Research paper

Characterization of Fe_2O_3/metal or alloy (Al, Mg, Ti or MgAl) / polyoxymethylene thermite compositions

Youichi Sano*† and Toshiyuki Nagaishi**

*Advanced Instruments Center, Kyushu Sangyo University, 2-3-1 Matsukadai Higashi-ku, Fukuoka-shi, Fukuoka 813-8503, JAPAN
Phone : +81-92-673-5662
†Corresponding author : youichi@ip.kyusan-u.ac.jp

**Professor Emeritus of Kyushu Sangyo University

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Abstract

This work investigated a new thermite formulation consisting of Fe_2O_3, metal or alloy (Al, Mg, Ti or MgAl) and polyoxymethylene (POM), with potential applications as a propellant in fireworks. Thermal analysis (TG/DSC) data indicated that all mixtures underwent a mass loss on heating, although only the Fe_2O_3/Mg and Fe_2O_3/MgAl systems generated exothermic peaks due to an oxidation-reduction reaction. Ignition activation energies of vigorously and lightly mixed Fe_2O_3 were determined as 32.6 and 47.8 kJ mol^{-1}, respectively. Also, ignition activation energies of Fe_2O_3/Mg, Fe_2O_3/Ti and Fe_2O_3/MgAl were determined as 48.8, 52.5 and 29.4 kJ mol^{-1}, respectively. These combinations of Fe_2O_3 with various metals were found to undergo intense combustion in air when ignited, thus confirming that the thermite reaction has occurred. The maximum pressures of vigorously and lightly mixed Fe_2O_3/Al/POM, Fe_2O_3/Mg/POM, Fe_2O_3/Ti/POM and Fe_2O_3/MgAl/POM were obtained as approximately 2100, 1200, 1100 and 250 kPa, respectively. A vigorously mixed Fe_2O_3/Al/POM (5/5/20) composition generated a particularly high gas pressure, greater than those of the other mixtures and comparable to the pressures generated by black powder, CuO/Al/POM and CaO_2/Al/POM systems.

Keywords : composition, thermite, fireworks, pressure, energy

1. Introduction

Thermite pyrotechnic compositions, typified by the reactive mixture of Fe_2O_3 with Al, have been in use since 1898, when they were applied to the welding of railroad tracks.[1] Since that time, various studies have reported on the radical propagation mechanism of thermite as well as the effects of composition and stoichiometry, and this pyrotechnic has been applied to the cutting and perforation of materials and the ***in situ*** production of alumina liners for pipes and used as a portable heat source, a high temperature igniter and an additive to propellants and explosives.[2),3)] Thermite has also been used as an ignition charge in various energetic devices, including airbags, electric detonators, rockets, pyrotechnics and ammunition.[3] In addition, thermite mixtures have been studied as heat sources for the vaporization of solid materials such as lithium in sounding rocket systems.[4]

In a previous paper[5], we reported a thermite composition augmented by the rapid decomposition of polyoxymetylene (POM), with applications in rock breaking and fireworks, and we have also reported the thermite-type reaction of Bi_2O_3 with various metal powders (Al, MgAl, Si and FeSi).[5),6),7)] During these studies, a 5/5/20 Fe_2O_3/Al/POM mixture was found to generate the highest pressure compared to other mixtures.[8]

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 various metal or alloy (Al, Mg, Ti or MgAl). In this paper, we report the thermite properties and pressure test results of a Fe_2O_3/metal or alloy (Al, Mg, Ti, or MgAl) thermite system, both with and without the addition of POM.

2. Materials

Ferric oxide (III) (Fe_2O_3) was kindly supplied by the

Titan Kogyo Co., Ltd. The metals or alloy used were aluminum (Al, Yamato Metal Co., Ltd., 95% pure w/w, average particle size of 50 μm), titanium (Ti, High Purity Chemicals Co., Ltd., 99.9%, 45 μm), magnesium (Mg, Kanto Metal Co., Ltd., 99.9%, 150 μm) and magnalium (MgAl, Minoru Chemical Co., Ltd., 5 : 5, 99.0%, 295 μm). Mixtures of Fe_2O_3 with Al were obtained by two different methods : employing either light mixing or vigorous mixing in an agate mortar. Light mixing refers to mixing Fe_2O_3 and metal or alloy using spoon, while vigorous mixing refers to mixing Fe_2O_3 and metal or alloy using ball mill. All other metals or alloy (Ti, Mg or MgAl) were combined with Fe_2O_3 using vigorous mixing. In each case, a metal or alloy and Fe_2O_3 were combined in a 1 : 1 mass ratio, except where noted. POM was the same as that reported in the literture.[8)]

