Decomposition, Pyrolysis, and Deflagration of Pure and Isomorphously Doped Ammonium Perchlorate

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Theme

Ammonium perchlorate (AP) is the oxidizer and principal ingredient in most composite solid propellants and its behavior in the cumbustion zone affects the overall combustion characteristics of the propellant. Because the written word can only partially describe this behavior, a 16 mm film has been prepared in which scanning electron micrographs (SEM), cinephotomicrography, graphs, charts, and plots are used to describe the phase changes orthorhombic to cubic and cubic to orthorhombic; the sublimation, isothermal decomposition, pyrolysis, and self-deflagration of pure AP; and the self-deflagration of AP crystals isomorphously doped with K^+, $Cr_2O_7^{2-}$ and MnO_4^- ions.

Content

The phase change from orthorhombic to cubic occurs at 240°C and proceeds, via slippage of planes moving parallel to each other, to give rectangular crystal faces. When AP is cooled to below 240°C the crystal forms many grains with each grain having the orthorhombic structure, but the macroscopic appearance of the whole crystal remains cubic. This state has been referred to as "relic cubic."

Sublimation of AP is a reversible surface process having an activation energy (obtained from determining rate as a function of sample temperature and then using an Arrhenius expression $r = Ae^{-E/RT}$) of approximately 28 kcal/mole.[1] Sublimation sites have a structure reflective of the crystal habit: sites on the *m*-face are rectangular while those on the *c*-face are rhomboidal. The rate of sublimation varies inversely with pressure, e.g., from 5×10^{-4} cm/sec at 290 mm Hg and 400°C to 2×10^{-4} cm/sec at 1 atm and 400°C.[1]

When a hot gas stream or flame is directed at an AP sample at 1 atm, the material usually sublimes, producing a step-like surface structure. This same structure is seen when samples subjected to "convective pyrolysis" at 1 atm are viewed, leading to the speculation that this technique, which has been billed as a means for studying phenomena intermediate between sublimation and deflagration, is causing sublimation when used at 1 atm. This conclusion is supported by the fact that the activation energy for this process is comparable to the value given for sublimation.

When sublimation is reduced, usually by increasing the pressure or performing the experiment at lower temperature ($T < 300$°C), decomposition can be observed. It differs from sublimation in several ways: it is irreversible, while sublimation is reversible; it takes place within the sample (often very near but not at the surface), whereas sublimation is a surface process; its activation energy is approximately 22 kcal/mole whereas the activation energy for sublimation is approximately 28 kcal/mole; and it is pressure-independent, whereas sublimation is pressure-sensitive.[2] The decomposition reaction takes place within the crystal, usually near the surface, and continues until the products can be vented to the atmosphere, at which point the reaction ceases. The surface therefore is marked by "blisters" and/or porous residue.

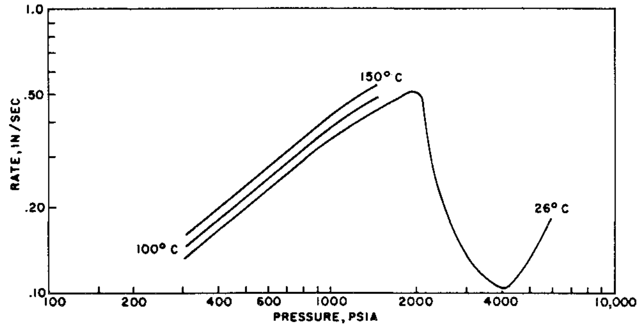

Fig. 1 The deflagration rate of ammonium perchlorate as a function of pressure and initial sample temperature.

Under the proper conditions of pressure and initial sample temperature, AP will sustain self-deflagration. Burning rate data as a function of pressure and initial sample temperature T_0 are presented in Fig. 1. For a given T_0 the deflagration rate curve can be divided into four pressure-dependent regimes, described in the following paragraphs, according to the character of burning, surface structure, subsurface profile, and energy transfer mechanisms.[3] For $T_0 = 26$°C pressure ranges (psia) for Regime I–IV, respectively, are 300–800, 1000–2000, 2000–4000, and > 4000 psia. Although the data in Fig. 1 for 100°C and 150°C were obtained only for pressures less than 1500 psia, the results (and those of others) suggest that one effect of T_0 is to alter the pressure range of a particular regime. Thus for $T_0 = 26$, 100°C, 150°C the transition from Regimes I to II (taken to be the point where the data no longer follow the $r = Cp^{0.77}$ relationship of Regime I) occurs at $p \simeq 800, 900, 1000$ psia respectively. This is confirmed when the data of other investigators, using less pure AP, is considered: for instance, one study[4] shows the region of negative slope (Regime III) to occur at $p > 2200$, 3500 and 4200 psi for $T_0 = 20, 100, 150$°C, respectively.

