

As derived, the displacement or strain expressions contain the three transverse strains. Other than boundary conditions, no further restrictions exist on these functions. One then could choose arbitrarily and independently a separate functional form for each of the transverse strains and evaluate the integrals. Such an approach would be acceptable but not necessarily satisfactory. Though two-dimensional shell theory is an approximate one, the degree of refinement and applicability of the theory is affected by the approximations. Hence, the more constraints satisfied the better the theory.

The expressions for the displacement or strain components presented in the paper could be used in conjunction with an energy variational theorem. Such an application would relate the transverse strains and the lateral surface loads so that bounds could be established regarding the choice of functional relations for the transverse strains. Ultimately, when the functional form of the transverse strain would be postulated, assurance would be had that the resulting shell theory satisfies the constraints of continuum compatibility and minimum potential energy.

It might be noted that what is being suggested in the previous paragraph as a means of establishing bounds on the functional forms of the transverse strains is utilized in thin shell theory as a means of obtaining the constitutive relations.<sup>9</sup> However, there are important differences between the two applications. In thin shell theory two assumptions are simultaneously introduced into the variational equations. Namely, an assumed linear displacement variation in the transverse coordinate and an assumed transverse stress or strain variation. The fact that the two sets of assumptions are incompatible with each other has been noted by Reissner<sup>10</sup> and also becomes obvious if the assumed strain variations are introduced into the displacement equations presented in the paper. Thus the thin shell application of the variational theorem when used in conjunction with an assumed linear displacement variation and an assumed transverse strain or stress variation leads to a shell theory which satisfies the minimum energy constraint but violates that of continuum compatibility. However, for sufficiently thin shells, the contradiction usually results in small errors.<sup>11,12</sup>

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## Surface Structure of Ammonium Perchlorate Composite Propellants

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THE surface structure of a burning solid propellant is an important aspect to be considered when attempting to mechanistically or mathematically model the propellant combustion process. The vast majority of models proposed for steady and nonsteady combustion of solid propellants treat the burning surface as a planar, dry, homogeneous entity with one simple Arrhenius expression describing the chemical reaction of the entire regressing surface. For composite propellants, this simplification does not fully describe the combustion. One justification for such simplification is that the complexity of the model can be reduced to a more tractable mathematical representation. Another reason is that detailed information defining the structure of the surface is not available to construct accurately a more physically realistic model. Because of the latter reason, an experimental investigation was undertaken to understand better the physical nature of the surface and determine, if possible, the extent of heterogeneous or subsurface reactions. In the study, burning propellant samples were extinguished and then examined by using a scanning electron microscope (SEM).

The test propellants consisted of ammonium perchlorate (AP) and either polyurethane (PU) or carboxy-terminated polybutadiene (CTPB) binder. The propellants were formulated with either a unimodal oxidizer particle size distribu-

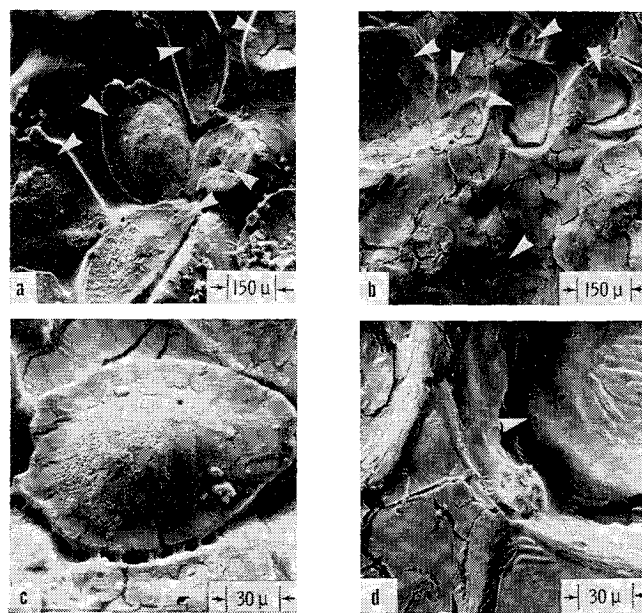


Fig. 1 Scanning electron microscope (SEM) micrographs of an ammonium perchlorate-polyurethane propellant quenched from (a,c) 100 psia and (b,d) 800 psia. The white arrows indicate the ammonium perchlorate particles. Note the different positions of these particles relative to the binder for the two cases.

