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Effect of Surface Microstructure on the Temperature Sensitivity of Burning Rate of Ammonium Perchlorate

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ABSTRACT

Considering Vielle's law and the new thermodynamic model which the authors have developed recently, the true dependence of temperature sensitivity of burning rate (σ_p) of ammonium perchlorate (AP) on pressure is resolved and experimentally verified for pellet burning. The value of σ_p decreases with pressure steeply in regime I' (below 20 atm), but gently in regime I (above 20 atm). The σ_p value of powder AP has been determined and it is observed that $\sigma_{p(powder)} > \sigma_{p(pellet)}$, which clearly suggests that σ_p is influenced by the surface temperature sensitive parameter $(\partial T_s/\partial T_o)_p$ and hence by the surface/subsurface microstructure. In powder burning, the buoyant lifting of the particles into the gas phase occurs, which constitutes the so-called 'free board region' (FBR) extending just above the true surface. Consequent to the decomposition of AP particles in FBR, the condensed phase heat release gets curtailed and $\sigma_{p(powder)}$ becomes larger. A general relationship for σ_p in terms of density and surface temperature is suggested, which is applicable to both pellet and powder AP.

1. INTRODUCTION

Ammonium perchlorate (AP) is one of the most extensively used oxidizer in high energy formulations. Due to its unique characteristic of self-supporting deflagration, AP combustion has been studied primarily to understand the more complex combustion phenomena in AP-based composite propellant systems. Despite the profusion of studies conducted, AP deflagration mechanism still remains elusive in its various facets. AP is only one of its kind that exhibits a critical low pressure deflagration limit, (LPL: 20 atm) below which it does not burn; by suitable augmentation of the initial temperature (T_o), it can be made to burn below LPL. The temperature dependence of burning rate is expressed in terms of temperature sensitivity of burning rate (σ_p), which has been observed to increase, decrease, or both as

a function of pressure (P). In a majority of cases, however, a decrease is observed[1-3].

We have determined the values of σ_p and have attempted here to resolve the perplexing dependence of σ_p on P. The present analysis is based on Veille's law and our novel thermodynamic model of AP deflagration[4], which clearly identifies a hitherto unknown subcritical pressure regime (christened as regime I'), mechanistically distinctive from regime I (20-70 atm), which succeeds regime I'.

Most of the studies on AP deflagration have been surprisingly done on pellets and single crystals but not on the powder, despite its use as a particulate in the actual propellant systems. We have studied the deflagration of powder AP and compared it with its deflagration in pellet form in

order to understand as to how the microstructure of the burning surface of AP influences σ_p.

2. EXPERIMENTAL PROCEDURE

The methods employed for preparation of the samples, measurement of burning rate ($\dot{r}$) as a function of T_o and pressure (P), the temperature profile imprinting and analyses, etc. have been discussed elsewhere[4]. Surface temperature (T_s, °K), at a given pressure (P) was obtained from the following empirical equation[4]

$$\ln T_s = 0.0484 \ln P + 6.6957 \qquad (1)$$

The value of T_s thus obtained was verified experimentally by recording the temperature profile[4] of AP deflagration at different pressures and T_o's. The temperature profile plot of $\ln T$ vs time is linear up to the temperature corresponding to the burning surface, and thereafter it deviates from linearity. The temperature corresponding to the point of deviation was taken as T_s. The surface temperature was thus obtained at different T_o's in regimes I' and I and from this data $(\partial T_s/\partial T_o)_p$ was computed.

The $\dot{r}$ and T_s values of tamped powder at different values of T_o and P were obtained from the $\dot{r}$ measurements of AP powder in a glass tube (diameter : 1.0 cm). About 1.5 g of AP of particle size 200 - 250 μm was packed in the tube as a lightly tamped powder accommodating nichrome ignition wire, fuse wires (5 amp) and chromel-alumel thermocouple (beed size 0.005 in.). The packing density was determined from the weight of AP packed to a certain volume in the glass tube and was found to be 1 g/cm^3. Care was taken to maintain the packing density same in all the experimental measurements.

