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Combustion and Sensitivity Characteristics of Mg/TF Pyrolants

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Abbrand- und Empfindlichkeitscharakteristiken von Mg/TF-haltigen pyrotechnischen Sätzen

Das Verhalten der Abbrandgeschwindigkeit und der Empfindlichkeit von energetischen Gemischen bestehend aus Metallpartikeln und Oxidationsmitteln (sogn. Pyrolants) wurde experimentell untersucht. Die Sätze wurden hergestellt aus Magnesium und Polytetrafluorethylen (TF) mit unterschiedlichen Partikelgrößen. Mg/TF-Sätze erzeugen hohe Flammentemperaturen, so daß sie verwendet werden können als Wärmequellen und als Zündsätze. Die maximale Flammentemperatur (Tf) beträgt 3271 K bei 0.1 MPa und 3483 K bei 1 MPa. Diese Werte werden erhalten, wenn die Mg-Konzentration 30% beträgt. Wenn die Mg-Konzentration geringer als 50% ist, dann können die Sätze bei einem Druck von 1 Atmosphäre nicht stabil abbrennen. Die Abbrandgeschwindigkeit bei konstantem Druck nimmt mit steigender Konzentration an Mg zu und nimmt mit zunehmendem mittlerem Durchmesser der Mg-Partikel ab. Die Energie des Explosivstoffs, berechnet aus dem Fallhammer-Test, nimmt mit zunehmender Abbrandgeschwindigkeit ab, somit besteht eine strenge Beziehung zwischen Abbrandgeschwindigkeit und Energie.

Caractéristiques de combustion et de sensibilité de compositions pyrotechniques à base de Mg/TF

Le comportement de la vitesse de combustion et de la sensibilité de mélanges énergétiques composés de particules métalliques et d'agents oxydants (appelés "pyrolants") a été étudié expérimentalement. Les compositions ont été synthétisées à partir de magnésium et de polytétrafluoréthylène (TF) possédant différentes tailles de particules. Les compositions Mg/TF engendrent des températures de flammes élevées et peuvent donc être utilisées en tant que sources de chaleur et compositions d'amorçage. La température de flamme maximale (Tf) est de 3271 K à 0.1 MPa et de 3483 K à 1 MPa. Ces valeurs sont obtenues lorsque la concentration de Mg est de 30%. Lorsque la concentration de Mg est inférieure à 50%, les compositions ne peuvent pas avoir une combustion stable à une pression de 1 atmosphère. La vitesse de combustion à pression constante augmente avec la concentration de Mg et diminue lorsque le diamètre moyen des particules de Mg augment. L'énergie de l'explosif, calculée à partir du test du marteau-pilon (Fallhammer) diminue lorsque la vitesse de combustion augmente et il existe donc une étroite relation entre la vitesse de combustion et l'énergie.

Summary

Burning rate characteristics and sensitivity characteristics of energetic mixtures composed of metal particles and oxidizers, the so called 'pyrolants', were studied experimentally. The pyrolants tested were made of various particle sizes of magnesium (Mg) and polytetrafluoroethylene (TF). Mg/TF pyrolant produces high combustion flame temperature, so it is used as heat sources and igniter pyrolants. The maximum flame temperature (Tf) is 3271 K at 0.1 MPa, and 3483 K at 1 MPa. These values are obtained when Mg concentration is 30%. When the Mg concentrations are less than 50% the pyrolants are not able to burn stably at one atmosphere. The burning rate increases with increasing the concentration of Mg and decreases with increasing the mean diameter of Mg particles at constant pressure. Explosive energy evaluated with drop hammer test decreased with increasing burning rate, so there is strong relationship between burning rate and explosive energy.

1. Introduction

Mg/TF pyrolants are high energy materials which produce high combustion temperatures and generate high temperature solid particles. The high temperature solid particles are easy to ignite propellants and are used to produce luminous flame. Accordingly, Mg/TF pyrolants have been used as igniters for solid rocket motors and pyrotechnics. The burning rate and sensitivity characteristics of Mg/TF pyrolants have been studied by a number of researchers[1–6]. However, their relationship has not been established[7]. In this study, the relationship between combustion and sensitivity characteristics was investigated using Mg/TF pyrolants.

