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NWC TP 4723

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TECHNICAL ARTICLE 20

THE ROLE OF THE SCANNING ELECTRON MICROSCOPE IN THE STUDY OF SOLID ROCKET PROPELLANT COMBUSTION

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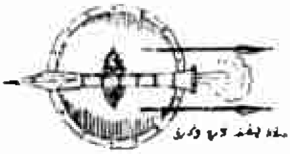

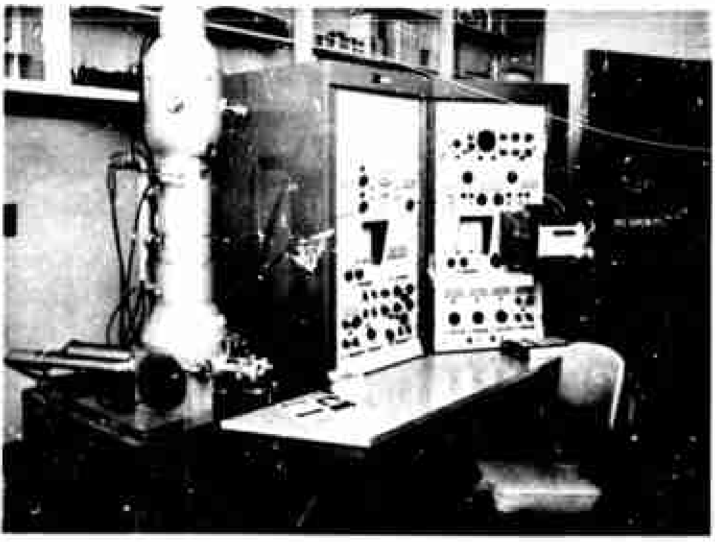

FIG. 1. Scanning Electron Microscope.

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The authors are indebted to Dr. W. R. McBride of the Naval Weapons Center for providing the large crystals of ammonium perchlorate used in our studies and to Dr. R. L. Derr of Lockheed Propulsion Co., Redlands, Calif., for providing some of the quenched samples and for helping to interpret the SEM micrographs taken of the quenched propellant samples.

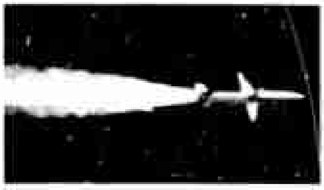
FOREWORD

The combustion of composite solid propellants is a complex process involving the interaction of a combustion wave with the various propellant ingredients. In order to understand the propellant combustion, the response of the various ingredients to the temperature and heating rates of the combustion wave must be known. One tool that has been used to provide such data is the scanning electron microscope (SEM).

The ammonium perchlorate decomposition and deflagration research was supported by the Office of Advanced Research and Technology of the National Aeronautics and Space Administration (NASA) under Work Order 6030 and by the Naval Ordnance Systems Command under ORD-033 129/200 1/R001-06-01, Problem Assignment No. 5. The metal agglomeration and combustion was supported by NASA under Work Order 6032. The surface structure of quenched composite propellants was a joint effort between Naval Weapons Center (NWC) (under NASA Work Order 6030) and Lockheed Propulsion Co., Redlands, Calif (under Air Force Contract F04611-67-C-0089).

This report has been prepared primarily for timely presentation of information. Because of the continuing nature of this research program, refinements and modifications may be made later in this study.

K. H. ROBINSON, *Head*
Technical Information Department



While attending the Berkeley campus of the University of California, Mr. Boggs participated in the Engineering Cooperative Work-Study Program (Co-op). Under a cooperative arrangement between the Naval Weapons Center and the University, Co-op students would spend a semester and a summer session at the University and the rest of the summer and the ensuing semester working at NWC. After graduation in December 1966, with a B.S. degree in mechanical engineering, Mr. Boggs returned to China Lake and subsequently joined the Aerothermochemistry Division of the Research Department. Currently he does research on oxidizer deflagration, propellant combustion mechanisms, and bulk mode combustion instability of solid propellants.

Mr. Boggs is an active member of the China Lake section of the American Institute of Aeronautics and Astronautics.

THE ROLE OF THE SCANNING ELECTRON MICROSCOPE IN THE STUDY OF SOLID PROPELLANT COMBUSTION

by

Thomas L. Boggs
Jack L. Prentice
Karl J. Kraeutle
James E. Crump

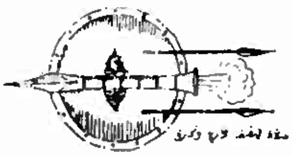
Jack L. Prentice received a B.S. degree in chemistry from California State Polytechnic College, San Luis Obispo, Calif., in 1959 and joined NWC following graduation. With the exception of a 1-year leave of absence to do graduate study in physical chemistry at the University of California, Davis, Calif., he has been continuously employed at NWC. Mr. Prentice has conducted research in the fields of high-temperature polymorphic transition of explosives, synthesis and characterization of properties of nitrogen complexes of light metal hydrides, flashdown combustion instability of solid propellants, and metal particle combustion. He has been engaged in the study of metal combustion for the past 6 years and is currently a member of the Fundamental Combustion Research Branch, Aerothermochemistry Division, Research Department.

Mr. Prentice is listed in *American Men of Science.*

Karl J. Kraeutle attended the University in Munich to study physics, chemistry, and meteorology. He did his thesis work in mass spectrometry and isotope research, and graduated with a Ph.D. degree in physical chemistry. After graduation, Dr. Kraeutle worked at Siemens and Halske Co. in Munich in the field of ferrite technology. His main endeavor was the application of laboratory results to large-scale production. Immigration to this country led him to the Naval Ordnance Station, Indian Head, Md., where he worked on problems of gas analysis (mass spectrometry) and solid decomposition. In June 1965, Dr. Kraeutle came to NWC. As a member of the Aerothermochemistry Division, he is currently studying the kinetics and mechanisms of oxidizer decomposition, the interaction and reactions of propellant ingredients during decomposition, and subignition phenomena of metal combustion.