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tion or a narrow cut bimodal distribution, with no additives such as burning rate catalysts or powdered metal. Small strands of these propellants were burned at pressures between one atmosphere and 800 psia in a combustion bomb containing an inert gas. While the samples were burning, high-speed, high magnification movies were taken. Once steady-state conditions were attained, the sample was extinguished by rapid depressurization of the combustion bomb. The extinguished samples were cut to an appropriate size, coated with gold-palladium of a few hundred angstroms thickness (the coating eliminates electrostatic charging of the sample surface), examined and photographed using the SEM. The SEM enabled viewing the structures, which were also seen using cinephotomicrography, at magnifications up to 100,000 $\times$  (up to 10,000 $\times$  was used in this study) while retaining depth of focus resolution not available with other devices such as the optical microscope. The marked correlation between the structures seen in the high-speed, high-magnification movies and the structures seen when the quenched samples were examined using the SEM indicates that any artifacts due to the quenching method seem to be of minor importance. The purpose of the metallic coating and the question of artifacts due to vacuum deposition of a metallic alloy has been discussed in Ref. 1.

### Results and Discussion

Results typical of this study are shown in Figs. 1-4. The SEM photographs of a propellant consisting of 26% polyurethane and 74% 200- $\mu$  AP (Fig. 1) illustrate the effects of pressure on the surface structure. The photographs on the left (Fig. 1a, 1c) show samples extinguished at a pressure of 100 psia and those on the right were obtained at 800 psia. Inspection of the photographs reveals that at the low pressure the regression rate of the AP particles was less than that of the binder and vice versa at higher pressures, thus confirming the observation reported by Bastress.<sup>1,2</sup> The smoothly contoured surface (the cracks on the surface of the right hand sample are due to cracking of the gold-palladium coating) indicates that the binder was molten during the combustion. The pressure dependence of the oxidizer particles' position with respect to the binder coupled with the ability of the binder to become molten could explain why some polyurethane-AP propellants do not sustain combustion at pressures above approximately 800 psia as reported in Refs. 3, 4,

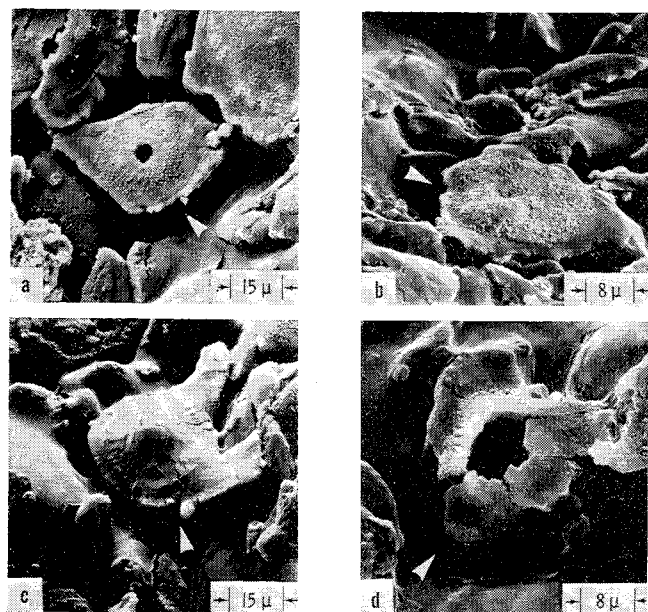


Fig. 2 SEM micrographs of ammonium perchlorate-polyurethane propellant quenched from 100 psia (a,b) and 200 psia (c,d). White arrow indicates undercutting.