3. RESULTS & DISCUSSION

3.1 Temperature Sensitivity and its Variation with Pressure

The LPL of AP can be brought down and it can be made to burn at atmospheric pressure by increasing T_o. Let us first consider the following relationship between $\dot{r}$ and P based on Veille's law[5]

$$\dot{r} = \left[\quad \right] P^n \qquad (2)$$

where

a_o is a constant, n is the pressure exponent and T_{ig} is the ignition temperature. From the basic definition of σ_p, we can write Eqn (2) as

$$\sigma_P = \left[\frac{\partial \ln \dot{r}}{\partial T_o} \right]_P \pm \frac{1}{T_{ig} - T_o} \qquad (3)$$

If $T_o = T_{ig}$, then the value of $\dot{r}$ will be infinity. However, in the range $T_o < T_{ig}$, which is normally prevalent in propellants, σ_p will vary with T_o. Besides, it is well known that the value of T_{ig} depends upon sample size and shape. Hence, the value of σ_p obtained from Eqn (2) will be erroneous. We have modified Eqn (2) by replacing T_{ig} with T_s

$$\sigma_p = 1/(T_s \quad T_o) \qquad (4)$$

Since T_s is independent of sample size and shape and rests only on chemical characteristics and pressure, it is a preferable parameter to T_{ig}. The value of T_s is also affected by T_o.

The variation of σ_p with P is examined by differentiating Eqn (3) with respect to P:

$$\frac{\partial \sigma_P}{\partial P} = -\sigma_P^2 \left[\frac{\partial T_s}{\partial P} \right]_{T_o} \qquad (5)$$

Since σ_p and $(\partial T_s/\partial P)_{T_o}$ are both positive quantities in both regimes I' and I, it is explicit from Eqn (5) that the value of σ_p should decrease with pressure.

In regime I, for instance, at 1 atm, the critical T_o below which AP does not burn is 245 °C; this critical T_o will have a unique value at a given pressure in the subcritical regime[4]. Similarly, T_s
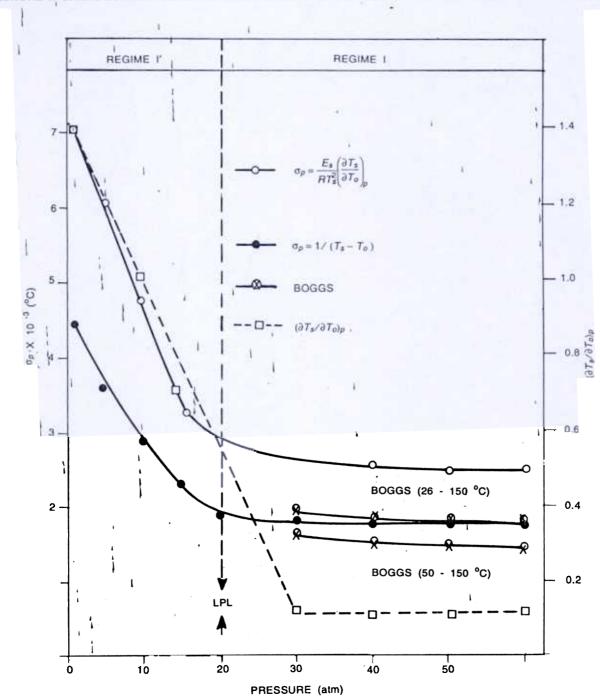
Figure 1. Dependence of σ_p and $(\partial T_s/\partial T_0)_p$ on pressure

will also have a unique value at a given pressure in the subcritical regime. Accordingly, for a given pressure, the critical T_o and the corresponding T_s (T_o and T_s taken from Ref. 4) were substituted in Eqn (3) and σ_p values obtained at various pressures in the regimes I' and I, and plotted against P in

Fig. 1; the figure also includes the experimental data of Boggs and Zurn[1] for regime I. The variation of σ_p with P shows a steep decrease in regime I' and a marginal decrease in regime I, which is comparable with that observed by Boggs and Zurn[1].

