Combustion of Magnesium/Polytetrafluoroethylene

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The combustion of magnesium (Mg) with polytetrafluoroethylene (TF) is a complex oxidation reaction accomplished by physical changes from solid to liquid and to gas. The burning rate characteristics were determined with Mg/TF propellant pellets made of various-sized Mg particles and different mixture ratios of Mg/TF. The adiabatic flame temperature of Mg/TF propellants is the maximum when the weight fraction of Mg particles (ξ) is 0.33. However, the experimental results indicate that the burning rate increases with increasing ξ for the propellants tested ($\xi = 0.2 \sim 0.7$), which shows that the burning rate does not depend on the final flame temperature. Furthermore, the burning rate increases when large Mg particles (200 μm diam) are replaced with small Mg particles (22 μm diam) at $\xi = 0.6$. The burning rate is correlated with the total surface area of the Mg particles mixed within the propellants. The burning rate increases with increases in the surface area of the Mg particles within the range of ξ tested in this study. The heat produced just above the burning surface has a dominant effect on the burning rate. This heat is generated by the oxidation of the surface layer of the Mg particles with fluorine produced by the thermal decomposition of the TF at the burning surface of the propellants.

Introduction

THE understanding of the oxidation process of magnesium by fluorine is an important subject in the field of combustion chemistry. This is because the heat produced by the oxidation of magnesium with fluorine is 16.8 MJ/kg of Mg and is higher than that produced by the oxidation of magnesium with oxygen. The combustion of magnesium (Mg) with polytetrafluoroethylene (TF) is a typical example of rapid oxidation of magnesium with fluorine. TF is composed of a $-C_2F_4-$ molecular structure, which contains 0.75 weight fraction of fluorine. Since Mg and TF are both solid materials, the complex reaction process between Mg and TF is accompanied by phase changes from solid to liquid and to gas.

The determination of the burning rate characteristics of a mixture of Mg and TF is important for developing pyrotechnic materials used for igniters and flares. There have been very limited studies on the combustion of Mg and TF.[1] No systematic studies on the effects of the mixture ratio of Mg/TF and the particle size of Mg on the burning rate have been conducted. In this study, experiments were carried out to determine the physicochemical parameters that control the burning rate characteristics of Mg/TF propellants.

Thermochemical Properties of Mg/TF Propellants

Figures 1 and 2 show the calculated flame temperatures and combustion products as a function of Mg weight fraction ξ. The calculations were based on the JANAF Thermochemical Tables.[2] The flame temperature is the maximum at $\xi = 0.33$. The temperature decreases rapidly as ξ increases in the concentration region high above 0.33.

The major combustion products are C(s) and MgF_2(g) at the maximum flame temperature. The combustion products of C(s) and MgF_2(g) decrease and Mg(g) and MgF_2(L) increase with increasing ξ. With further increased ξ above 0.6, Mg(g) and MgF_2(L) decrease and Mg(L) increases.

Experimental Methods

Propellant Preparation

In order to determine the effects of the concentration and the particle size of Mg on the burning rate of Mg/TF propellants, various types of Mg/TF propellants were formulated. The propellant samples were prepared as pressed pellets. Mixtures of Mg and TF particles were kept in a cylindrical-shaped container made of steel and pressed with a hydraulically operated piston. The force on the piston ranged from 20 to 200 MPa in order to make the density of the pellets 1.80×10^3 kg/m^3. The size of each pellet was 7 mm in diameter and 30 mm in length. The chemical compositions and the particle sizes of Mg and TF used are shown in Table 1. A small amount of binder (Viton: $C_5H_{3.5}F_{6.5}$) was also mixed within the propellant samples in order to improve the mechanical properties of the samples.

Measurements of Burning Rate Characteristics and Combustion Wave Structures

The burning rate of the Mg/TF propellants were measured with a chimney-type strand burner pressurized with nitrogen. Three low-melting-point fuse wires (0.25 mm in diameter) were threaded through each propellant sample. Each sample was ignited by an electrically heated nichrome wire attached to the top of the sample.

The combustion wave structure of the Mg/TF propellants was studied with microthermocouples embedded within the samples. The microthermocouples were made of Pt-Pt10%Rh wires (50 or 5 μm diam). The temperature profiles in the combustion waves during propellant burning were measured with these microthermocouples.

Thermal Decomposition Measurements

The thermal decomposition process of the Mg/TF propellants was measured using thermal gravimetry (TG) and a differential thermal analysis (DTA). Both experiments were operated with a heating rate of 0.167 K/s in an argon atmosphere at 0.1 MPa. The weight of the sample used for each

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test was 10×10^{-6} kg and was kept in a container made of nonreactive quartz.