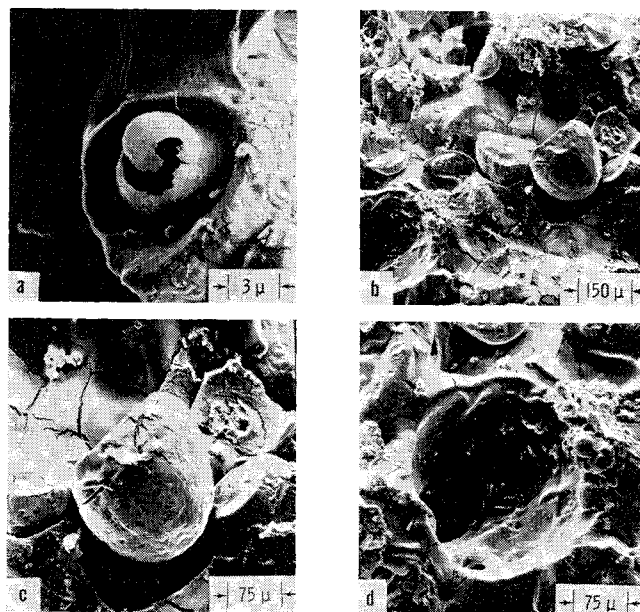


Fig. 3 SEM micrographs of quenched samples of ammonium perchlorate-polyurethane propellant.

5, and 6. As the pressure is increased the regression rate of the AP eventually becomes greater than the binder regression and the molten binder then is able to flow over the AP crystals inhibiting their combustion and causing extinguishment. Other SEM pictures taken during this study confirm this hypothesis.

The samples obtained at 100 psia (Fig. 1a, c) also indicate that the oxidizer particles were undermined. Figure 2 presents SEM photographs of samples consisting of 22% polyurethane binder and 78% 50-micron AP which were burned at pressures of 100 psia (Fig. 2a and b) and 200 psia (Fig. 2c and d). All views shown in this figure indicate definite undercutting of the PU at the oxidizer particles' boundary. Although some investigators may interpret undercutting as indicating that interfacial reactions occurred between the AP and the binder, this is unlikely in view of the investigations of Hightower and Price.<sup>7</sup> In any case, such undercutting shows the error in using a one-dimensional description of the combustion.

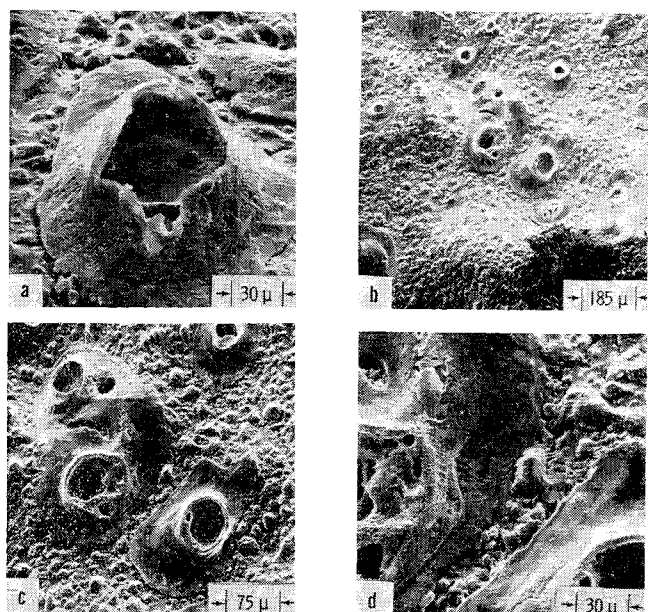


Fig. 4 SEM micrographs of ammonium perchlorate-carboxy terminated polybutadiene propellant quenched at 600 psia.

Figure 3 contains photographs of samples, burned at 600 psia, of the same propellant as seen in Fig. 1. The bubble formation on the AP crystal shown in Fig. 3a is typical of structures that have been observed in studies of AP deflagration using single crystals,<sup>8</sup> and has been interpreted as indicating that the surface of the AP is covered by a thin molten layer. Gases formed from the decomposition within the molten layer expanded during rapid depressurization causing the bubble formation as the AP "froze." Indeed it would be difficult to explain the bubble-like structure without assuming the existence of a liquid state. Similar types of structures are evident in Fig. 2 and 4 as well as the majority of the samples studied. The volcano-like structure seen in Fig. 2a and 2d, and the vented structure shown in Fig. 2c also indicate that subsurface reactions have taken place within the liquid portion of the AP prior to quench.