According to our newly proposed thermodynamic model[4], the surface activation energy (E_s) is represented as

$$E_s = E_{s,c} + E_{s,g}$$

$$= \frac{\sigma_P RT_s^2}{(\partial T_s / \partial T_o)_P} + \frac{(n/P)RT_s^2}{(\partial T_s / \partial P)_{T_o}} \quad (6)$$

where

$E_{s,c}$ and $E_{s,g}$ are the condensed and gas phase activation energies just below and above the apparent surface respectively; R is the gas constant and $(\partial T_s / \partial T_o)_P$ and $(\partial T_s / \partial P)_{T_o}$ are the surface temperature sensitive parameters related to condensed and the gas phase, respectively. σ_P was examined by rearranging Eqn (6) as follows[4]

$$\sigma_P = \frac{E_{s,c}}{RT_s^2} \left[\frac{}{\partial T_o} \right]_P \quad (7)$$

Substituting the appropriate values of $E_{s,c}$, T_s and $(\partial T_s / \partial T_o)_P$ in Eqn (7), σ_P was calculated at various pressures in regimes I′ and I. The plots obtained are shown in Fig. 1. It may be seen that the extent of decrease in regime I′ is large, and it is marginal in regime I. This may be attributed to a steep decrease in the value of $(\partial T_s / \partial T_o)_P$ in regime I′ compared to regime I (Fig. 1). Hence, it is said that σ_P strongly depends upon $(\partial T_s / \partial T_o)_P$. In the present investigation, at LPL, $(\partial T_s / \partial T_o)_P$ is 0.5 (Fig. 1) and hence Eqn (6) becomes[4]

$$\sigma_P = E_{s,c} / RT_s^2 \quad (8)$$

Equation (8) is similar to that obtained from Belayaev-Zel'dovich model[6]. By applying the condition that at higher pressures, $T_s \simeq T_{m'}$ we get the following equation

$$\sigma_P = \left[\frac{E}{2RT_s^2} + \frac{L}{RT_s^2} \frac{T_{m'} - T_s}{T_s - T_o} \right] \left[1 + \frac{L}{RT_s^2} (T_{m'} - T_s) \right] \quad (9)$$

Strunnin and Manelis used the following simplified equation for σ_P

$$\sigma_P = E_s / 2RT_s^2 \quad (10)$$

which is similar to the equation obtained on the basis of Belayaev-Zel'dovich model[6]. Eqns (10) and (8) are similar and hence it may be concluded that they can be used for calculating values of σ_P for AP, but only at LPL.

Above LPL (beyond 20 atm), as seen from Fig. 1, $(\partial T_s / \partial T_o)_P$ is almost constant having a value of 0.1 in regime I, σ_P can, therefore, be written as[4]:

$$\sigma_P = E_{s,c} / 10RT_s^2 \quad (11)$$

Dependence of σ_P on pressure can also be examined by differentiating Eqn (10) with respect to P

$$\frac{\partial \sigma_P}{\partial P} = -\frac{E_{s,c}}{5RT_s^3} \left[\frac{\partial T_s}{\partial P} \right]_{T_o} \quad (12)$$

The quantities $E_{s,c}$, T_s and $(\partial T_s / \partial P)_{T_o}$ are all positive and hence the value of σ_P should decrease with P. This is yet another evidence to show that σ_P should decrease with P.

3.2 Calculations of T_s from σ_P

In regime I, for constant T_o, Eqn (4) suggests that the value of σ_P varies with $1/T_s$, whereas it is proportional to $1/T_s^2$ according to Eqn (11). To verify which of the dependences is better, experimental data of Boggs and Zurn[1] and Cohen Nir[8,9] were used and a plot of σ_P as a function of both $1/T_s$ and $1/T_s^2$ was drawn. The correlation coefficient for both, σ_P vs $1/T_s$ and σ_P v$ 1/T_s^2$ plots was found to be 0.98 for the Bogg-Zurn's data, and 0.99 for Cohen Nir's data. Although, both the curves fit well, Cohen Nir's data shows a slightly better fit than that of Boggs-Zurn for the dependence of σ_P with both $1/T_s$ and $1/T_s^2$. Apparently, the σ_P data are not sufficiently precise to decipher the superiority of the dependence of σ_P either on $1/T_s$ or $1/T_s^2$. However, Eqn (11) can be used to calculate T_s at different pressures in
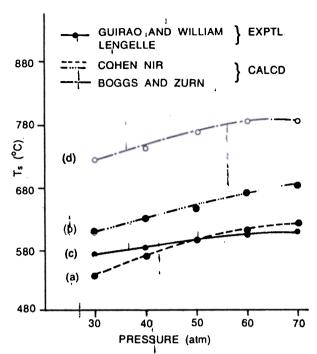
Figure 2. Dependence of T_s on P; T_s calculated using the σ_p data, (a) particle size: 200-315 µm, (b) particle size: > 1000 µm, (c) experimental and (d) at T_o = 26-150 °C.