James E. Crump received his B.S. degree in physics from Purdue University in February, 1953. Upon graduation he joined the Rocket Department at NWC. After a year in the Junior Professional Development Program, he worked on the design of small caliber air-to-air rockets and later was assistant project engineer on the original Sidewinder 1C propulsion system. In 1958 he transferred to the Research Department, where he has done work in combustion instability in solid propellant motors and steady-state combustion of metallized propellants. Currently he is engaged in the study of the combustion of fuel-rich plumes in ducted air combustion chambers and is Head, Applied Combustion Research Branch.

Mr. Crump is a member of the Research Society of America and the American Institute of Aeronautics and Astronautics.



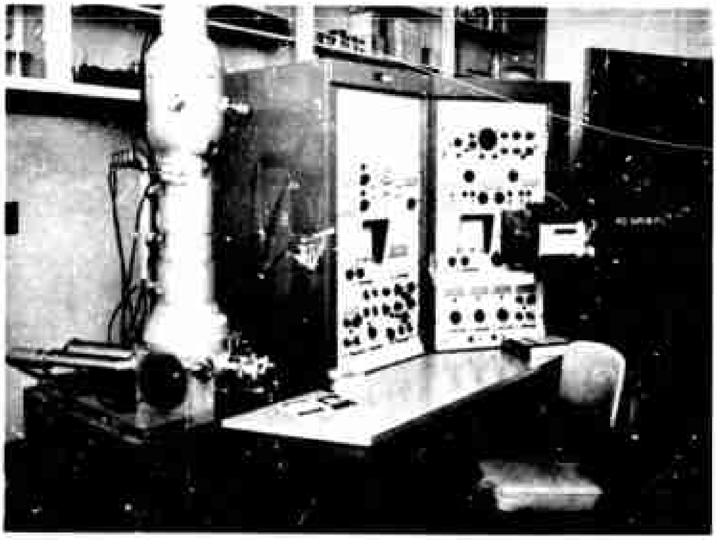


FIG. 1. Scanning Electron Microscope.

INTRODUCTION

Since the 13th century, when the Chinese introduced primitive powder rockets, man has been intrigued by the idea of reaction propulsion: a means of locomotion whereby a force is imparted to a device by the momentum of ejected matter. Unfortunately, ever since those first rockets were fired, the art of rocket propulsion has advanced more rapidly than the science of reaction propulsion. This discrepancy is due to our inability to describe qualitatively and predict quantitatively the combustion behavior of propellants. Until complete knowledge of the physicochemical reactions and interactions of all the various propellant components is obtained, the formulation, testing, and use of propellants will remain an empirical process. This is no reflection on the scientific competence of those engaged in combustion research, but merely reflects the realities of an exceedingly difficult area of applied science.

A typical composite solid propellant is a heterogeneous mixture of a crystalline oxidizer (usually ammonium perchlorate), a polymeric fuel binder, and often a powdered-metal fuel additive. The combustion of this mixture is a complex process involving the interaction of a combustion wave with the propellant ingredients.

Our investigations were undertaken to provide insight into the reactions of individual ingredients, first singly and then in combination with other ingredients. An essential tool used in the investigation was the scanning electron microscope (SEM) shown in Fig. 1. The photomicrographs obtained with this device have enabled us to infer mechanisms of the following processes: (1) oxidizer decomposition and deflagration, (2) metal-particle agglomeration and combustion, and (3) the interactions of oxidizer, binder, and metal particles during combustion. In many cases, SEM analysis permitted a choice to be made among several competing hypotheses or else the proposition of a new hypothesis.

It is the purpose of this paper to discuss the role of the SEM in investigating solid propellant combustion, rather than to present a detailed description of combustion processes. For a more detailed treatment of propellant combustion dynamics, Ref. 1 through 14 may be consulted.

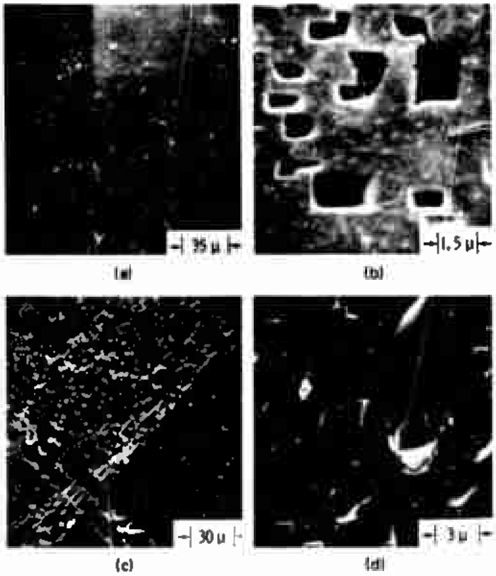


FIG. 2. Decomposition Site on m-Face of Ammonium Perchlorate Single Crystal After 90-Minute Decomposition (a, b) and on c-Face After 120-Minute Decomposition (c, d) at 226°C and Atmospheric Pressure.