3. Experimental

3.1 Scanning electron microscopy

The surfaces of Al, Mg, Ti and MgAl samples were observed via scanning electron microscopy (SEM) and they were also analyzed using an elemental analysis system (EDS, Hitachi High-Technologies Miniscope® TM 3000) for lightly mixed or vigorously mixed Fe_2O_3/Al mixture.

3.2 Thermal analysis

Simultaneous differential scanning calorimetry (DSC) and thermogravimetry (TG) was performed for each metal sample and each thermite sample (Fe_2O_3/Al, Fe_2O_3/Ti, Fe_2O_3/Mg and Fe_2O_3/MgAl), using a STA449F3 Jupiter instrument (NETZSCH Japan Co., Ltd.). Measurements were conducted over the temperature range of 20 to 1200 K or 20 to 900 K at a rate of 10 K min^{-1} under He gas, using an alumina cell. All measurements were performed in He atmosphere.

3.3 Ignition temperature measurements

Ignition temperature specimens were obtained by forming samples of each thermite composition (Fe_2O_3/Al, Fe_2O_3/Ti, Fe_2O_3/Mg and Fe_2O_3/MgAl) of approximately 30 mg total mass into pellets, again employing a 1 : 1 mass ratio. These molded pellets were placed in a heated electric furnace and the time required for ignition was recorded at various temperatures.

3.3 Pressure tests

Pressure tests was carried out using a pressure vessel (Matsuki Science Ltd.) in which a sample of 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 and evolved gas pressures were digitally recorded using the Extra Taff software package.

4. Results and discussion

4.1 Surface observations with SEM

Figure 1 depicts SEM images showing the shapes and sizes of the ingredients, *i. e.* Al, Mg, Ti, MgAl and Fe_2O_3. From these images, it is evident that the Al powder was in the form of flakes and that the average particle size of the spherical Mg powder was larger than that of the other metals. The MgAl and Ti powders are seen to have sharp, angular morphologies, while the Fe_2O_3 powder is hardened and agglomerated into needle-like crystals.