regime I where $E_{s,c}$ is 35 kcal/mole. A plot of T_s [calculated from Eqn (11)] as a function of P is shown in Fig. 2. From a comparison with the data[8-11] of Guirao and Williams[10], Lengelle, et al[11], Cohen Nir[8,9] and Boggs & Zurn[1], it may be seen that Cohen Nir's data[8,9] gives a better dependence of T_s on P, comparable to the experimental curves of Guirab and Williams[10] and Lengelle[11].

3.3 Temperature Sensitivity of AP Deflagration as Tamped Powder

It is apparent from Eqn (7) and our analysis of pellet AP deflagration that σ_p depends on the condensed phase sensitive parameter $(\partial T_s/\partial T_o)_p$. This suggests that any variation in the surface/subsurface microstructure of deflagrating AP would alter this paramater and, hence σ_p. We have, therefore, examined the deflagration behaviour of AP as tamped powder, where the burning surface will be more particulate and σ_p different from that observed for the pellet form.
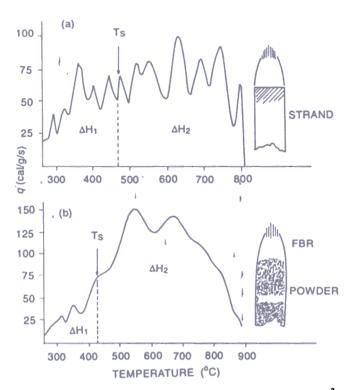

Figure 3. $\dot{q}$ vs T profiles for AP (a) pellet strand (1.93 g/cm^3) (b) powder (1 g/cm^3) burning at T_o = 245 °C and P = 1 atm.

The $\dot{r}$ and T_s values for powder AP deflagration were obtained experimentally, as described elsewhere[4]. The identification of true T_s is much easier in the case of compressed pellets because of a distinct gas-solid interface. In powder form, however, such a clear surface demarcation is not possible, because AP particles at the surface are so loosely held that some of them are carried away bouyantly by the upstream gases from the surface into the gas phase. In the process, exothermic decomposition of AP particles continues all along their travel from the surface into the gas phase, thus adding to the gas phase exothermicity. As a result, the proportion of the heat of decomposition in the condensed phase will be curtailed compared to that for pellet burning. In view of such a deflagration behaviour, the surface in the case of powder burning can be best called as 'interfacial region' or 'transition region'. The zone in which the driven AP particles are present in the gas flame is called

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pellet and the powder are 1.93 g cm^{-3} and 1.0 cm^{-3}, respectively compared to the AP single crystal density (d_o) of 1.95 g cm^{-3}. Hence, the approximate numerators in Eqns (4) and (13) are 1 and 2 respectively.

Thus, the higher value of σ_p for the powder, obtained from (a) Eqn (13), (b) ln $\dot{r}$ vs T_o plot and (c) Eqn (7) may be attributed to the substantial decrease in ΔH_1 value due to the upstream lifting of the particles in the gas phase as well as to the surface erosion caused by it, resulting in an apparent enhancement in the value of $\dot{r}$. Further, from T_s, σ_p and $(\partial T_s/\partial T_o)_p$ data, the $E_{s,c}$ value, calculated using Eqn (6), is found to be 10.4 kcal/mole for powder AP, which matches with the $E_{s,g}$ for pellet AP in regime I^4 which suggests that the burning surface and hence T_s is actually in FBR in the gas phase.

4. CONCLUSION

The value of σ_p has been estimated (i) by modifying the well-known identity equation derived from Veille's law, and (ii) from our thermodynamic model. The elusive variation of σ_p value with pressure has been verified. It has been found to decrease with increase in pressure. Further, it is also found to depend on the surface temperature sensitive paramater, which is condensed phase-related. The larger value of σ_p observed for AP burning as a tamped powder compared to its burning as pellet is attributed to the curtailed surface/subsurface heat release owing to the bouyant lifting of AP particles into the gas phase. This study reveals that the σ_p value of AP is influenced by the surface microstructure, depending upon whether it is compact as in pellet or particulate form as in the tamped powder.

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