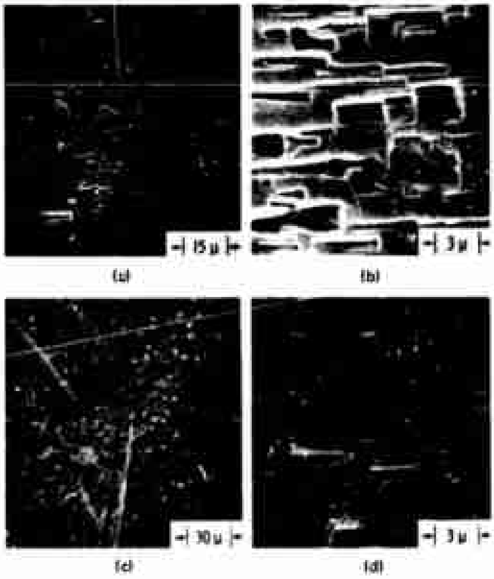


FIG. 3. Decomposition Site on m-Face of Ammonium Perchlorate Single Crystal After 40-Minute Decomposition (a, b) and on c-Face After 60-Minute Decomposition (c, d) at 226°C and a Pressure of 20 mm Hg.

OXIDIZER DECOMPOSITION AND DEFLAGRATION

Crystalline ammonium perchlorate, used in granular form, is the oxidizer and principal ingredient (about 70 to 80% by weight) in most composite solid propellants, and its behavior in the combustion zone greatly influences the overall combustion of the propellant.

The crystal structure of ammonium perchlorate is orthorhombic below 240°C and cubic above 240°C. This material decomposes at low temperatures (200 to 350°C) and at low heating rates (below 100°C/min) by a proton transfer process:

$$NH_4ClO_4 \underset{k_2}{\overset{k_1}{\rightleftarrows}} NH_3 + HClO_4 \qquad (1)$$

At high pressures (300 psia or higher), ammonium perchlorate is capable of self-deflagration. The crystals will continue to burn in an inert atmosphere once they have been ignited. Our research has been concerned with both low-pressure, low-temperature decomposition and high-pressure, high-heating-rate deflagration.

Decomposition of Ammonium Perchlorate

Ammonium perchlorate decomposes under the conditions given above until approximately 30 to 35% by weight of the sample has reacted. The product is a highly porous residue that cannot be satisfactorily studied with the optical microscope because the residue (1) appears opaque in transmitted light, (2) causes strong diffused reflection of incident illumination, and (3) cannot be resolved because of the inadequate resolution and depth of focus of the optical microscope. By contrast, the SEM offers resolution and depth of focus necessary to study the microstructure of partially decomposed ammonium perchlorate.

Decomposition occurs at active sites scattered over the surface rather than on the whole surface at once. Figure 2 shows decomposition sites on an m-face and on a c-face of a crystal that was deocmposed for 90 and 120 minutes at atmospheric pressure at 226°C. The sites on an m-face are composed of many rectangular holes, while those on a c-face are composed of rhombic holes. The decomposition sites therefore reflect the growth habit of the orthorhombic crystals, which have rectangular m-faces and rhombohedral c-faces.

Micrographs of decomposition sites taken at atmospheric and subatmospheric pressures have been used to illustrate the pressure dependence of ammonium perchlorate sublimation. As shown in Fig. 2 and 3, the samples that were decomposed at atmospheric pressure and 226°C for 90 to 120 minutes (Fig. 2) have smaller holes than do the samples that were decomposed in vacuum at 226°C for 40 to 60 minutes (Fig. 3).

The decomposition of a single crystal in vacuum includes two simultaneously occurring reactions: namely, (1) the interface decomposition leading to a porous residue (30 to 35% weight loss) and (2) the vacuum sublimation of the porous residue. Due to this sublimation, only a thin (approximately 100-micron) residue layer envelopes the undecomposed crystal core. Figure 4 shows the surface typical for a residue that sublimed in vacuum. The c-face at the top of the picture is characterized by a streak structure, whereas the two visible m-faces exhibit shallow dips.

Deflagration of Ammonium Perchlorate

The deflagration of single crystals of pure ammonium perchlorate was studied to determine (1) the variation of the deflagration rate as a function of pressure, (2) the surface structure of the deflagrating samples, and (3) the subsurface profile associated with the deflagration. From these observations we postulated energy transfer modes.

FIG. 4. Ammonium Perchlorate Single Crystal in an Advanced State of Decomposition in Vacuum (20 mm Hg).

Data on the variation of deflagration rate versus pressure in a nitrogen atmosphere, from our investigations and those of other laboratories, are compared in Fig. 5. Above 2,000 psia, the data are in disagreement. Levy and Friedman (Ref. 1), in explaining their findings, suggest that the rate simply continues to rise as a function of pressure. Bobolev and others (Ref. 2) and Glaskova (Ref. 3) suggest that above 2,000 psia, the rate decreases with increased pressure until a pressure of 4,000 psia is reached, at which time the rate again increases. Our results, obtained by cinemicrophotography, confirm the latter view. Some difference in the actual values obtained might be expected because they used pressed pellets of ammonium perchlorate and we used single crystals.