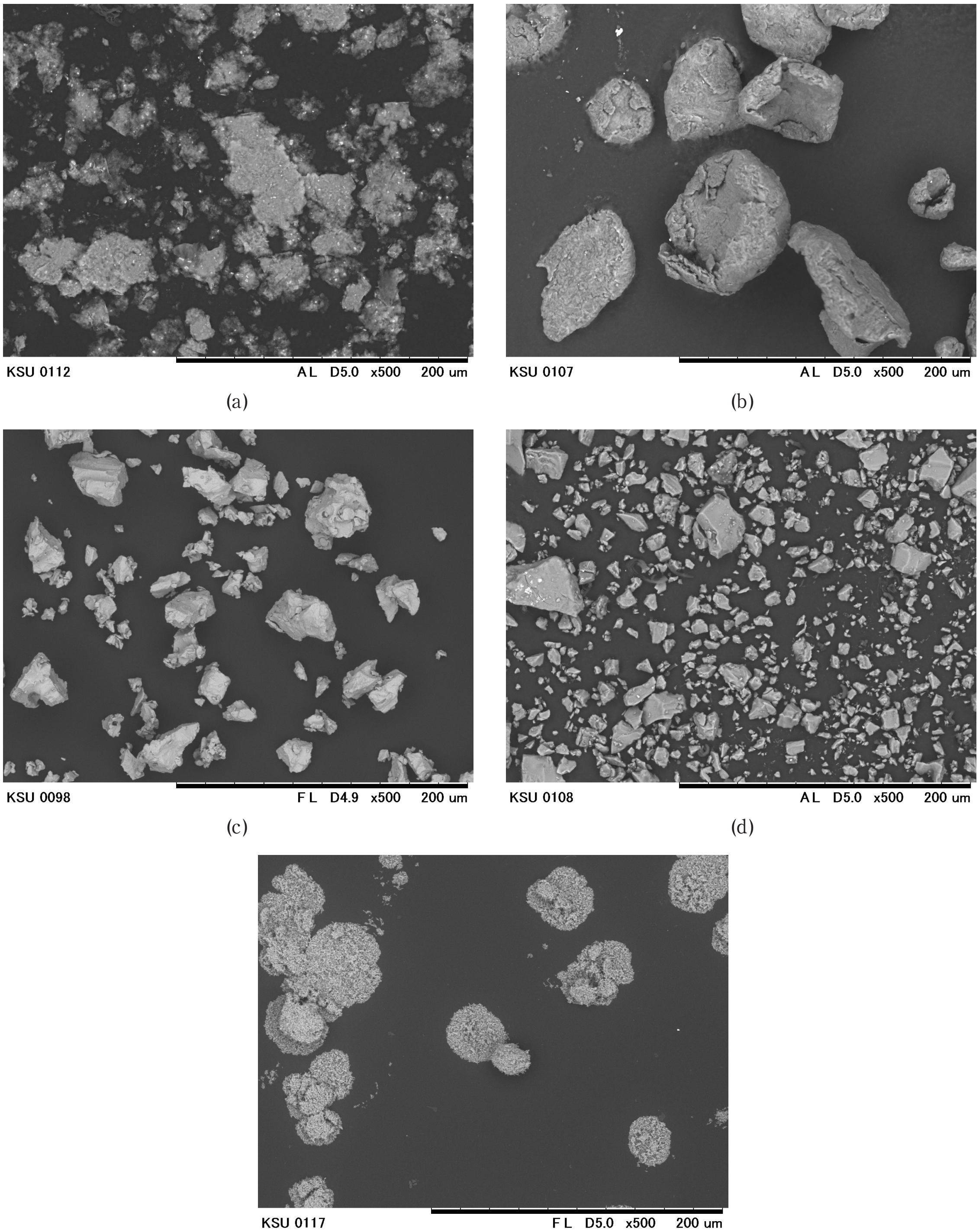
Figure 2 shows EDS and SEM images of the surfaces of Fe_2O_3/Al mixtures prepared by both light and vigorous mixing. Both samples present similar morphologies in the SEM images, although the EDS data show that the lightly mixed sample exhibits unmixed Al regions, while the vigorously mixed sample is more homogeneous.

4.2 TG-DSC

Figure 3 shows the TG-DSC curves obtained from samples composed of Al, Ti, Mg and MgAl or Fe_2O_3/metal mixtures under He at atmospheric pressure.

The Al data in Figure 3a exhibits an endothermic peak due to melting at approximately 656 K and shows a mass loss at about 20.2% between the initial temperature and the maximum temperature of 1200 K. The Mg plot in Figure 3b has an endothermic peak due to melting at 652 K, and an endothermic peak at 711 K is attributed to the evaporation of some of the Mg. Mg combusting are easily evaporated even below the melting point in air.[9)] From this, it is suggested that Mg was evaporated after melting. The weight loss evident from the TG plot up to the maximum temperature of 900 K is about 53.7%. Figure 3c shows the TG-DSC plot of Ti, which has neither exothermic nor endothermic peaks and indicates a mass loss up to the maximum temperature of 1200 K of approximately 3.8%. The MgAl plot in Figure 3d exhibits an endothermic peak at the eutectic point in the vicinity of 435 K then shows a gradually developing endothermic peak around 690 K. The weight loss shown from the TG plot up to the maximum temperature of 900 K is about 53.6%.

Figure 3e depicts the TG-DSC curve for Fe_2O_3/Al. Here, an endothermic peak is observed at 653.9 K due to the melting of Al and the total mass loss is 6.1%. There was evidently no reaction between Al and Fe_2O_3 since no other exothermic peaks were observed. The same general results are seen when using Ti, as shown in Figure 3 g. Figures 3f and 3h show the TG-DSC curves of Fe_2O_3/Mg and Fe_2O_3/MgAl mixtures, which contain sharp exothermic peaks at 637.6 K and 590.6 K, respectively. This phenomenon was not observed in the mixtures containing Al and Ti. It is thus suggested that Fe_2O_3/Mg and Fe_2O_3/MgAl samples has undergone oxidation-reduction reactions even during this relatively slow heating process. Here, each vapor pressure of the metals is : Al 160, Mg 293, Ti 1123.9 Pa at melting points. This was attributed to the high vapor pressure of Mg compared to Al and Ti, as well as the evaporation of a portion of the Mg in the MgAl alloy. These samples showed mass losses of 23.6% and 23.0%, respectively.



