The Burning Surface Temperature and Boiling Point of Ammonium Nitrate

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1 Introduction

Most solid rocket motors currently use ammonium perchlorate (AP) as the main oxidizer. However, one of the primary products of combustion of AP-based propellants is hydrochloric acid (HCl). Therefore, ammonium nitrate (AN) is also used as an energy source in solid-fuel rockets because of its relatively low cost, low vulnerability, and nontoxic combustion products compared with conventional solid propellants.

The burning surface temperature and its pressure dependence are important parameters to predict the regression rate of the propellant, because the burning surface is a boundary condition for all combustion models of solid propellants. Measurements of the surface temperature of burning AN were performed by Whittaker and Barham [1] using thermocouples over a range of pressures from 6.7 to 327 MPa. Based on observations made by Hildenbrand et al. [2], and using burning liquid strands and a 25 µm diameter wire thermocouple, the surface temperature of burning AN was determined to be approximately 300 °C and did not vary with pressure. High-speed photography was utilized to photograph the thermocouples as they approached the surface of the liquid. However, the photographs were not shown.

Andersen et al. [3, 4] reported measured results for the burning surface temperature and the regression rate using the “hot plate” technique: the AN sample was pressed against a heated plate and the surface temperature was measured with a thermocouple embedded in the hot plate. These studies showed that the AN burning surface temperature was approximately 170 °C and independent of the regression rate for rates less than 0.4 mm/s. On the other hand, the AN surface temperature depends on the regression rate when it is greater than 0.4 mm/s. Furthermore, the AN surface temperature is also shown to be independent of the pressure [3]. The boiling point of AN was reported to be 210 °C [5]. However, in more recent work, this value was shown to be the melting point [6]. Therefore, the AN surface temperature of 170 °C [3, 4] measured using a hot plate may not be appropriate.
The mechanism of AN decomposition in a propellant has been examined and discussed based on applying Arrhenius’ law in the surface pyrolysis as follows [7, 8]:

\[ r = Z \exp \left( -\frac{E_s}{RT_s} \right), \]

where \( r \) is the regression rate, \( T_s \) is the burning surface temperature, \( E_s \) is the surface activation energy, \( R \) is the universal gas constant, and \( Z \) is a pre-exponential factor.

The thermal decomposition of AN has been examined using a rapid-scan FTIR/thermal profiling technique [9]. AN was heated to 150 °C/s under 0.1 MPa. The temperature profile of the condensed phase exhibited a region of constant temperature near 310 °C as the endotherm occurred.

Many studies have examined the relationship between the regression rate and the burning surface temperature for AN. However, the effect of pressure on the burning surface temperature has not been clarified. Previous studies [10, 11] have examined the relationship between the burning surface temperature and the pressure of fuels. These studies showed that the surface temperature is independent of the regression rate. In the present study, detailed experiments were performed to obtain the relationship between the burning surface temperature and the pressure for AN.

2 Experiments

Three methods were used to examine the pyrolysis of AN. The first was a bulk heating experiment in which AN was heated in a vessel. The second was an imitated-combustion experiment, in which the top of the AN specimen was rapidly heated using a high-temperature gas to simulate combustion conditions. The third was a thermochemical experiment, using thermogravimetric analysis (TGA).

In the first method (the bulk heating experiment), an AN specimen was heated in either a 30 ml glass beaker or a 5 ml stainless steel cell, as shown in Fig. 1. A vacuum pump and chamber were used to examine the pressure dependence of the AN temperature. A type K sheath-type thermocouple was used to measure the temperature. The sheath diameter was 1.0 mm or 3.2 mm, and the tip of the thermocouple was placed at the center of the sample. Nitrogen was used as the purge gas. The condition of the specimen was monitored using a video camera.