We observed that the data on single-crystal deflagration rate define a curve that appears to fall naturally into four regimes (Fig. 6). Such a division is important only if it allows one to correlate observations from many sources by the regimentation so imposed. SEM micrographs, cinemicrophotography films, and other observations confirmed the existence of the four regimes, which are described in Table 1. The four

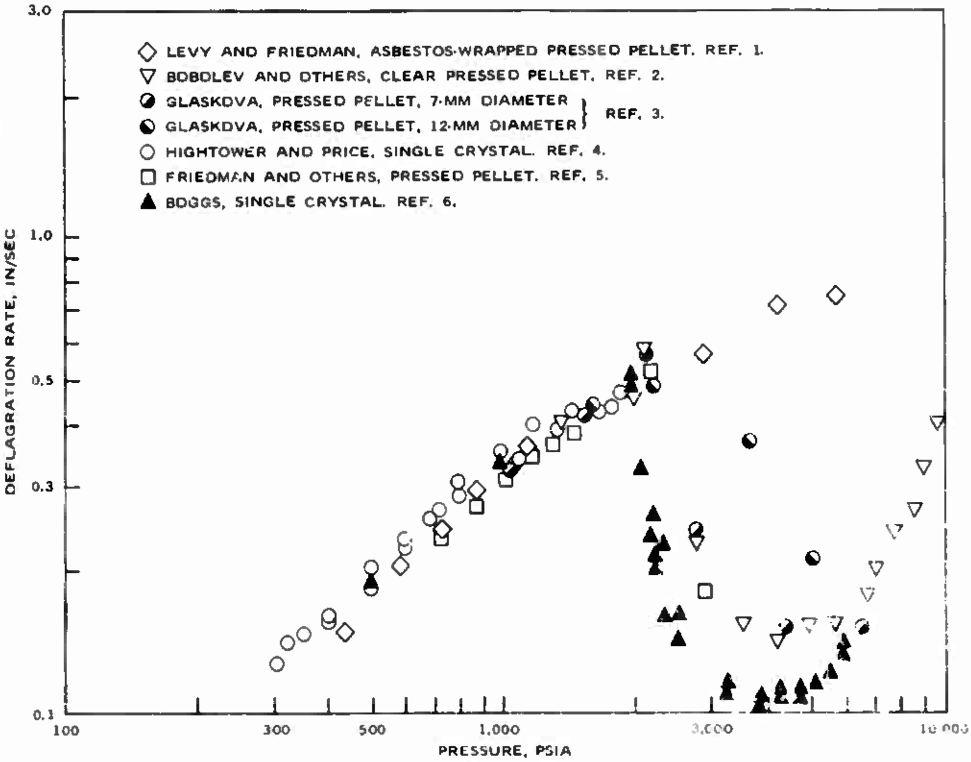


FIG. 5. Deflagration Rate of Ammonium Perchlorate in a Nitrogen Atmosphere.

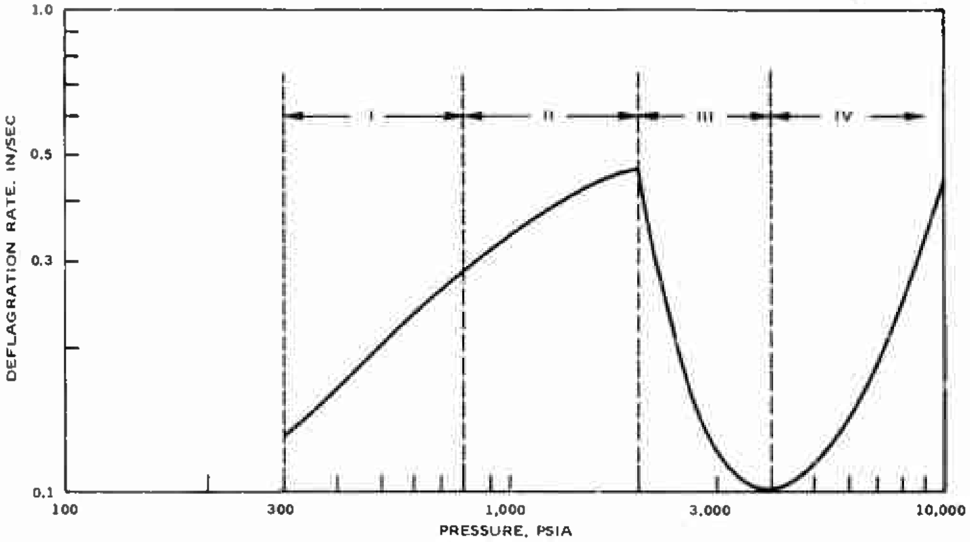


FIG. 6. Deflagration Rate of Single Crystals of Ammonium Perchlorate in a Nitrogen Atmosphere, Showing the Four Regimes.

TABLE 1. Deflagration Behavior of Single Crystals of Pure Ammonium Perchlorate.

Behavior	Regime I	Regime II	Regime III	Regime IV
Pressure, psia	300 to 800	1,000 to 2,000	2,000 to 4,000	Greater than 4,000
Deflagration rate, in/sec	0.13 to 0.34	0.34 to 0.48	0.48 to 0.10	Greater than 0.10
Rate (r) as a function of pressure (p) increase	$r = cp^n$ where pressure exponent $n = 0.77$, and c is a constant	Decreasing positive dr/dp	Negative dr/dp	Positive dr/dp
Surface				
Regression	Steady; planar	Steady; macroscopically planar	Intermittent; nonplanar	Steady; macroscopically planar
Characteristic	Gas entrapped in liquid, resulting in a froth	Ridges and valleys with activity sites in valleys; surface pattern spatially invariant with time	Needles in areas of maximum regression	Entirely covered by needles
Change in characteristic as a function of pressure increase	Thickness of liquid layer decreases, amount of gas increases	Length of ridges decreases; activity sites change from froth to vigorous gas reaction sites (and a few needles)	. . .	Degree of erosion increases
Subsurface				
Characteristic	Froth on cubic phase; cubic phase on orthorhombic phase	Ridges and valleys composed of cubic phase; activity sites extend depth of cubic phase	Thickness of layer of needles about 200 to 300 μ; no needles at areas of minimum regression	Surface layer of needles on crystal
Changes in characteristic as a function of pressure increase	Cubic-phase thickness decreases; froth appears to decrease	Cubic layer under valleys decreases; height between ridges and valleys increases	. . .	Insufficient data
Energy transfer	"Exothermic froth"	Condensed phase and gas phase coupled	Intermittent flame; localized decomposition in needle array	Steady flame, with uniform array of needles

