Combustion of Ti/C Pyrolants

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ABSTRACT

The thermochemical characteristics of pyrolants composed of titanium (Ti) and carbon (C) were studied in order to develop high energy release materials used for igniters and fireworks. Since the Ti and C reaction occurs only at temperatures above 1200 K, polytetrafluoroethylene (PTFE) was mixed with the Ti/C pyrolants as an oxidizer. Various types of experiments were performed to gain information on the role of each ingredient. The results, measured by differential thermal analysis and thermal gravimetry, indicated that PTFE melts at about 605 K and reacts exothermically at about 830 K with Ti. The burning rate of the pyrolants increases as the mixing ratio of Ti and C approaches the stoichiometric ratio, (i.e., the burning rate increases as the adiabatic flame temperature increases within the range of the samples tested). Since the reaction starts from the surface of the Ti particles, the burning rate increases as the total surface area of the Ti particles increases.

Keywords: pyrolant, titanium, carbon, polytetrafluoroethylene, PTFE

Introduction

Energetic materials composed of metal particles and oxidizing materials, the so-called pyrolants, are used for igniters and fireworks. Typical pyrolants are made with titanium (Ti), zirconium (Zr), magnesium (Mg), or aluminum (Al) as fuel components and crystalline oxidizers such as potassium perchlorate ($KClO_4$), potassium nitrate (KNO_3), or ammonium perchlorate (NH_4ClO_4).

Polytetrafluoroethylene (PTFE) consisting of $–C_2F_4–$ is a typical polymeric oxidizer for metal fuels. PTFE decomposes thermally and produces F_2, which acts as an oxidizer. The mixture of Mg and PTFE is a typical pyrolant.[1-4] It is known that Ti reacts with carbon to form titanium carbide, TiC, as

$$Ti + C \rightarrow TiC + 184.1 \text{ kJ/mol}$$

accompanied with high heat release.[5,6] Based on a theoretical computation, the adiabatic flame temperature is 3460 K for the stoichiometric ratio of Ti and C. However, this reaction occurs only at temperatures well above 1200 K. Accordingly, to initiate the reaction requires that a high heat flux be given to the pyrolants.

Since the reaction between Ti and PTFE occurs with relatively low ignition energy, the addition of PTFE aids the ignition of the mixture of Ti and C particles. The heat produced by the reaction between Ti and PTFE is provided to the remaining Ti, which then reacts with C in the high temperature region.

Experimental Methods

Formulation of Ti/C Pyrolants

Four types of pyrolant samples were made to determine the effect of the mass fraction of Ti, ξ(Ti), on the burning rates of this class of pyrolants. The mass fraction of PTFE, ξ(PTFE), mixed within the Ti/C pyrolant samples was ξ(0.091), which included a small amount of Viton: $C_5H_{3.5}F_{6.5}$ (VT). The VT was used as a binder for the Ti, C, and PTFE particles. The size of Ti, C, and PTFE particles were 20, 0.5, and 5 μm in diameter, respectively. Each pyrolant sample was prepared as a pressed pellet. The Ti and C particles with PTFE particles were placed in a cylindrical-shaped container made of steel and pressed with a hydraulically operated piston. The piston pressure was about 200 MPa in order to make the density of the pyrolant pellets more than 0.95 theoretical density. The size of each pellet was 10 mm in diameter and 10 mm in length. The chemical compositions of the pyrolant samples tested are listed in Table 1.

Table 1. Chemical Compositions of the Ti/C Pyrolants Tested in this Study.

	Chemical Composition (mass %)		
ξ(Ti)	Ti	C	PTFE/VT
ξ(0.8)	72.7	18.2	9.1
ξ(0.6)	54.5	36.4	9.1
ξ(0.4)	36.4	54.5	9.1
ξ(0.2)	18.2	72.7	9.1

Thermal Decomposition and Burning Rate Measurements

The thermal decomposition process of the Ti/C pyrolants was measured using thermal gravimetry (TG) and differential thermal analysis (DTA). Both experiments were operated with various heating rates (0.083 K/s to 0.25 K/s) in argon atmosphere at 0.1 MPa. The mass of the sample used for each test was approximately 2.0 mg and was kept in a cell made of non-reactive quartz.

The burning rate of the Ti/C pyrolants was measured with a chimney-type burner that was pressurized with nitrogen gas. Each pressed pellet was set on a holder in the burner and was ignited from the top. The ignition was accomplished by using an electrically heated nichrome wire. The regressing surface was recorded with a high-speed video camera through a transparent quartz window that was mounted on the side of the burner. The burning rate was obtained from the recorded video tape.