2. Theoretical Combustion Characteristics of Pyrolants

The relationship between the theoretical adiabatic flame temperature and the concentration of Mg, ξMg is shown in Fig. 1. The concentration of Viton is 12% constant, and ξMg plus ξTF are 88% and calculation condition pressures are 0.1 MPa and 1 MPa. ξMg is changed from 0 to 88%. The maximum adiabatic flame temperatures (Tf) are 3271 K at 0.1 MPa, and 3483 K at 1 MPa and these values are obtained when Mg concentration is 30%. Tf decreases with increasing the concentration of Mg when ξMg is larger than 30%, and when pressure is 1 MPa it reaches 1729 K at ξMg = 70%. When ξMg is larger than 70%, Tf is constant. The Tf at 1 MP is larger than that at 0.1 MPa.

In order to identify the role of metals with TF on the thermochemical properties several types of metals have been evaluated. Theoretical adiabatic flame temperatures are shown in Fig. 2 when the metals, titanium (Ti), aluminum (Al), and boron (B) are used at pressure of 1 MPa. When the concentration of Ti is larger than 50%, or that of B is larger than 70%, or those of Al and Mg are larger than 80%, theoretical adiabatic flame temperatures could not be obtained, for solid produced compositions are too much to calculate. The maximum flame temperature of B contained pyrolant is 3301 K at the concentration of B = 10%. Flame temperature of Al contained pyrolant is a little larger than that of B contained pyrolant, and the maximum value reaches 3764 K at the concentration of Al = 30%. The maximum flame temperature of Ti contained pyrolant is

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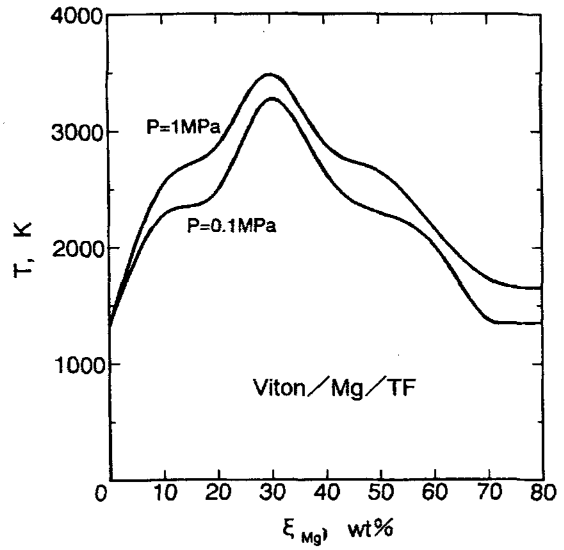

Figure 1. Theoretical flame temperature as a function of the concentration of Mg.

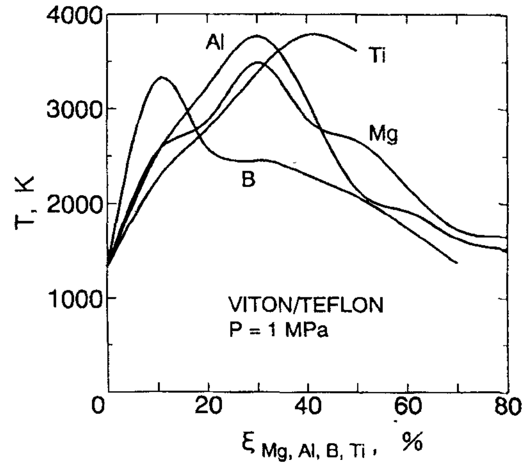

Figure 2. Theoretical flame temperature as a function of the concentration of metals.

3781 K at the concentration of Ti = 40% and this value is the highest in the 4 kinds of pyrolants.

3. Experimental Apparatus

The thermal decomposition process of TF/metal pyrolants was measured by differential scanning calorimetry (DSC) and thermal gravimetry (TG). Heating rate was 0.17 K/s at 0.1 MPa in helium (He) gas. Burning rates of the pyrolants were measured with a chimney-type strand burner, and nitrogen gas was used to pressurize the burner. Pyrolants were pressed to pellets at 1500 kgf (~15 kN) and shaped into 10 mm in diameter and 10 mm in length for combustion characteristics measurements. Fallhammer sensitivity test is based on JIS K 4810, Japanese Industrial Standard (JIS). The fallhammer weights were 5 kgf. The results were represented by 'class' which was defined by the same standard. The smaller number of the class means higher sensitivity.