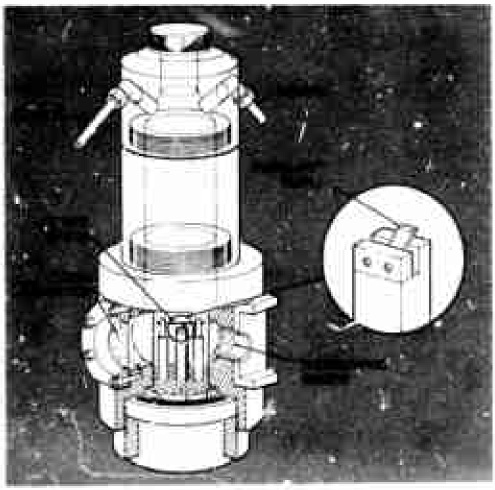


FIG. 7. Combustion Chamber.

regimes characterize the deflagration of ammonium perchlorate crystals at pressures from 300 to 10,000 psia, thus permitting predictions of crystal behavior during deflagration from a knowledge of the pressure.

The descriptions of surface and subsurface profile characteristics listed in Table I are based on SEM micrographs of single crystals that were rapidly quenched while undergoing deflagration. This deflagration and quenching took place in the combustion chamber shown in Fig. 7. The sample was held in a copper vise and ignited by a hot wire in an inert, but upward-moving, atmosphere of dry nitrogen gas at the desired pressure. The flow of this gas carried away exhaust products and permitted a clear view of the burning sample. Motion pictures were taken of the burning sample with a high-speed camera at rates of 400 and 4,000 frames per second and magnifications of 2X and 4X. These motion pictures provided us with a view of the combustion process and in many cases helped us to interpret the SEM pictures taken later. As the deflagration wave approached the copper vise, the sample lost energy to the metal of the vise and was thermally quenched. The quenched samples were coated

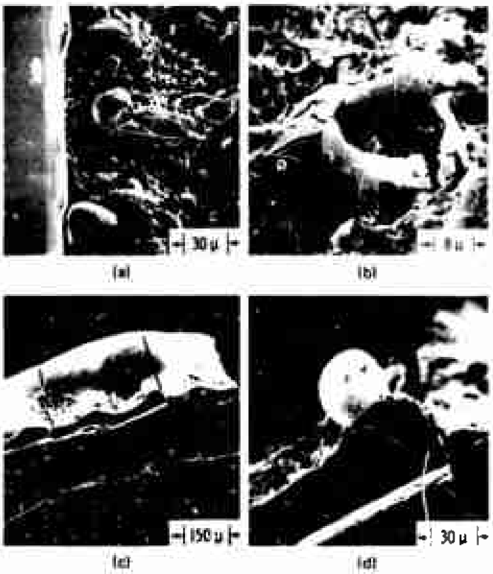
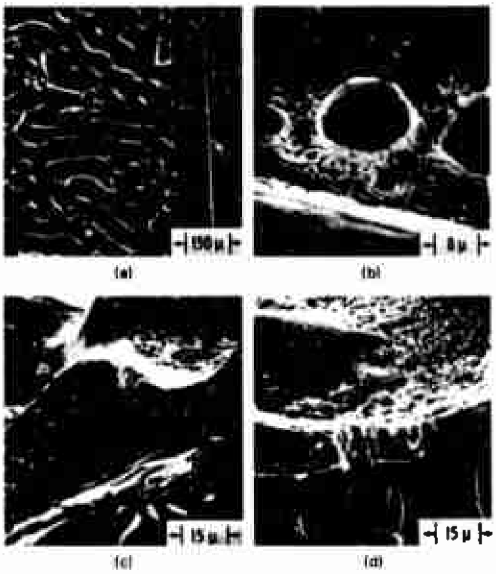


FIG. 8. Quenched Ammonium Perchlorate Samples From Regime I. (a, c, d) About 300 psia; (b) 600 psia.

with a gold/palladium alloy and examined with the SEM. The samples were then removed from the SEM, cleaved perpendicular to the quenched surface (thus exposing the deflagration profile), and again examined with the SEM, this time to see the details of the subsurface profile.

SEM micrographs taken of samples from Regime I indicate that the surface was covered with a froth caused by gas that evolved through a liquid layer (Fig. 8). This observation permitted a choice to be made between two competing hypotheses. The widely accepted assumption that the mechanism of ammonium perchlorate deflagration is the same as that of decomposition (i.e., sublimation) was not seriously questioned until Hightower and Price (Ref. 4) observed a cooled froth on the surface of quenched samples that they examined with an optical microscope. SEM analysis revealed the details of this froth, and it was apparent that a melt had been present on the surface of the deflagrating sample. Such observations proved that the sublimation hypothesis does not describe the deflagration. The froth on the ammonium perchlorate crystal surface was shown to be roughly 1 to 5 microns thick on the 300- and 600-psia samples and present only in patches on samples burned at 800 to 900 psia. Examination of the profile showed that the thickness of this froth decreased with increased pressure and that it covered a layer of cubic-phase ammonium perchlorate overlaying the original orthorhombic phase. The well-defined interface between the cubic and orthorhombic phases indicates the location of the 240°C isotherm within the crystal. Knowledge of the position of this isotherm and of the regression rate as a function of pressure allows a calculation of the surface temperature of the deflagrating crystal (Ref. 15). The results obtained with the SEM were more precise than those that Beckstead and Hightower (Ref. 15) obtained with the optical microscope and were in agreement with the best line drawn through their data.