By mechanically stressing the quenched samples it was possible to break the AP-binder bond, thereby releasing the AP particles, as seen in Fig. 3b-d. The unreacted surfaces of the AP particles which were in the binder, and the sharp edges of the resulting craters seem to indicate that no subsurface or interfacial reactions took place between the binder and the AP particles.

In order to explore a possible effect of binder-type on the surface structure, a propellant containing a CTPB binder was tested at pressures of 200, 500, and 600 psia. Results from the tests at 600 psia are shown in Fig. 4 and are typical of the results obtained at the other pressures (at the lower pressure the oxidizer particles protruded above the binder to a greater height). Figure 4a again indicates that the surface of the AP crystals was molten and that subsurface reactions resulted in gas liberation within the molten phase. The photograph seen in Fig. 4d seems to indicate that interfacial reactions did not occur at the CTPB-AP interface.

### Conclusions

- 1) Previous observations that AP crystals protrude above the binder at low pressures and are recessed at high pressure were verified.
- 2) The polyurethane binder melts during burning to the extent that at higher pressures, where the oxidizer particles are recessed, the molten binder is able to flow over the AP crystals providing an explanation for the self-extinguishment of polyurethane propellants at high pressure.
- 3) Interfacial or subsurface heterogeneous reactions between the AP and binder were not apparent at all pressures for either the PU or the CTPB propellants. However, at low pressures where the AP protruded above the binder, there appeared to be an undermining of the AP crystals in the PU propellant but not in the CTPB propellant.
- 4) The AP crystals were observed to form a thin, surface melt and undergo subsurface reactions in the molten phase with in-depth liberation of gas resulting in bubbles and volcano-like fumaroles.

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## Ion Density Profile across a Shock in a Partially Ionized Gas

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IT is very important to investigate a shock structure in a partially ionized gas in relation to the problem of a vehicle in an ionosphere. In order to investigate whether ions follow the Rankine-Hugoniot relation in a partially ionized gas, an ion density profile across a shock has been measured with the Langmuir probe technique in a plasma jet wind tunnel,<sup>1</sup> and the experimental result has been compared with the theoretical one. Schematic diagram of the measurement configuration is shown in Fig. 1. Measured profiles of ion density across the shock and in the free stream are shown in Fig. 2, which shows that the ion density upstream of the shock decreases due to the effect of recombination or diffusion and that the ion density behind the shock does not increase up to the value given by the Rankine-Hugoniot relation. Assuming that all particles have the same velocity  $u_1$  upstream of the shock and that  $u_1$  is constant, the relation between  $1/n_i$  and  $z/u_1$ , where  $n_i$  is the ion density and  $z$  the distance along the flow, can be obtained from Fig. 2 as shown in Fig. 3. The following equation can be obtained easily from Fig. 3:

$$1/n_i = (\eta z/u_1) + K \quad (K: \text{constant}) \quad (1)$$

where  $\eta$  is the coefficient of the ion density decay. Equation (1) shows that the ion density decreases with time in the recombination type, but, when  $\eta z/u_1$  is very small, the relation between  $1/n_i$  and  $\eta z/u_1$  is approximately linear even in the diffusion-type decay. Equation (1) leads us to the following

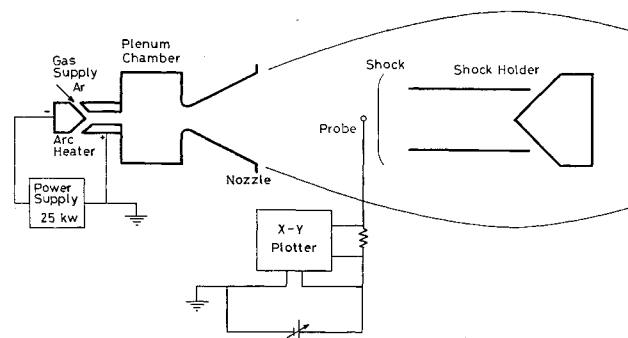


Fig. 1 Schematic diagram of measurement configuration.

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