4. Results and Discussion

4.1 Decomposition Characteristics

DSC/TG result of TF is shown in Fig 3. The endothermic peak was as appeared at 615 K and the weight of TF was not changed, so TF was only melting over 615 K and not decomposed. DSC/TG result of Mg/TF pyrolant is shown in Fig. 4. The exothermic peak started at 673 K and this temperature is over the TF melting peak of 615 K, so Mg reacted in liquid TF.

The thermal decomposition process of TF/metal pyrolants was measured with DSC and TG. The temperature in the DSC and TG increased at 1073 K and after that it was cooled down at 300 K. Concentrations of TF/metals are 60/40% and not pressed to pellets. Relationships between decomposition characteristics and temperature are shown in Fig. 5. The endothermic peaks of TF appeared at 615 K and 861 K. TF was decomposed at 861 K and there was no residue in the DSC/TG equipment. The endothermic peak of

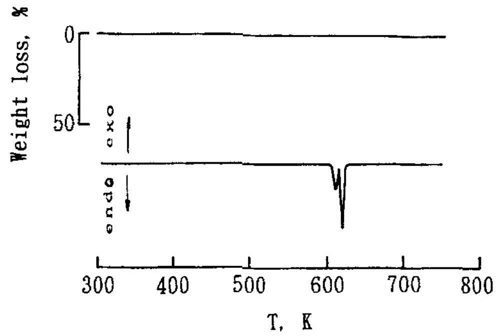

Figure 3. Decomposition characteristics of TF.

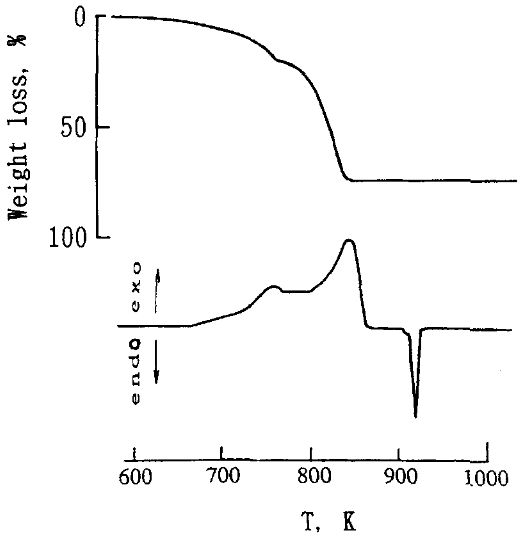

Figure 4. Decomposition characteristics of Mg/TF pyrolant.

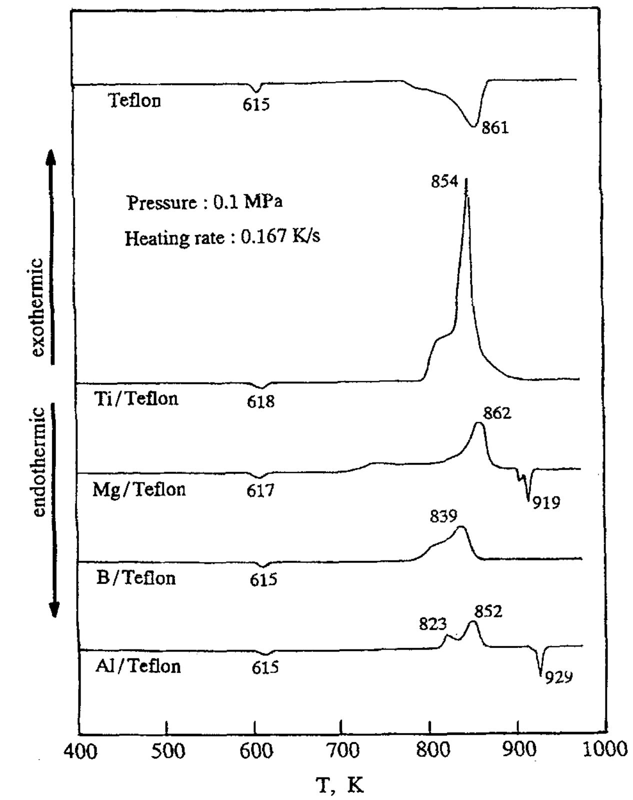

Figure 5. Decomposition characteristics of metal/TF pyrolant.