Samples from Regime II differed from those of Regime I in that there was no longer a liquid on the surface; rather, the surface was characterized by a pattern of ridges and valleys (Fig. 9a), with sites of increased activity at the bottom of the valleys (Fig. 9b). Ridge length was found to vary inversely with the



(a) (b)

(c) (d)

FIG. 9. Quenched Ammonium Perchlorate Samples From Regime II. (a, b, d) 1,200 psia, (c) 1,500 psia.

pressure (over 500 microns long at 1,000 psia, and less than 100 microns at 1,800 psia). Just as the ridge structure was pressure dependent, so were the sites of increased activity (reaction) at the bottom of the valleys. The samples quenched at 1,000 psia show frothy residue in the valleys. The samples quenched at 1,200 psia also show frothy material as well as holes of complex geometry indicative of localized activity. At 1,500 psia, an array of needle-like structures appeared in some of the holes. This feature becomes increasingly evident with increasing pressure.

The profiles of Regime II samples present evidence of the complex nature of the combustion. The cubic-phase thickness was greater under the ridges than under the valleys (Fig. 9c). This difference in thickness indicates that the regression rate of the ridges was less than that of the valleys, that the temperature gradient through the ridges was not as steep as that under the valleys, and that heat was transferred in three dimensions (including conduction of heat in a direction perpendicular to the direction of surface regression). This interpretation would explain why the ridges frequently peeled off from the surface without burning, as seen in the high-speed motion pictures. Figure 9d indicates that the activity sites of the valley extended below the surface for a depth almost equivalent to the cubic-phase thickness.

The surfaces of the Regime III samples show pronounced depressions with extensive areas of needles (Fig. 10). The micrographs of the profiles indicate that the needles extend 200 to 300 microns from the surface of the pocket. Studies using cinemicrophotography identified the origin of these depressions and helped explain why the needles exist only in the depressions. The high-speed motion pictures show localized orange flamelets over the surface; these flamelets change location as the burn progresses. Parts of the surface are seen to regress locally (causing the depressions seen in the micrographs) while adjoining areas seem temporarily stationary, with the flame standing over the recessed areas. Because the flame was observed to be in the depression, the lip seen in Fig. 10 provides an opportunity to view a portion of the sample that was partially exposed to the flame and at the same time

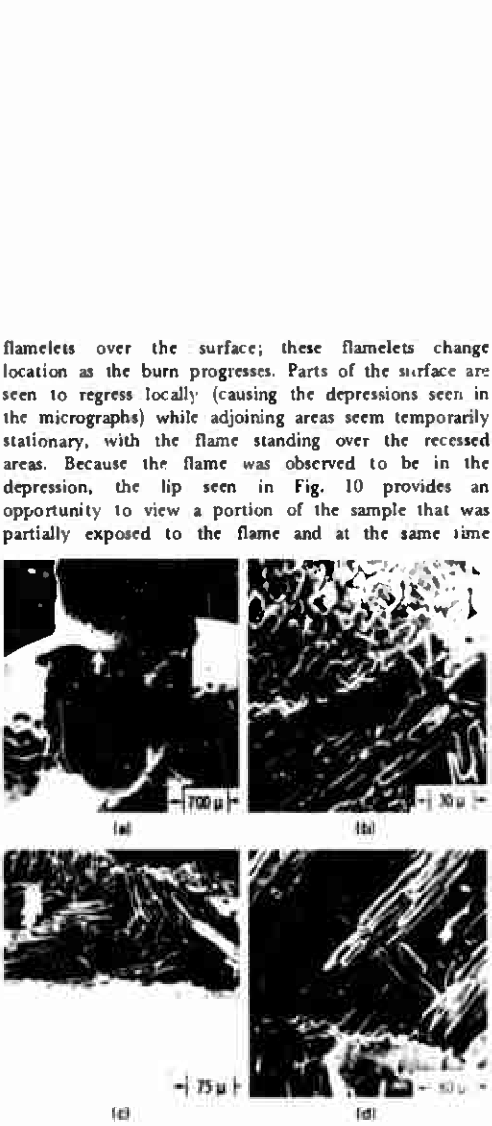
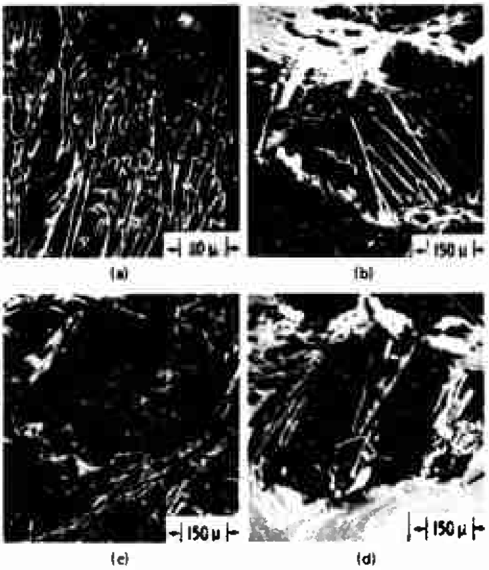


FIG. 10. Quenched Ammonium Perchlorate Samples From Regime III. (a, b, c) 3,300 psia; (d) 4,000 psia. Arrow in (a) points to lip.

view a portion that was shielded from the flame. The portion that the flame contacted exhibits the needle structure, whereas the shielded portion exhibits a different surface structure. Thus, by combining the SEM results with those obtained by cinemicrophotography, it is possible to show that the needle structures are indicative of proximity to the flame.