(e)

Figure 1 SEM images of (a) Al, (b) Mg, (c) Ti, (d) MgAl and (e) Fe_2O_3 used in this study.

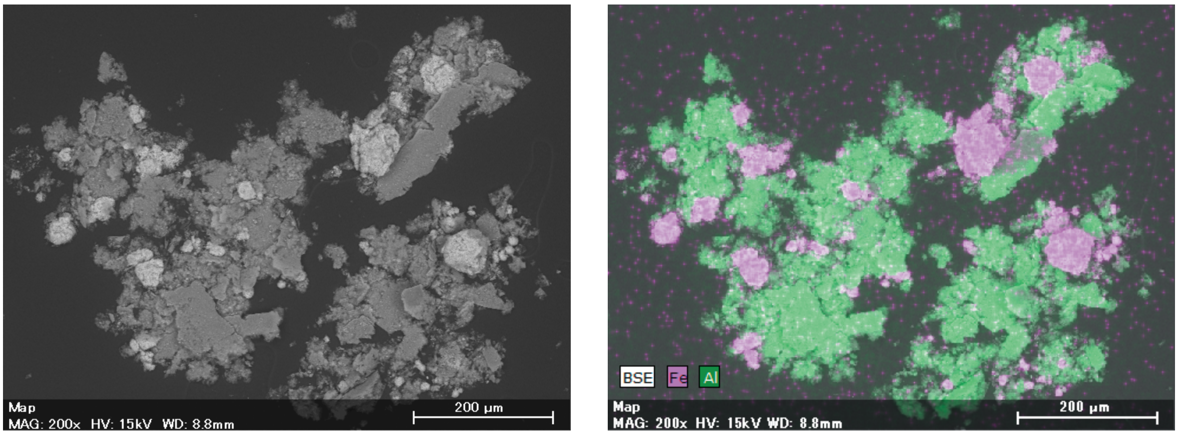
4.3 Ignition point measurements of Fe_2O_3/metal or alloy mixtures

The activation energy and minimum ignition results for the Fe_2O_3/Al (vigorously and lightly mixed), Fe_2O_3/Mg, Fe_2O_3/Ti and Fe_2O_3/Ti mixtures are summarized in Table 1. These ignition energies were obtained from the slopes of the relation between $\ln t$ and $1/T$ (K^{-1}). It is evident from these data that the vigorously mixed material had a minimum ignition temperature that was approximately 170 K lower than that of the lightly mixed sample, which is likely due to the improved contact between the two phases, leading to improved thermal conductivity.

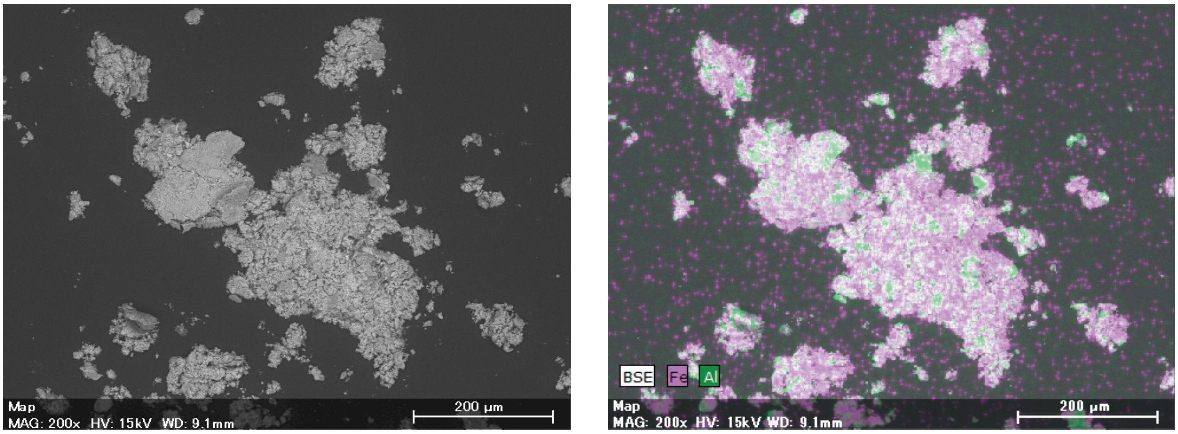
4.4 Pressure testing of Fe_2O_3/metal/POM mixtures