Ti/TF pyrolant appeared at 618 K and this is TF melting point. The maximum exothermic peak of Ti/TF pyrolant is 854 K and exothermic heat capacity is 112.3×10^3 J/kg. So, the flame temperature and the exothermic heat capacity of Ti/TF pyrolant is the maximum value in the 4 kinds of pryrolants. The maximum exothermic peak of Mg/TF pyrolant is 862 K and the exothermic heat capacity is 43.9×10^3 J/kg and also TF melting peak appeared at 617 K. The maximum endothermic peak is 919 K and this coincides with melting temperature of Mg, so Mg has not completely reacted with TF. There are two exothermic peaks of Al/TF pyrolant at 823 K and 852 K and the exothermic heat capacity is 21.9×10^3 J/kg which is the smallest in the 4 kinds of pyrolants. The maximum endothermic peak appeared at 929 K and this coincides with melting temperature of Al, so Al has not reacted completely with TF. When B is used for pyrolant there are the endothermic peak of TF melting point at 619 K and the exothermic peak at 839 K and the exothermic heat capacity is 30.2×10^3 J/kg.

4.2 Burning Rate Characteristics

(1) Burning rate

Figure 6 shows the relationship between burning rate and pressure at ϕMg = 49 μm, ξMg = 50%, 70%, 80%. The burning rate increases with increasing pressure, and the burning rate at ξMg = 70% is higher than the others. It is

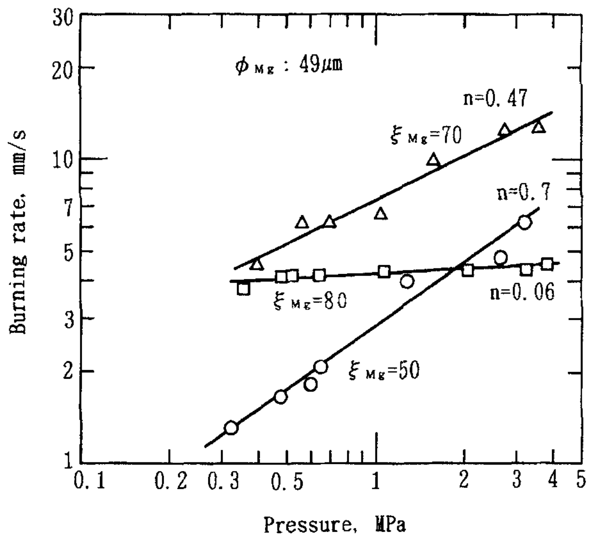

Figure 6. Burning rate characteristics (Mg; 49 μm).

evident that the burning rate of Mg (70%) contained sample attained 2.6 times as fast as the burning rate of Mg (50%) contained sample at 1 MPa. Pressure exponent of burning rate 'n' decreases with increasing the concentration of Mg, so 'n' of Mg (50%) contained sample is 0.7 and 'n' of Mg (80%) contained sample is 0.06. The relationship between burning rates and pressures are shown in the following equations,

$$r = 2.9P^{0.7} \quad (\xi Mg = 50\%)$$
$$r = 7.4P^{0.47} \quad (\xi Mg = 70\%)$$
$$r = 4.2P^{0.06} \quad (\xi Mg = 80\%) \qquad (1)$$

and burning rates of pyrolants are shown by the function of pressure like propellants.

Figure 7 shows the relationship between burning rate and pressure at ϕMg = 78 μm, ξMg = 70% and 80%. The burning rate of Mg (70%) contained sample was smaller than that of Mg (80%) contained sample when pressure was lower than 1.3 MPa, however higher when pressure was

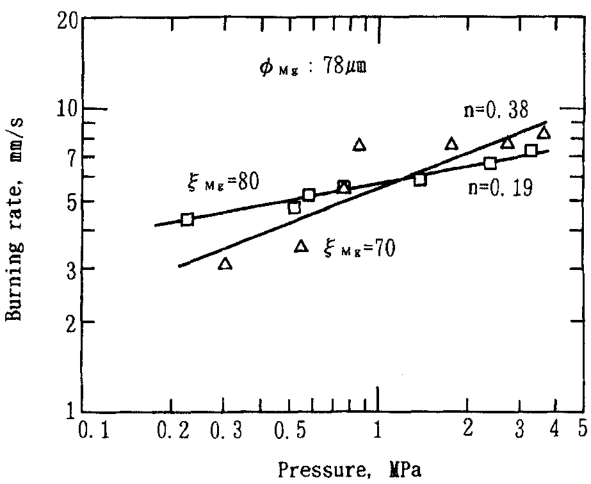

Figure 7. Burning rate characteristics (Mg; 78 μm).

higher than 1.3 MPa. Pressure exponent of burning rate 'n' is 0.38 of Mg (70%) contained sample and it decreased 0.19 of Mg (80%) contained sample. Burning rate of Mg (70%) contained sample is 5.5 mm/s and that of Mg (80%) contained sample is 5.7 mm/s at pressure = 1 MPa.