Results and Discussion

Burning Rate Characteristics

The measurement results of burning rate of Mg/TF propellants are shown in Figs. 3 and 4. The burning rate increases with increasing weight fraction of Mg (ξ) at a constant pressure. The burning rate also increases with increasing pressure at a constant ξ. The pressure exponent of burning rate defined by $n = (d\ln r / d\ln p)$ at a constant initial propellant temperature is also determined, where r is the burning rate and p is pressure. The pressure exponent is relatively constant for the propellants with high concentration of Mg throughout the pressure range tested. However, the pressure exponent increases rapidly with increasing pressure for the propellant with low concentration of Mg. The maximum pressure exponent is observed at 4 MPa for the propellant consisting of Mg/TF = 40 (22 μm diam)/60 (25 μm diam) in the pressure range tested in this study.

The effects of the particle size of Mg and TF on the burning rate are shown in Fig. 4. The results shown in Fig. 4 are obtained for the propellants consisting of Mg/TF = 60/40. It is evident that the burning rate increases with decreasing the particle size of Mg. Furthermore, the burning rate is dependent not only on the particle size of Mg but also on the particle size of TF. The burning rate is higher for the propellant containing larger-sized TF (450 μm diam) than for the propellant containing smaller-sized TF (25 μm diam).

Since Viton is composed of hydrocarbon and fluorine, it acts as a fuel component similar to TF when it is mixed within Mg/TF propellants. Measurement results indicated that no detectable effect on the burning rate characteristics was seen when 3% Viton was removed from the Mg/TF propellants tested in this study.

Figure 5 shows the relationship between the burning rate and the adiabatic flame temperature. The burning rate decreases with increasing the flame temperature for all the propellants tested and in the pressure range tested in this study. It is important to note that the burning rate decreases with increasing energy contained in the unit mass of Mg/TF propellants. In general, the burning rate of solid propellants, such as composite and double-base propellants, increases with increasing energy contained in the unit mass of propellant. This is a significant difference between the burning rate characteristics of Mg/TF propellant and conventional solid propellants.

Thermal Decomposition Characteristics

The measurement results with TG and DTA are shown in Fig. 6 for TF and in Fig. 7 for Mg/TF propellants

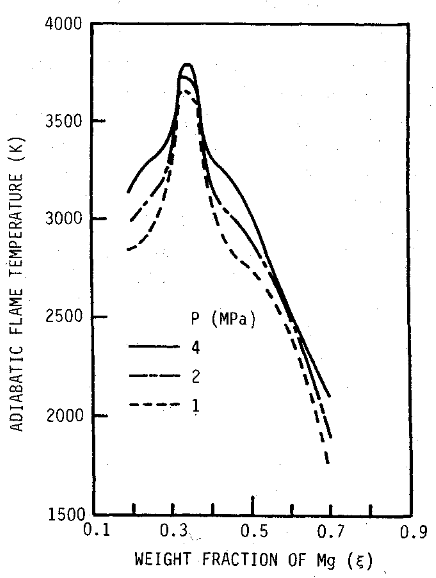

Fig. 1 Adiabatic flame temperature of Mg/TF propellants as a function of the weight fraction of Mg.

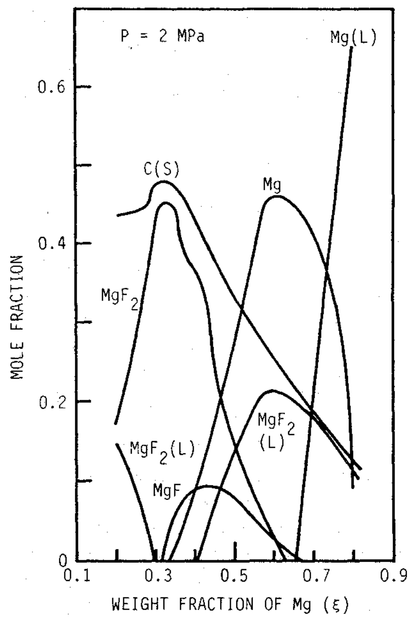

Fig. 2 Combustion products of Mg/TF propellants as a function of the weight fraction of Mg.