Figure 4 shows the pressure curves obtained for Fe_2O_3/Al/POM (lightly or vigorously mixed). Under these conditions, the maximum pressures generated by the Fe_2O_3/Al (lightly mixed) and Fe_2O_3/Al (vigorously mixed) were about 1200 kPa and 2100 kPa, respectively. It is also evident that the initial reaction rate was different between the two samples. Based on the SEM/EDS images in Figure 2, it was suggested that these different behaviors were caused by improved contact between Fe_2O_3 and Al particles in the vigorously mixed sample.

Figure 5 summarizes the changes in the maximum pressures obtained from Fe_2O_3/Al mixtures made with



(a)



(b)

Figure 2 SEM and EDS images of Fe_2O_3/Al mixture used in this study, following (a) light and (b) vigorous mixing.

varying ratios and when adding POM. Fe_2O_3/Al samples generated pressures ranging from 800 to 1200 kPa, while these pressures were significantly increased by the addition of POM, which is likely due to the additional gases generated by the decomposition 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. It was considered to be due to the increase in the combustion speed with an increases in the content of metals or alloy.[10)]

The results of pressure tests of various Fe_2O_3/Al/POM, Fe_2O_3/Mg/POM, Fe_2O_3/Ti/POM (5/5/20) and Fe_2O_3/MgAl/POM (4/6/20) mixtures are shown in Figure 6. The maximum pressures obtained were approximately 2100, 1200, 1100 and 250 kPa when testing the Fe_2O_3/Al/POM, Fe_2O_3/Mg/POM, Fe_2O_3/Ti/POM and Fe_2O_3/MgAl/POM mixtures, respectively. As a benchmark, it is helpful to consider that the pressure generated by black powder using the same test method is about 1400 kPa.[8)] In the previous report, the pressure was reduced by increasing the amount of POM in Fe_2O_3/Al mixed system.[8)] It was considered that POM acted as an inert diluent.[10)]

For comparison purposes, the pressures obtained with and without the addition of POM are given in Figure 7. The maximum pressures are seen to increase on the addition of POM in all compositions with the exception of Fe_2O_3/MgAl, which actually exhibited a significant decrease in pressure due to the addition of POM. Analysis of the combustion residue from the Fe_2O_3/MgAl pressure test confirmed the presence of residual uncombusted Fe_2O_3/MgAl. From the results of the pressure test on adding varying amounts of POM to Fe_2O_3/MgAl, it was observed that the uncombusted portion increased and the pressure was decreased as greater amounts of POM were added. The pressure difference due to differences in the amount of Fe_2O_3 and metals or alloy addition is considered to be because the oxygen balance or particle size are different, but this matter should be discussed in more detail.

5. Conclusions

A number of conclusions can be drawn from the results of this study. The SEM observations and EDS data for the vigorously and lightly mixed Fe_2O_3/Al show that the Fe_2O_3 particles are in close contact with Al particle in the vigorously mixed material. From the TG-DSC results of Fe_2O_3/metal mixtures (Al, Mg, Ti and MgAl), both of Fe_2O_3/Mg and Fe_2O_3/MgAl combinations generated sharp exothermic peaks, which is likely due to the higher vapor pressure of Mg and evaporation of Mg in MgAl alloy. The ignition energies of the vigorously and lightly mixed Fe_2O_3/Al were found to be 32.6 and 47.8 kJ mol^{-1}, respectively while the minimum ignition temperatures of the same materials were 560 and 760 K, respectively. The maximum pressures obtained were approximately 2100, 1200, 1100