The theoretical adiabatic flame temperature is the maximum value at Mg (30%) concentration, however if concentration of Mg is less than 50% a stable combustion is impossible. The combustion residue was analyzed with a differential scanning calorimeter (DSC). The maximum endothermic peak at 923 K was observed, which was recognized to be the melting-point temperature of Mg. Thus, it was found that the Mg particles contacting with TF were oxidized and the surface layer of each Mg particle reacted effectively.

(2) Burning rate and adiabatic flame temperature

The relationship between the burning rate and the adiabatic flame temperature is shown in Fig. 8 at pressure = 1 MPa. The mean diameter of the Mg particles used was 49 μm and 78 μm. The burning rate increases with decreasing flame temperature. It should be noted that no relationship existed between the burning rate and the adiabatic flame temperature. In general, the burning rate increases with increasing the adiabatic flame temperature for energetic materials[8].

4.3 Fallhammer Sensitivity

(1) Fallhammer sensitivity test

Fallhammer sensitivity test is the test to examine the sensitivity of explosives referring to impact which is produced by falling hammer. Test results are classified into some classes by the relation between fallhammer height and explosion. The sensitivity of Mg (70%) contained sample was class 2 at ϕMg = 49 μm, and it was the most sensitive in this study. The sensitivities of other pyrolants were class 3; also, the diameter of TF was changed and it was seen that the sensitivity was not changed and so it was class 3. Residue of sensitivity test was analyzed with DSC, there was endothermic peak at 919 K of Mg melting temperature and it was found that Mg had only reacted with TF near the surface of Mg particles.

(2) Mg concentration and impact energy

Figure 9 shows the relationship between Mg concentration and fallhammer sensitivity which was converted to impact energy (E). Impact energy was obtained as a product of the fallhammer height and fallhammer weight, 5 kgf. The minimum energy of E was obtained with Mg (70%) contained sample at ϕMg = 49 μm. When ϕMg = 78 μm, impact energy was not changed with changing the concentration of Mg and it was a little larger than that at ϕMg = 49 μm.

(3) Adiabatic flame temperature and impact energy

The relationship between the adiabatic flame temperature (Tf) and the impact energy is shown in Fig. 10. The impact energy increases with increasing the adiabatic flame temperature (Tf), so the impact energy increases with increasing the energy of pyrolants. Generally, the impact energy E increases with decreasing the flame temperature. There was no relationship between the impact energy and the adiabatic flame temperature.

(4) Burning rate and sensitivity

The relationship between the burning rate (r) and the fallhammer sensitivity (E) is shown in Fig. 11. Fallhammer sensitivity tests were conducted under atmospheric condition, so that the burning rate at low pressure should be considered in order to compare these results. The burning rate at pressure = 1 MPa was used for comparison. The

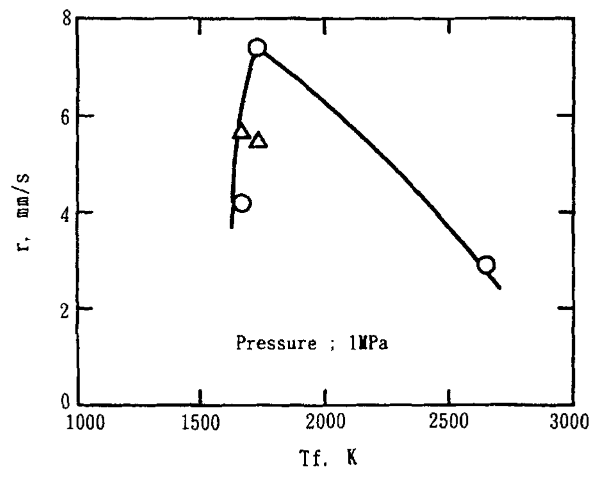

Figure 8. Relationship between the adiabatic flame temperature and the burning rate (O: diameter = 49 μm).