SEM micrographs taken of Regime IV samples show that needles cover the entire surface (Fig. 11), and the high-speed motion pictures show a pronounced orange flame adjacent to the burning surface, thus confirming the above hypothesis.



(a) (b) (c) (d)

FIG. 11. Quenched Ammonium Perchlorate Samples From Regime IV. (a, b) 4,200 psia; (c, d) 6,200 psia.

The use of cinemicrophotography to examine the dynamics of the combustion and the SEM to examine the microstructure of quenched samples has made it possible to study not only the self-deflagration of ammonium perchlorate crystals but also the burning of propellants and the agglomeration of metals. To illustrate how valuable these two tools are when used in conjunction, consider what we have learned about the energy transfer mechanisms occurring during self-sustained deflagration of a single crystal of ammonium perchlorate. At the low pressures of Regime I, we have seen that the surface is covered by a froth. It is our hypothesis that decomposition occurs either within or beneath the melt and that the exothermically reacting gas products are entrapped within the melt. The heat produced by the exothermic reaction is transferred by conduction through the froth to the unreacted solid, thereby providing the energy required for further decomposition. As the pressure is increased, the liquid becomes so thin that it ruptures into droplets, and it is these droplets that produce the valleys. The reactions become concentrated within the valleys, and three-dimensional heating occurs within the solid.

In Regimes I and II, energy is transferred from exothermic reactions occurring on the surface. In Regime I, reactions occur within the froth; in Regime II, they occur at activity sites (Fig. 9b) in the valleys. Energy is transferred to Regime III and IV samples by conduction from the gas flame. In Regime III this flame is unsteady, and consequently the deflagration rate of the crystal decreases as seen in Fig. 6. In Regime IV the flame is steady, and the deflagration rate increases.

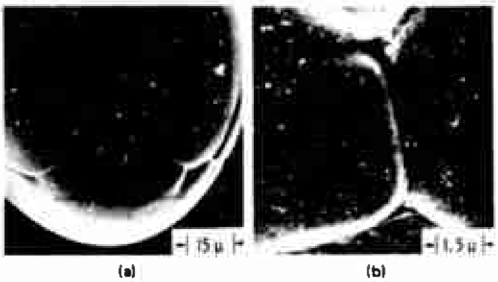


FIG. 12. Two Magnifications of an Unheated Spherical Aluminum Particle. Diameter is 105 µ.

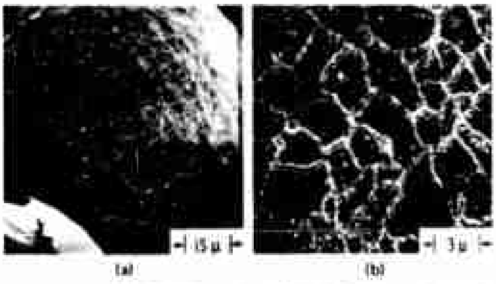


FIG. 13. Two Magnifications of an Aluminum Particle After Heating to 1,490°C at Atmospheric Pressure.

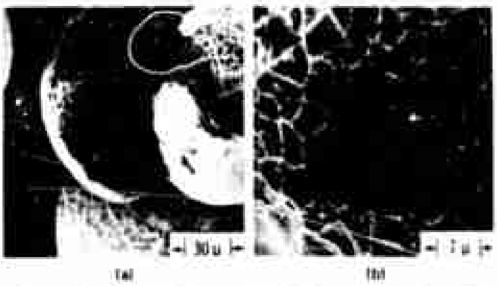


FIG. 14. Broken Aluminum Oxide Shell (a) and Close-Up of Inner Surface (b).

METAL AGGLOMERATION AND COMBUSTION

Metals are a useful propellant ingredient only if they react completely to finely subdivided products and do not impair other combustion characteristics such as stability and burning rate.

When a metallized propellant burns, metal tends to accumulate on the burning surface, agglomerate into larger particles, ignite only reluctantly (compared with other reacting ingredients), and burn relatively slowly while moving away from the surface. The process is complex, but the mechanisms have been substantially clarified by studies of behavior of single and multiple particles in simple laboratory situations. SEM analysis of the residues from these experiments has contributed to our understanding of the processes. These experiments reveal the nature and behavior of protective oxide on unignited particles, the breakdown of the oxide to permit sintering the agglomeration, and the ignition and combustion of particles. The observations allow us to interpret the behavior of metal ingredients during propellant combustion.

Preignition Behavior of Metals

The accumulation of metal particles on the surface of the propellant and subsequent agglomeration of these individual particles into larger particles have a marked effect on the combustion efficiency and stability of the combustion. For this reason, knowledge of the mechanism of agglomeration is of considerable importance in solid propellant research. Prior to this SEM study, no systematic laboratory-scale investigation of the agglomeration phenomenon had been reported.

When aluminum particles are incorporated in the propellant mix, they have an oxide coating resulting from exposure of the metal to the atmosphere. Once this oxide attains a thickness of a few hundred angstoms, it serves as a diffusion barrier to additional oxidation of the metal. Since rapid oxidation is necessary for efficient ignition, it was thought that the oxide layer would also hinder the combustion of the aluminum. It was assumed that the oxide coating would continue to be protective until the individual aluminum particles, exposed by the regression of the burning propellant, were convected from the surface and ignited in the flame; ignition would occur only after the aluminum oxide had reached its melting temperature (2067°C).