In the second method (the imitated-combustion experiment), AN was cured in a Plexiglas mold with the dimensions: outside diameter = 20 mm; length = 30 mm; and thickness = 1.5 mm. The AN was rapidly heated using a propane–air premixed flame burner, as shown in Fig. 2. A vacuum pump and chamber were used to examine the pressure dependence of the AN temperature. A type K sheath-type thermocouple was used to measure the temperature. The sheath diameter was 1.0 mm or 3.2 mm, and the tip of the thermocouple was placed at the center of the sample. Nitrogen was used as the purge gas. The condition of the specimen was monitored using a video camera.

In the second method (the imitated-combustion experiment), AN was cured in a Plexiglas mold with the dimensions: outside diameter = 20 mm; length = 30 mm; and thickness = 1.5 mm. The AN was rapidly heated using a propane–air premixed flame burner, as shown in Fig. 2. The apparatus used in this experiment was similar to that used previously [10–12]. Heated gas was applied to the top of the specimen. The AN surface was held in the same position relative to the burner by moving the specimen upward. The regression rate was measured by a dial gauge mounted below the specimen, and monitored by a video camera. The burner was cooled with water to prevent any temperature change in the burner. The temperature profile was measured using a type R (platinum/platinum–13% rhodium) thermocouple, which was embedded in the AN at least 10 mm into the specimen from the surface. The diameters of the thermocouple wires were 100 µm and 50 µm, respectively. The lead angle between the two leads was set to approximately 150°. The heat loss from the two leads in this experiment was previously confirmed as small compared with the experimental scatter [13, 14]. In addition, the temperatures were also measured with a thermocouple that was quartz coated using dimethyl siloxane [15]. However, the measured results did not differ.

The burning surface was observed and recorded using a video camera. A flash lamp was used to synchronize the videotape time with that of the temperature measurement via the thermocouple. The experimental procedure in this study has been described in previous papers [10–12].

In the thermochemical experiment, TGA experiments were carried out in flowing nitrogen at a pressure of 0.1 MPa. For TGA, a Rigaku TG/DTA-8120 module with a nitrogen flow rate of 50 ml/min was used. Heating rates between 2 °C/min and 20 °C/min were usually employed, and the
sample mass used was approximately 10 mg. The initial weight of the sample was the same for all TGA experiments.

3 Results

Temperature measurement in bulk heating experiments

In this experiment, the AN specimen was observed and the temperature was measured while being heated in vessels. As the temperature increased, bubbles were generated from the bottom of the beaker. At 0.1 MPa, near \( T = 300 \degree C \), the rate of temperature increase slowed and then stopped, as shown in Fig. 3. Then the AN bubbled violently. This temperature was specified as \( T_b \). After this point, the AN completely disappeared. Therefore, the boiling point of AN is considered to be 300 \degree C at 0.1 MPa. The relationship between the AN temperature \( T_b \) and the rate of temperature increase is shown in Fig. 4. The rate of increase in Fig 4. was defined by a gradient at 220 \degree C in the temperature curve of Fig. 3. In addition, Russell and Brill’s experimental result [9], which was obtained using a rapid-scan FTIR/thermal profiling technique, was also plotted. Therefore, the temperature \( T_b \) of AN was independent of the heating rate in the bulk heating experiment.

\( T_b \) was measured at different pressures. It obviously decreased as the pressure decreased. The relationship between reciprocal temperature and pressure is plotted in Fig. 5. The resulting graphs may be expressed by the following equation:

\[
P = Z \exp\left(-\frac{k_p}{T_b}\right),
\]

where \( P \) is pressure, \( Z \) is the pre-exponential factor, and \( k_p \) is a factor obtained from the gradient of Fig. 5. The value of \( k_p \) was about 11,500 K.