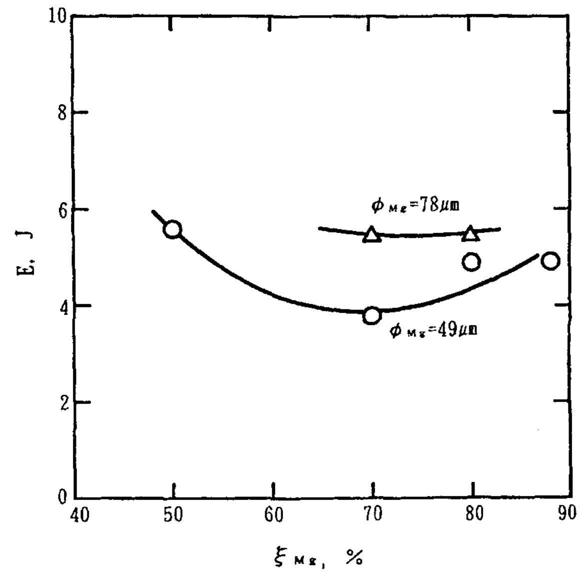

Figure 9. Relationship between the concentration of Mg and the explosive energy.

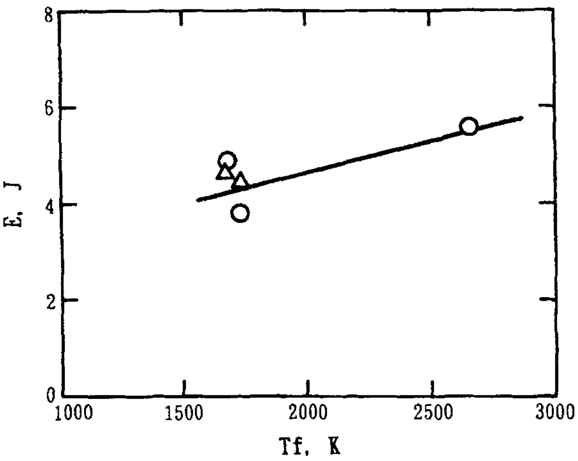

Figure 10. Relationship between the adiabatic flame temperature and the explosive energy.

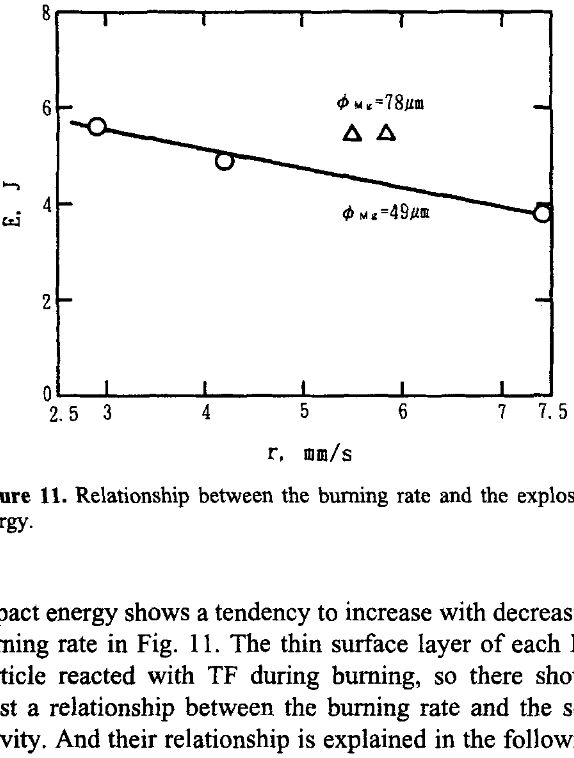

Figure 11. Relationship between the burning rate and the explosive energy.

impact energy shows a tendency to increase with decreasing burning rate in Fig. 11. The thin surface layer of each Mg particle reacted with TF during burning, so there should exist a relationship between the burning rate and the sensitivity. And their relationship is explained in the following equation,

$$E = -0.37r + 6.6 \qquad (2)$$

so sensitivity energy E of pyrolant decreases with increasing burning rate r.

5. Conclusions

The results can be summarized as follows:

(1) The maximum burning rate is obtained with Mg (70%) contained sample at $\phi Mg = 49$ μm, and the pressure exponent of the burning rate decreases with increasing concentration of Mg.
(2) The sensitivity of the Mg/TF pyrolants is classified as 'class 2 or 3' by fallhammer sensitivity tests.
(3) The thin surface layer of Mg particles reacts with melting TF during burning.
(4) The sensitivity increases as the burning rate increases for Mg/TF pyrolants.
(5) The sensitivity energy E is the function of the burning rate r, $E = -0.37r + 6.6$.

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