The first of these regimes, $300 \leqq p \leqq 800$ psia, is characterized by a macroscopically smooth, planar regression of the surface. When the profiles of samples quenched[5] from these pressures are examined, what appears to have been a thin layer ($\simeq 5\mu$) of reacting, gas entrapping liquid is seen existing on a layer of relic cubic material, the thickness of which varies with pressure according to $X_{tr} \propto p^{-0.77}$ (for the significance of this measurement see Refs. 6 and 7), which in turn exists on the orthorhombic phase which had never experienced the cubic phase change. It was hypothesized that much of the energy transfer necessary to sustain self-deflagration occurs in the froth, and several recent analyses[8,9] have supported this hypothesis. In Regime II, $1000 < p < 2000$ psia, the surface exhibits a conspicuous and intricate surface pattern of ridges and valleys which

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Received May 26, 1971; revision received July 26, 1971. The film that serves to back this synoptic is available on loan from the authors upon direct request to them. This work is sponsored by the Naval Ordnance Systems Command under ORDTASK 331–001/200–1/URO 24–02–02.

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is relatively invariant as the burn progresses. The reaction sites are localized within the valleys.

In Regime III, the region of negative slope of the burning rate ($2000 < p < 4000$ psia), a visible, spatially variant flame is seen, accompanied by a sporadic, uneven regression of the surface. The quenched samples show pockets of "needles." In Regime IV ($p > 4000$ psia) a steady flame is present over the entire surface. The quenched samples show a surface entirely covered with the "needles."

Samples made by pressing granular AP are shown to exhibit combustion behavior similar to that of the single crystals in terms of burning rate, surface structure, and subsurface profile.

The self-deflagration behavior of isomorphously doped AP is compared as a function of dopant type, concentration, and pressure change. The results show that each of these parameters has a significant effect on the deflagration rate, surface structure and subsurface profile, and other combustion behavior. The phenomena described in Ref. 5 are shown.

The effects of K^+ dopant are evident from 300 to 6000 psia (highest pressure used), Fig. 2, but are concentration-dependent only at pressures less than approximately 2500 psia. For these pressures the effect of K^+ is to either increase or decrease the burning rate relative to that of pure AP: at low-concentration levels ($[K^+] < .3$ w%) the rate can be greater while higher concentrations depress the rate. Similarly, a pressure increase can increase or decrease the rate. This irregular behavior is due in part to competing effects of K^+, which enhances the quantity of surface liquid and decomposition within the liquid but also leads to the formation of the rather inert KCl as a decomposition product.[10] A small initial amount of K^+ in the crystals enhances melt but yet not much KCl is formed, and thus the burning rate is increased. Samples with high K^+ concentration form more KCl, thereby decreasing the rate. Pressure can also cause an accumulated amount of KCl to exist on the surface by retarding the vaporization of the material. Evidence to support this hypothesis is presented.

The effects of $Cr_2O_7^{2-}$ doping are manifested at both low and high pressures and are concentration-dependent, with higher amounts of $Cr_2O_7^{2-}$ increasing the rate. The inclusion of 0.030 w%MnO_4^- ion increased the low pressure deflagration limit to $\simeq$ 1700 psia and also resulted in long (up to 2 sec) ignition delays.

The dynamic progression of the phase change, the differences between sublimation, decomposition and deflagration, the differences between a smooth planar regression and a sporadic regression, and the differences in burning rates caused by the inclusion of a very small amount of foreign ion, can be much better appreciated by viewing the film, which is available for loan upon request to the authors.

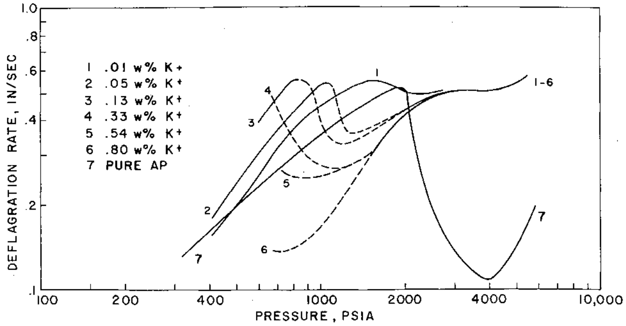

Fig. 2 The deflagration rate of K^+ doped ammonium perchlorate as a function of pressure. Initial sample temperature 25°C.

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