Results and Discussion

Figure 1 shows the result of the TG and DTA experiments (heating rate of 0.25 K/s) of the Ti/C pyrolant ξ(0.8) sample done in an argon atmosphere. An exothermic reaction initiated at 805 K and terminated at 850 K. The peak exothermic temperature was observed at 837 K. The mass loss started at the same temperature as the onset of the exothermic reaction (805 K). The mass loss terminated at about 10% at 850 K when the observed exothermic reaction terminated. No thermal changes or mass loss changes were observed above 850 K within the range of the temperature tested. The results indicate that the observed mass loss is due to the thermal decomposition of PTFE as

$$\text{PTFE } (\text{–}C_2F_4\text{–}) \rightarrow C_s + F_2$$

This thermal decomposition probably includes some oxidation reaction of F_2 and Ti, which is considered by the observed exothermic reaction.[1]

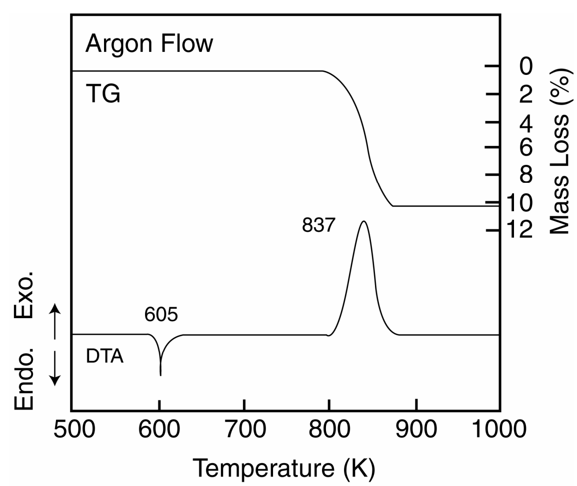

Figure 1. Thermal decomposition of Ti/C pyrolant ξ(0.8) with PTFE in an argon atmosphere (heating rate of 0.25 K/s).

Figure 2 shows an Arrhenius plot, the relationship between the reciprocal temperature of the exothermic peak temperature versus heating rate, of the DTA experiments. The results indicate that the peak temperature increased linearly as the heating rate increased in the log (reciprocal temperature) versus log (heating rate) plot. The activation energy of the observed exothermic reaction and the mass loss reaction was determined to be 210 kJ/mol for all samples tested, ξ(0.2) to ξ(0.8), in this study.

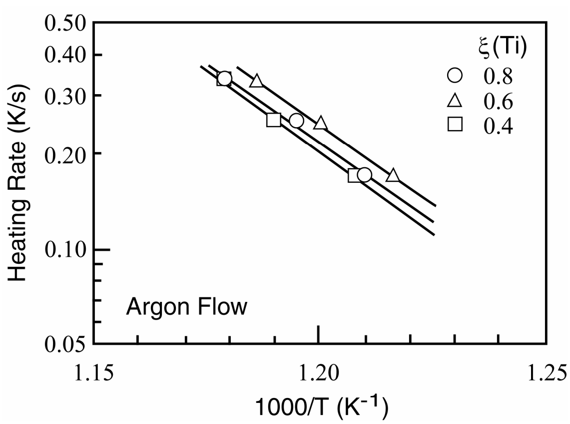

Figure 2. Arrhenius plot of DTA exothermic peak temperature.

The burning rate increased linearly in the log (pressure) versus log (burning rate) plots for the pyrolants of both ξ(0.6) and ξ(0.8) as shown in Figure 3. The pressure exponent of burning rate n defined in $r = a{\cdot}p^n$ was determined to be relatively independent of ξ(Ti), n = 0.45 for ξ(0.6) and n = 0.40 for ξ(0.8). Though the burning rate increased as ξ(Ti) increased at pressure of 0.1 MPa, the burning rate of the pyrolant ξ(0.4) was very low, and no self-sustaining combustion occurred when the pyrolant ξ(0.2) was ignited. The self-sustaining combustion limit was determined to be about ξ(~0.3) at pressures below 1.0 MPa.