Table 1 Mg/TF propellant compositions tested in this study

	Mg		TF		
Propellant	22 μm	200 μm	25 μm	450 μm	Viton
A	20	—	80	—	3
B	30	—	70	—	3
C	40	—	60	—	3
D	60	—	40	—	3
E	60	—	—	40	3
F	—	60	40	—	3
G	—	60	—	40	3
H	70	—	30	—	3

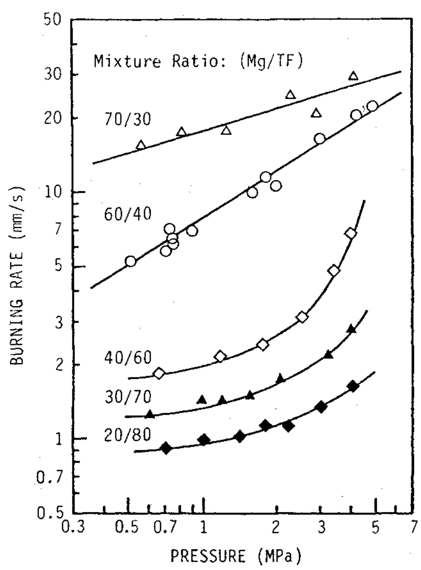

Fig. 3 Burning rate characteristics of Mg/TF propellants.

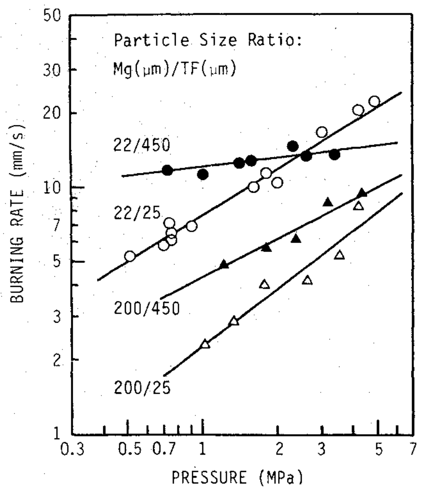

Fig. 4 Burning rate characteristics of Mg/TF (60/40) propellants.

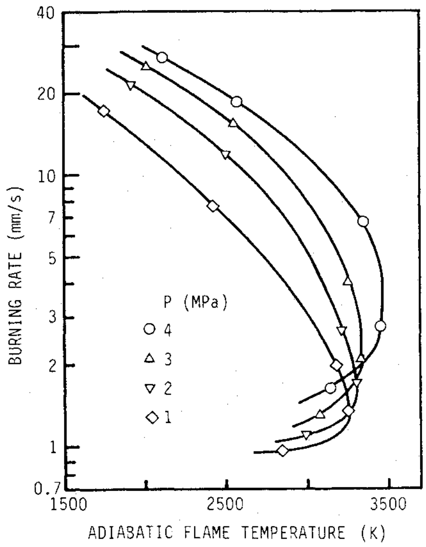

Fig. 5 Burning rate characteristics of Mg/TF propellants as a function of adiabatic flame temperature.

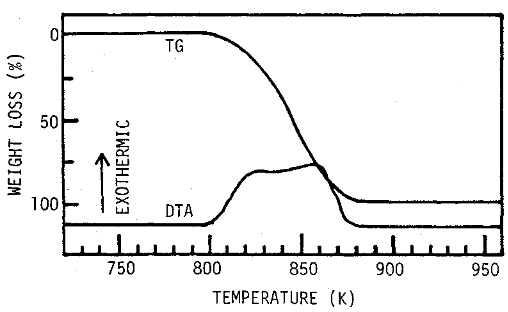

Fig. 6 TG and DTA data of TF.

(Mg/TF = 60/40). The decomposition of TF begins at 803 K and is completed at 893 K. During this decomposition, an exothermic gasification reaction occurs. It must be noted that no endothermic reaction is observed in this overall decomposition process. Furthermore, no undecomposed residue is seen above 893 K.

The decomposition of Mg/TF propellants begins at 763 K and is completed at 893 K. The gasification accompanied with an exothermic reaction between 763 and 803 K is determined to be caused by the decomposition of the binder (3% Viton)

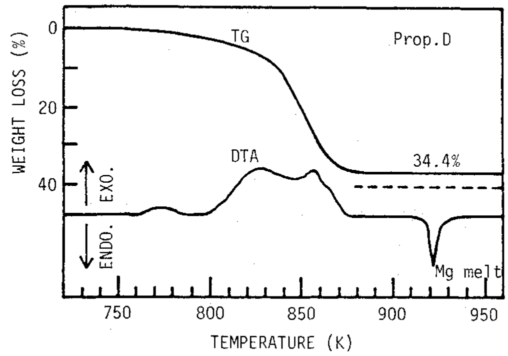

Fig. 7 TG and DTA data of Mg/TF propellants.