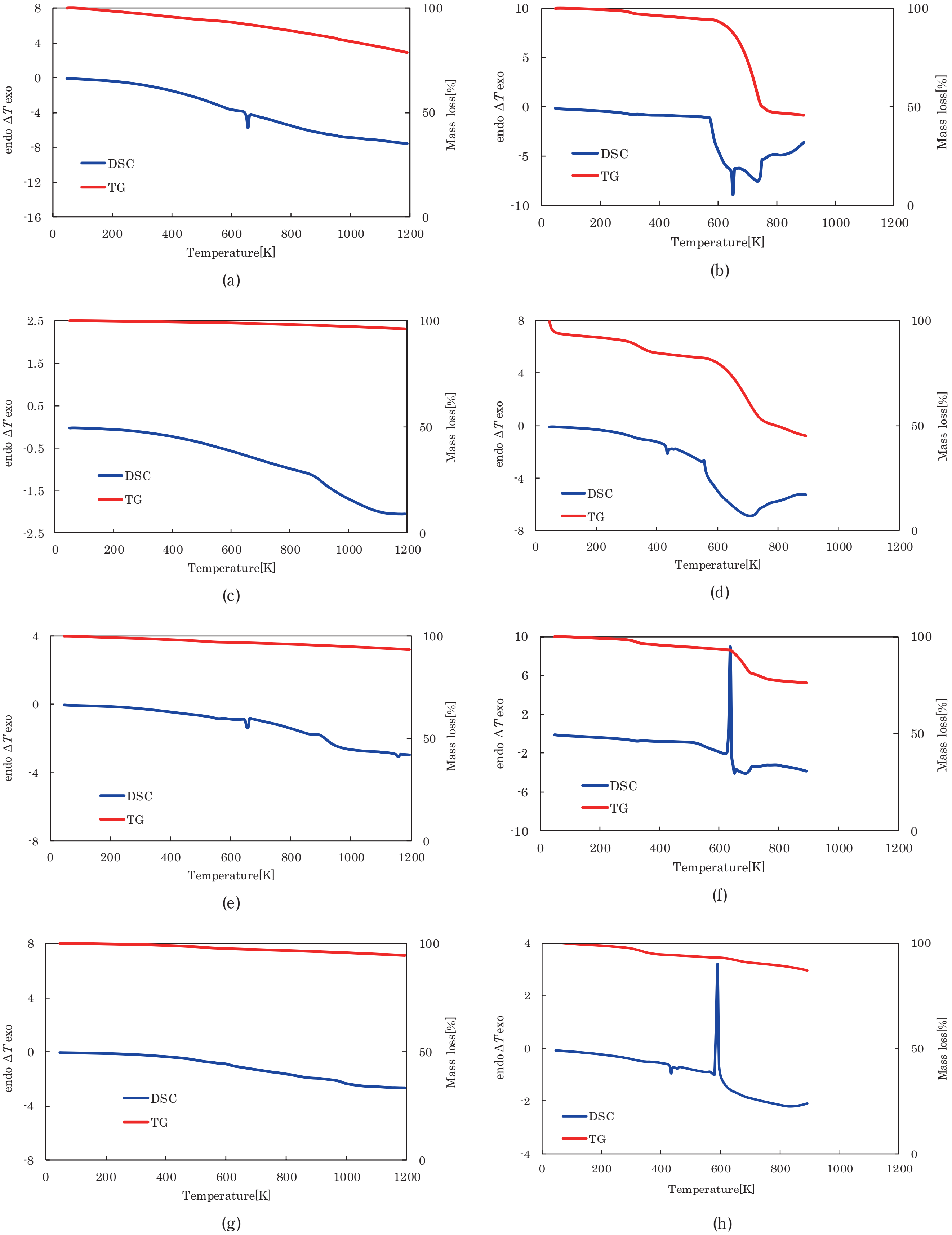


Figure 3 TG-DSC curves obtained for (a) Al, (b) Mg, (c) Ti, (d) MgAl and 1 : 1 (e) Fe_2O_3/Al, (f) Fe_2O_3/Mg, (g) Fe_2O_3/Ti and (h) Fe_2O_3/MgAl mixtures.

and 250 kPa, respectively when testing Fe_2O_3/Al/POM, Fe_2O_3/Mg/POM, Fe_2O_3/Ti/POM and Fe_2O_3/MgAl/POM mixtures. Pressure tests carried out on Fe_2O_3/metal/POM mixtures containing Mg, Ti and MgAl have shown that the highest maximum pressure (2100 kPa) was obtained with the Fe_2O_3/Al/POM (5/5/20) mixture.

Table 1 Ignition energy and minimum ignition temperature data.

Samples	Ignition energy [kJ mol^{-1}]	Minimum ignition temperature [K]
Fe_2O_3/Al[V]	32.6	560
Fe_2O_3/Mg	48.8	540
Fe_2O_3/Ti	52.5	690
Fe_2O_3/MgAl	29.4	410
Fe_2O_3/Al(L)	47.8	730

Legend : V = vigorously mixed, L = lightly mixed.