The burning rate was also dependent on the particle size of Ti mixed within the pyrolants. As shown in Figure 4, the burning rate of the pyrolant composed of Ti particles of 20 µm in diameter was higher than that for particles of 50 µm in diameter at 0.1 MPa in the ξ(Ti) range tested. This increased burning-rate effect appeared as ξ(Ti) increases. It is evident that the reaction of Ti occurs at the surface of each Ti particle. Thus, the reaction of Ti and C is considered to be dependent on the total surface area of Ti particles, ζ(Ti), mixed within the pyrolant. Figure 5 shows the results of the relationship

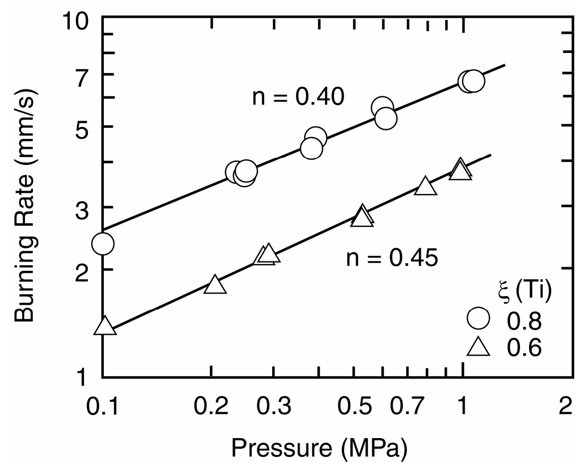

Figure 3. Burning rate characteristics of Ti/C pyrolants as a function of pressure and ξ(Ti).

between the burning rate and ζ(Ti) at 0.1 MPa. The burning rate increased as ζ(Ti) increased when the same sized Ti particles were used. In addition, the burning rate appeared to be high when large sized Ti particles were used at the same ζ(Ti).

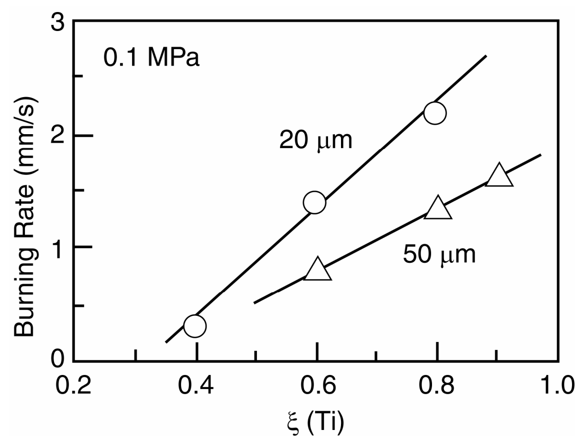

Figure 4. Burning rate characteristics of Ti/C pyrolants as a function of ξ(Ti) and the particle size of Ti.

The combustion process of the pyrolants was observed by using a high-speed video camera. Though whitish-yellow flames were seen on and above the burning pellet ξ(0.8), the light emission from the combustion product decreased as ζ(Ti) decreased. Porous, agglomerated materials were formed continuously above the burning pellets. TiC was found in the materials using an X-ray micro-analyzer. However, a quantitative analysis has not been done yet.

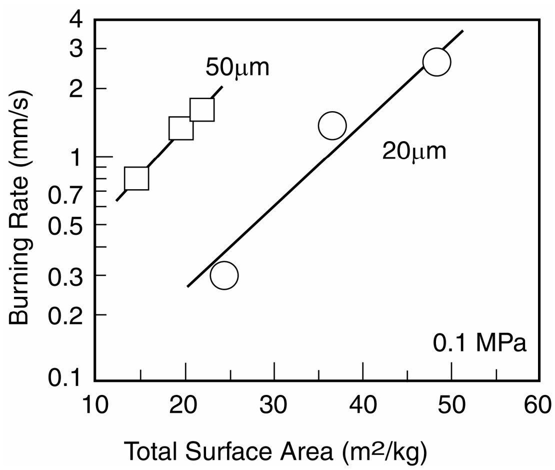

Figure 5. Burning rate characteristics of Ti/C pyrolants as a function of ζ(Ti) and the particle size of Ti.

Conclusions

Stable and continuous burning of the pyrolants composed of Ti and C was obtained by the addition of a small amount of PTFE. The thermal analysis using TG and DTA indicated that the reaction between Ti and C with PTFE started an exothermic reaction at 805 K in an argon atmosphere. This is considered to occur due to the decomposition reaction of PTFE.

The burning rate measurements and the observation of the combustion process indicate that the burning rate of Ti/C pyrolants increases linearly in log (pressure) versus log (burning rate) for the mass fractions of Ti, $\xi(0.8)$ to $\xi(0.6)$ tested in this study. The pressure exponent of the burning rate was determined to be from 0.40 to 0.45 in the pressure range from 0.1 MPa to 1.0 MPa. The burning rate is dependent on the total surface area of the Ti particles mixed within the pyrolants. Though the detailed combustion mechanism of Ti/C pyrolants has not been identified, the results indicate that the addition of PTFE plays a significant role in the observed stable burning of Ti/C pyrolants.

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