignition temperatures spanned the range of 560 to 600K in the case of the Fe_2O_3/Al mixtures, whereas the Fe_2O_3/Al/POM mixtures had ignition temperatures from 420 to 560 K. The decrease in the activation energy and the minimum ignition temperature observed in the POM mixtures is assumed to be associated with the low decomposition temperature of POM.

The relationship between ln (A) and ignition energy (in kJ mol^{-1}) is shown in Figure 4-(2), where it can be seen that the Fe_2O_3/Al and Fe_2O_3/Al/POM mixtures maintain the same reaction rate at all mixing ratios, since all data points for each system lie on straight lines. The Fe_2O_3/Al and Fe_2O_3/Al/POM mixtures, however, each plot exhibit different slopes and thus have differing reaction rates.

4.4 X-ray diffraction pattern of pressure test residues

An X-ray diffraction pattern of the solid residues resulting from pressure testing of the Fe_2O_3/Al (5/5) mixture are shown in Figure 5. Since the sole products present were Fe and Al_2O_3, the associated reaction scheme is believed to be $Fe_2O_3+2Al \rightarrow Al_2O_3+2Fe$. And the solid residues resulting from pressure testing of when

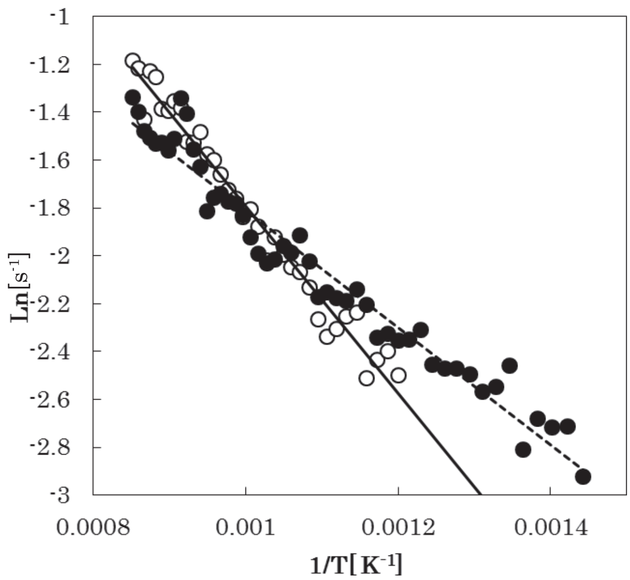

Figure 4-(1) Relationship between Ln (1/s) and1/T based on data from autoignition tests.

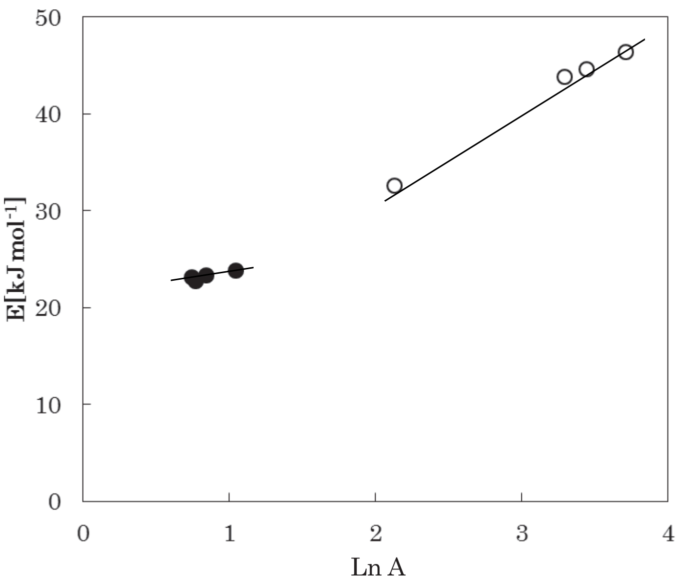

Figure 4-(2) Relationship between ln A and ignition energy (E) based on data from autoignition tests.

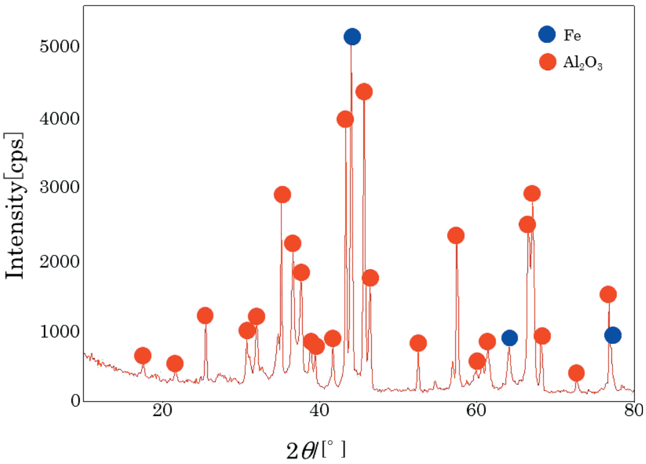

Figure 5 X-Ray diffraction pattern of the solid residue resulting from pressure testing of Fe_2O_3/Al (5/5).