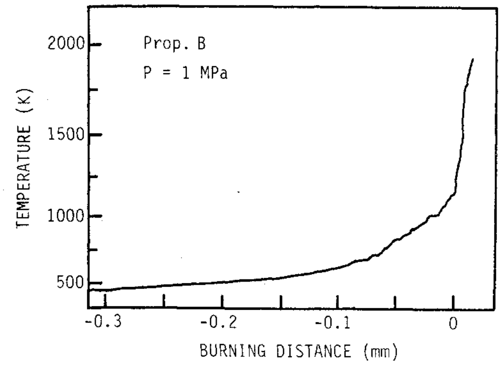

Fig. 8 A typical temperature profile of Mg/TF propellants.

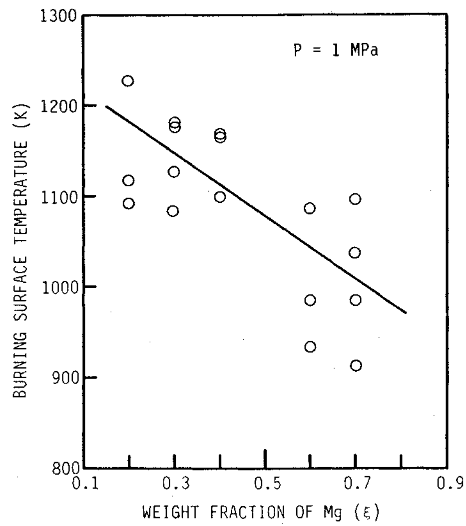

Fig. 9 Burning surface temperature of Mg/TF propellants as a function of the weight fraction of Mg.

within the Mg/TF propellants. The exothermic reaction observed in the temperature range 818–893 K is probably caused by the exothermic gasification reaction of the TF mixed within the propellants, which is the same exothermice reaction shown in Fig. 7. The endothermic peak at 923 K is the heat of phase change of Mg from a solid to a liquid.

There exists a residue remaining undecomposed above 893 K, as shown in Fig. 7. The weight fraction of the residue is 0.656, whereas the weight fraction of the Mg contained within the propellant is 0.600. This indicates that the weight fraction of 0.056 is produced by the oxidation of the Mg with the fluorine produced by the thermal decomposition of the TF. An x-ray analysis revealed that the residue remaining above

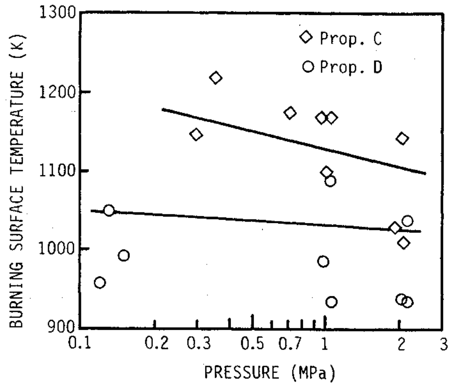

Fig. 10 Burning surface temperature of Mg/TF propellants as a function of pressure.

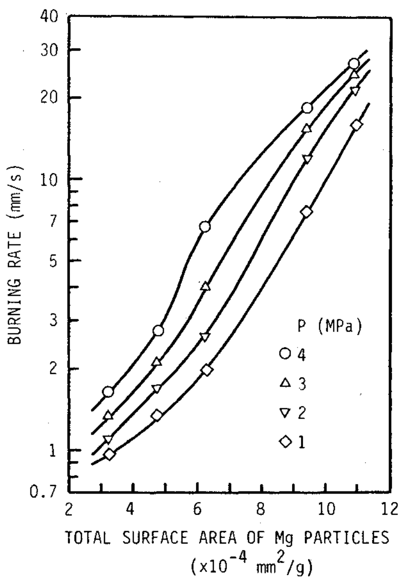

Fig. 11 Burning rate of Mg/TF propellants as a function of the total surface area of the Mg particles mixed within the propellants.

893 K in the TG experiments consisted of Mg and MgF_2. One assumes the following oxidation reaction during the decomposition of Mg/TF propellants:

$$Mg + F_2 \rightarrow MgF_2$$

The weight fraction of the fluorine 0.056 reacts with the weight fraction of the Mg 0.062. Since the oxidation reaction occurs at the surface of each Mg particle, the oxidized surface layer of MgF_2 is formed on the surface of each particle. The calculated results show that the thickness of the MgF_2 surface layer is 0.19 μm.