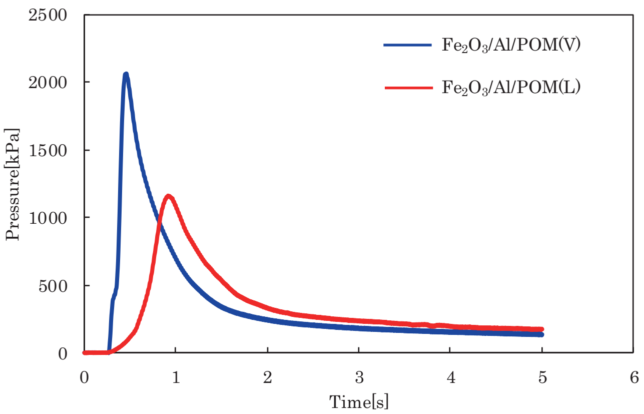


Figure 4 Combustion test results for Fe_2O_3/Al/POM mixtures formulated with vigorous (V) and light (L) mixing.

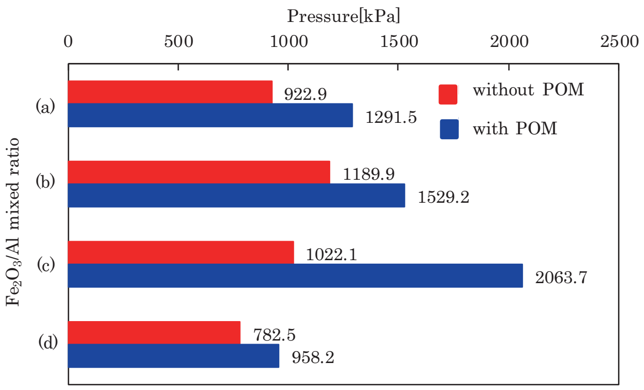


Figure 5 Comparison of the maximum pressures obtained from Fe_2O_3/Al and Fe_2O_3/Al/POM mixtures, following (a) 7/3, (b) 6/4, (c) 5/5 and (d) 4/6.

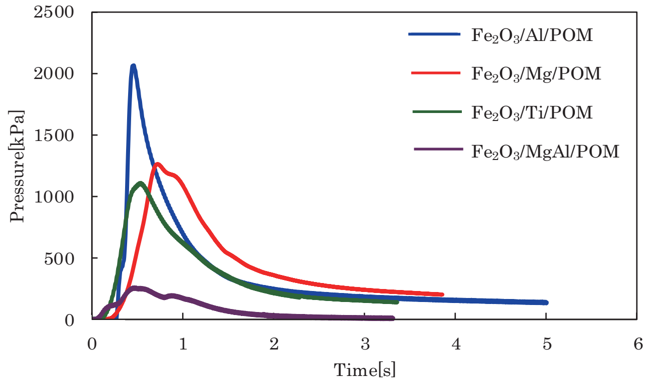


Figure 6 Combustion test results for Fe_2O_3/metal/POM mixtures.

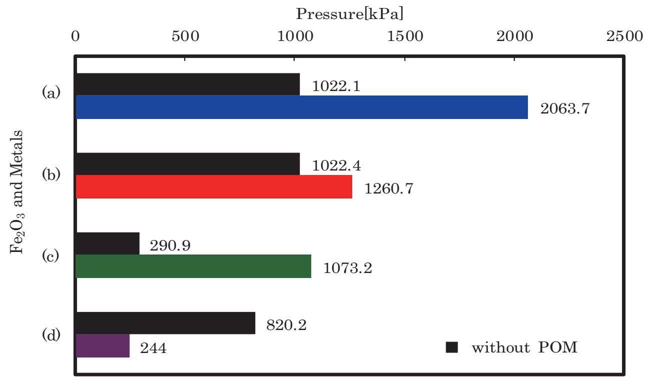


Figure 7 Comparison of the maximum pressure obtained from Fe_2O_3/metal and Fe_2O_3/metal/POM (5/5/20) mixtures, following (a) Fe_2O_3/Al, (b) Fe_2O_3/Mg, (c) Fe_2O_3/Ti and (d) Fe_2O_3/MgAl.

Acknowledgement

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