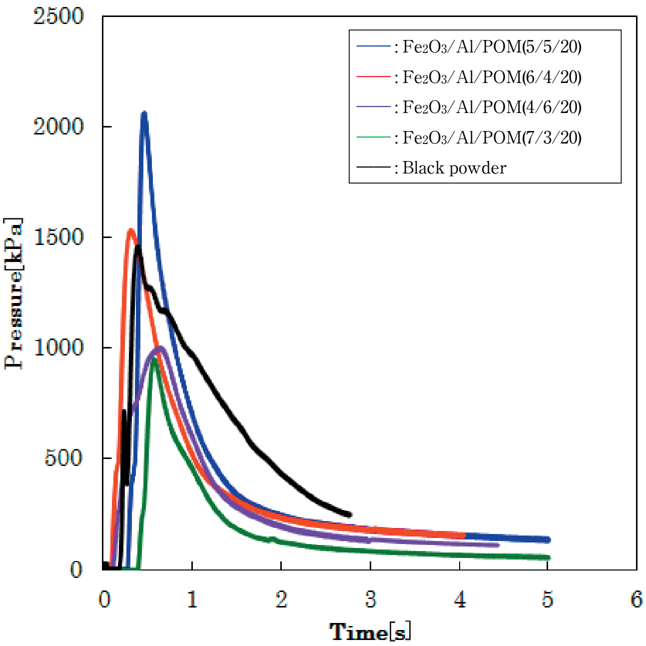

Figure 6 Combustion test plots for Fe_2O_3/Al/POM mixtures formulated with varying ratios of Fe_2O_3 to Al.

added to the POM were indicated the same pattern as in Figure 5.

A stoichiometry of Fe_2O_3 and Al mixture is 7.5 vs. 2.5 in weight ratio. This experimental was carried out on weight ratio (5/5) mixed of Fe_2O_3/Al, but amount to Al excessive. But from the results of X-ray diffraction, Al an unreacted was not confirmed. It was considered that the excessive Al is oxidized by oxygen in the air by fierce combustion of thermite reaction.

4.5 Combustion testing of Fe_2O_3/Al/POM mixtures

The results of combustion tests of various Fe_2O_3/Al/POM mixtures (4/6/20, 5/5/20, 6/4/20 and 7/3/20) are shown in Figure 6. For comparison purposes, the pressure plofile of black powder is given in Figure 7. The maximum pressures obtained were approximately 1000, 2100, 1500 and 1000 kPa when testing the 4/6/20, 5/5/20, 6/4/20 and 7/3/20 mixtures, respectively. The maximum pressure obtained from the black powder was about 1400 kPa.

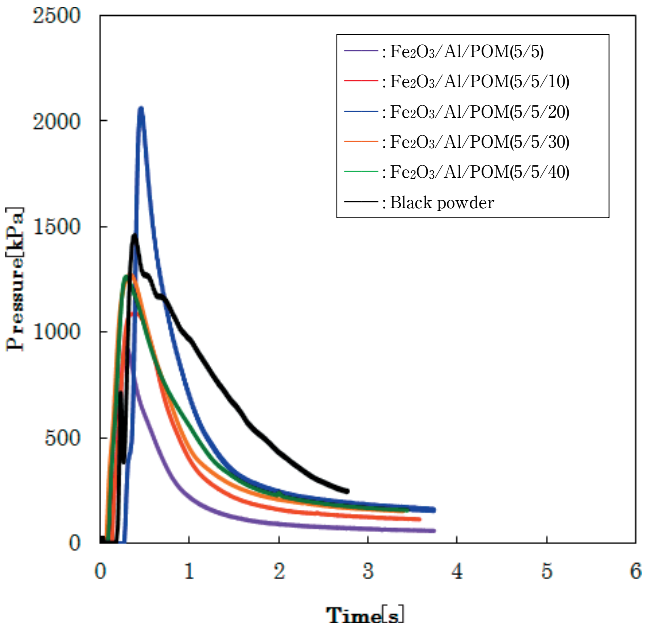

Figure 7 Combustion test plots for Fe_2O_3/Al/POM mixtures formulated with varying proportions of POM.