Combustion Wave Structure of Mg/TF Propellants

In order to determine the mode of the burning rate control of Mg/TF propellants, the combustion wave structure of the propellants was measured with microthermocouples. Figure 8 shows a typical example of the temperature profile during propellant burning. The temperature increases exponentially by the thermal conduction from the initial propellant temperature T_0 to the burning surface temperature T_s. The temperature in the gas phase just above the burning surface increases rapidly. However, the detailed analysis of the temperature in the gas phase was not possible because the thermocouple junction was too large to measure the fine structure of the gas phase.

An inflection point exists in the recorded temperature profile, as shown in Fig. 8. At the inflection point, the temperature increases rapidly. Thus, this inflection point is defined as the burning surface of the propellant. The measurements of the burning surface temperature are shown in Figs. 9 and 10. Since the burning surface was highly heterogeneous because of the propellants consisting of the particles of Mg and TF, the scatter in the data of the burning surface temperature was observed. Therefore, the determination of the effects of the particle size and concentration of Mg on burning surface temperature was not possible from the data obtained in this study. However, it is evident that the burning surface temperature is higher than the melting-point temperature of Mg (923 K) and is also higher than the decomposition temperature of TF (800~900 K). Thus, the magnesium particles mixed within the propellants are considered to melt on and above the burning surface. The burning surface temperature tends to decrease with increasing ξ at a constant pressure. It is also shown in Fig. 10 that the burning surface temperature tends to decrease with increasing pressure at a constant ξ.

Although the detailed analysis of the combustion process of Mg/TF propellants was not done in this study, the following combustion scheme can be drawn from the measurement results of the burning rate characteristics and the temperature profiles: The magnesium particles melt on the burning surface and are partially oxidized by the fluorine produced by the thermal decomposition of the TF particles. On the other hand, the TF particles decompose completely to produce fluorine and other gaseous fragments. During this TF particles decomposition, the Mg particles on the burning surface are ejected into the gas phase. In the gas phase, the oxidation of the Mg particles by the fluorine occurs rapidly. This oxidation of each Mg particle is considered to occur from the surface of the particle.

Thus, the rate of heat generation on and above the burning surface appears to depend on the surface area of the Mg particles and the concentration of the fluorine in the gas phase. Figure 11 shows the relationship between the surface area of the Mg particles and the burning rate of Mg/TF propellants. The burning rate increases with increasing surface area. In other words, the burning rate increases with decreasing particle size of Mg at a constant Mg/TF ratio or increases with increasing ξ within the range of the Mg concentration tested in this study.

As shown in Fig. 4, the burning rate of Mg/TF propellants depends on the TF particle size as well as the Mg particle size. This behavior is considered to be caused by the difference in the local concentration of the Mg particles distributed within the Mg/TF propellant. For example, the local concentration of Mg particles is high when large-sized TF particles are used at a constant ξ. The concentration distributions of the Mg particles and the fluorine produced from the large-sized TF particles are different when compared with the use of small-sized TF particles. Thus, the rate of the oxidation reaction of the Mg particles depends on the local concentration of the fluorine in the gas phase on and above the burning surface of the propellant. Accordingly, the heat-transfer process from the gas phase to the burning surface is affected by the size of the TF particles used, and the burning rate of the Mg/TF propellants appears to depend on the TF particle size.

Conclusions

Although the adiabatic flame temperature of Mg/TF propellants is maximum at $\xi = 0.33$, the burning rate increases monotonously with increasing ξ. This burning rate behavior demonstrates a significant contrast when compared with conventional solid propellants, such as composite and double-base propellants. The burning rates of solid propellants increase with increasing the flame temperature of combustion products.

The burning rate of Mg/TF propellants increases with decreasing Mg particle size at a constant ξ and at a constant pressure. Since the oxidation reaction of the Mg particles occurs from the surface, the surface area is a dominant factor in the burning rate. At the burning surface of the Mg/TF propellants, TF decomposes and produces fluorine, which acts as an oxidizer. The concentration of the fluorine produced at the surface is determined by the weight fraction of TF contained in the propellant.

On the other hand, the Mg particles on the burning surface are ejected into the gas phase. The oxidation reaction of the Mg particles with fluorine is considered to complete far downstream from the burning surface of the propellant. Thus, the consumption rate of the fluorine just above the burning surface increases with increasing the surface area of the Mg particles. In other words, the rate of heat production just above the burning surface increases with increasing surface area of the Mg particles at a constant ξ.

References

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[2]Gordon, S. and McBride, B. J., "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations," NASA SP-237, 1971.