The following reversible dissociation is considered to occur on the surface:

\[
\text{NH}_4\text{NO}_3(\text{l}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HN}0_3(\text{g}).
\]  

Therefore, using the Clausius–Clapeyron relation:

\[
P_{AS} \sim \exp\left(-\frac{\Delta H}{2 R_a T}\right),
\]

where \( P_{AS} \) is the saturation pressure and \( \Delta H \) is the heat of evaporation. From \( k_p \) obtained from Fig. 8, \( \Delta H = 190 \text{ kJ/mol} \). This value of \( \Delta H \) is approximately the same as the value of 173 kJ/mol calculated from the heats of formation of Eq. (3) [16], or the value of 170 kJ/mol obtained from the vapor pressure of AN [16].

Thermochemical experiments

Figure 6 shows typical TGA traces for AN measured at atmospheric pressure. At point A, a decrease in mass begins; at point B, 50% of the initial mass is depleted; and at point C, the entire mass is depleted. Points A, B, and C in Fig. 6 were determined for each heating rate. The Arrhenius plots, obtained using TGA, are shown in Fig. 7.

The temperatures at point C were compared with the values obtained by the bulk heating experiment in Fig. 4. In this figure, the rate of temperature increase corresponds to the heating rate of the TG experiment. At low heating rates of less than 0.4 \degree C/s, the temperature of AN decreased as the heating rate decreased. At higher heating rates of greater than 0.4 \degree C/s, the temperature was independent of the heating rate. This situation is similar to evaporation and boiling.
The burning rate of a typical AN-based propellant is thought to be approximately 0.1–0.3 mm/s at atmospheric pressure [17, 18]. The rate of temperature increase in a solid phase can be approximately estimated using the following equation, neglecting the latent heat in the solid or liquid phase and the cross-flow effect on the burning surface.

\[
\frac{dT}{dt} = (T - T_0) \left( \frac{r^2}{a} \right). \quad (5)
\]

The rate of temperature increase \(\frac{dT}{dt}\) at temperature \(T = 220 \, ^\circ\mathrm{C}\) of an AN-based propellant is approximately \(20\, ^\circ\mathrm{C}/\mathrm{s–200\, ^\circ\mathrm{C}/s}\) using the values of initial temperature \(T_0 = 20\, ^\circ\mathrm{C}\) and thermal diffusivity \(a = 1.0 \times 10^{-7}\, \mathrm{m}^2/\mathrm{s}\). The rate in the bulk heating experiment of Fig. 4 is almost the same as that of the true AN propellant combustion. Therefore, the burning surface temperature is considered independent of the burning rate. On the other hand, at rates of temperature increase less than 0.4 °C/s, the surface temperature depends on the regression rate or the evaporation rate. This phenomenon is similar to that of a lower molecular species such as water.

The gradient of each line in Fig. 7 is defined by \(k_c\). This figure shows that the values for each line are approximately the same. The values obtained in Fig. 7 using TGA were averaged and are discussed in the next section.

**Effect of pressure on the burning surface temperature**

The values for \(k_p\) and \(k_c\) obtained by the two sets of experiments are compared in Fig. 8, along with the \(k_p\) values for AP, hydroxyl-terminated polyester (HTPE), and glycerin obtained in previous papers [10–12]. The values of \(k_p\) obtained by the imitated-combustion experiment are in close agreement with the values of \(k_c\) obtained by TGA.

### 4 Conclusions

The pressure dependence of the burning surface temperature of AN was examined using a thermocouple. The burning surface temperature was the same as the boiling point, which was approximately 300 °C at 0.1 MPa, independent of the rate of temperature increase, but dependent on pressure. A thermochemical experiment using TGA was also conducted. It was found that these thermochemical methods can be used to derive an approximate pressure dependence of the burning surface temperature of oxidizer and fuels.
Figure 3. Temperature–time diagram of AN in the bulk heating experiment.

Figure 4. Relationship between AN surface temperature and the rate of temperature increase.

Figure 5. Relationship between pressure and AN temperature.

Figure 6. Typical TGA trace for AN.

Figure 7. Arrhenius plot measured using TGA.

Figure 8. Relationship between kp and kc.
References