Interestingly, although a stoichiometric ratio between Fe_2O_3 and Al is achieved at a weight ratio of approximately 7 to 3, the Fe_2O_3/Al mixture with a 5 to 5 ratio exhibited the best performance in this test series. At present, the reason for this unexpected result is not clear.

Figure 7 shows plots of pressure profile for six samples in which varying amounts of POM were added to Fe_2O_3/Al (5/5), along with data for black powder. The maximum pressure obtained from the thermite composition containing only Fe_2O_3/Al (5/5) was about 950 kPa, while elevated pressures of 1100, 2100, 1300 and 1300 kPa were obtained from the combustion of mixtures containing 10, 20, 30 and 40 POM ratios. Previous studies found that maximum pressure values of 1200 kPa were generated from both CuO/Al and CaO_2/Al mixtures while a pressure of 1400 kPa was obtained from black powder[8]. It should be noted that the pressure curves of the Fe_2O_3/Al mixtures containing both 30 and 40 POM ratios are similar to that of black powder, while the Fe_2O_3/Al/POM (5/5/20) mixture generated a higher pressure than either of the CuO/Al or CaO_2/Al mixtures and black powder. The pyrolysis mechanism of POM is known to involve the generation of gaseous products by scission of the primary polymer chain, moving inward from both chain ends, as well as by standard depolymerization reactions.[5] Therefore, during the combustion of a Fe_2O_3/Al/POM mixture, the initial stages likely involve an exothermic reaction between Fe_2O_3 and Al which releases sufficient heat to initiate decomposition of the POM. This decomposition produces the large volume of gases compared to black powder, CuO/Al and CaO_2/Al systems which in turn generates high pressures.

5. Conclusions

Some conclusions can be drawn from the results of this study. The TG-DTA data for the Fe_2O_3/Al and Fe_2O_3/Al/

POM mixtures demonstrated thermal reactions of Fe_2O_3, Al and POM. The ignition energies of the Fe_2O_3/Al mixtures were found to fall within the range of 30 to 40 kJ mol^{-1}, while the Fe_2O_3/Al/POM mixtures all had ignition energies of approximately 20 kJ mol^{-1}. The addition of POM to the Fe_2O_3/Al mixtures was observed to lower the minimum ignition temperature by about 100 K, although the ignition energy and minimum ignition temperature were not affected by difference in the ratios of the Fe_2O_3/Al mixtures. Pressure tests carried out on Fe_2O_3/Al/POM mixtures with varying ratios showed that the highest pressure (2100 kPa) was obtained with the Fe_2O_3/Al/POM (5/5/20) mixture. The Fe_2O_3/Al/POM thermite formulation was further found to generate a higher pressure than had previously been obtained when testing CuO/Al/POM, CaO_2/Al/POM and black powder compositions, and thus may be a viable candidate for use as a propellant in fireworks. Since the only solid residue products obtained were Fe and Al_2O_3, the reaction in this formulation may be described by the equation $Fe_2O_3+2Al \rightarrow Al_2O_3+2Fe$.

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Fe_2O_3／Al／ポリオキシメチレン混合系における テルミット組成のキャラクタリゼーション

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本研究は，テルミット反応を利用した酸化鉄／アルミニウム／ポリオキシメチレン混合系の煙火用発射薬についての研究をおこなった。

発火エネルギーは酸化鉄／アルミニウム系で約30~40 kJ mol^{-1}が得られ，これにポリオキシメチレンを添加させた酸化鉄／アルミニウム系では約20 kJ mol^{-1}が得られた。最低発火温度は酸化鉄／アルミニウム系ではいずれの重量混合比（4/6, 5/5, 6/4, 7/3）でも約500～600 Kであり，これにポリオキシメチレンを20％添加すると最低発火温度は約400～500 Kとなり，約100 K低温側へ移行することがわかった。

圧力試験による最大圧力は酸化鉄／アルミニウム／ポリオキシメチレン（5/5/20wt%）において，2100 kPaが得られた。これは酸化銅／アルミニウム／ポリオキシメチレン，過酸化カルシウム／アルミニウム／ポリオキシメチレンおよび黒色火薬に比べて高い圧力であることがわかった。

燃焼生成物は鉄と酸化アルミニウムが同定され，反応式は$Fe_2O_3+2Al \rightarrow Al_2O_3+2Fe$であり，テルミット反応が起こっていることがわかった。

酸化鉄／アルミニウム／ポリオキシメチレン混合物は煙火用発射薬として利用できることが示唆された。

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