The occurrence of particle agglomeration on the burning propellant surface, which is at a temperature of about 700°C, contradicts the above assumption and indicates that reaction of the metal is occurring at these relatively low temperatures and that oxide protection, in the sense described above, is not controlling.

Agglomeration is undesirable for several reasons. It has a dilatory effect on the particle ignition; it decreases metal combustion efficiency because of the formation of very large particles (200 to 1,000 microns); and it produces thermal and velocity losses in the gas stream, thereby reducing overall propulsion efficiency.

To determine the details of the aluminum agglomeration, spherical aluminum particles (about 100 microns in diameter) were heated to temperatures between 600 and 1400°C in different gases at atmospheric pressure, and the resulting agglomerates were examined with the SEM. Figure 12a, b shows a typical aluminum particle before heating. Figure 13a, b shows a similar particle that was heated to 1400°C at a rate of more than 1000°C/sec. It can be seen that the unheated particle has a relatively smooth surface, whereas the heated particle has a network of "welded" seams covering a coarse surface.

Some of the heated particles displayed a network of seams on the surface and were also hollow (Fig. 14), indicating that the aluminum was molten and was able to flow out of the oxide shell. These observations are important because they indicate that the molten aluminum flowed out through cracks in the oxide shell and, on exposure to an oxidizing atmosphere, formed aluminum oxide that welded the crack closed. This flowing of molten metal and subsequent oxidation, or welding, is believed to be responsible for the formation of bridges between two or more particles (Fig. 15).

Samples heated at lower rates were also examined with the SEM, and they provided an explanation for the formation of the cracks. Micrographs in Fig. 16 show the surfaces of aluminum particles that were heated at a moderate rate (less than 900°C/min) in air to preset temperatures. The surfaces are still smooth at 690°C (Fig. 16a), cracked at 845°C (Fig. 16b), and granular at 1040 and 1200°C (Fig. 16c, d). The cracking, flowing, and welding (oxidation) sequence begins at the melting temperature of the aluminum and grows more severe due to the large difference in the coefficients of thermal expansion of liquid aluminum and solid aluminum oxide, the ratio being about 3:1. The aluminum oxide expands less rapidly than does the molten aluminum, and it therefore cracks.

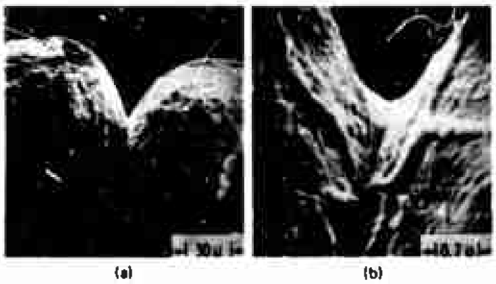


FIG. 15. Two Aluminum Particles Joined by Bridging (a) and Close-Up of Bridge Area (b).

Combustion of Single Metal Particles

Aluminum and beryllium are the most important metal fuels for rocket propulsion. The combustion of single particles of these and other metals has been the subject of extensive research. Application of the SEM as the major diagnostic tool in the study of the evolution of burning particle geometry has permitted significant progress in the interpretation of droplet combustion behavior.

In these experiments, a single particle (foil, sphere, or granule) is ignited by either a xenon-flash-discharge lamp or a neodymium-doped glass laser and permitted to burn while freely falling through a reaction chamber having

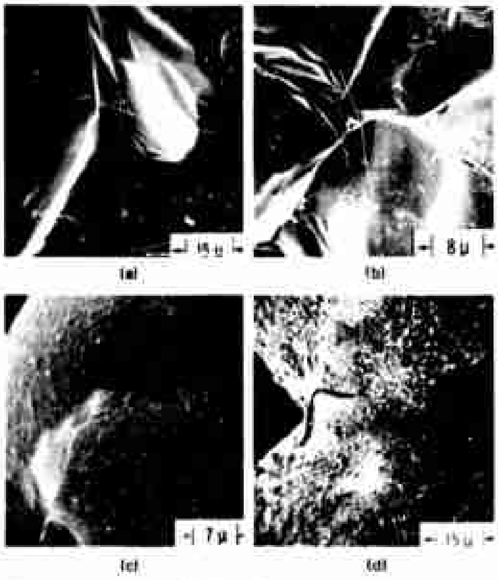


FIG. 16. Aluminum Particles After Heating in Hot Stage at Atmospheric pressure to 690°C (a), 845°C (b), 1040°C (c), and 1200°C (d).

an appropriate oxidizing atmosphere. To study the evolution of burning particle geometry, single particles are quenched on Pyrex plates located at various heights in the reaction vessel. These samples are then withdrawn for examination with the SEM.

Aluminum and beryllium are both said to burn by a "vapor-transport" mechanism. Most of the combustion is a reaction between metal diffusing from a vaporizing droplet and an oxidizer. This reaction is illustrated in Fig. 17. A characteristic feature of metal combustion reactions is the production of condensed oxide, usually in the form of smoke. In the combustion of many metals (especially aluminum and beryllium), this condensed oxide also diffuses back to the droplet surface, where it often accumulates in significant amounts. SEM examination of product accumulation on the burning droplet has provided a major advance in metal combustion research.

Aluminum. During the early days of aluminum particle combustion research, one of the hypotheses enjoying widest acceptance held that burning aluminum particles possessed a molten skin of aluminum oxide that became inflated during combustion by vaporization of the enclosed metal droplet. It was thought that continued vaporization caused the vapor pressure to exceed the surface tension of the oxide skin, resulting in the catastrophic droplet fragmentations that were widely observed. Quenched specimens examined with an optical microscope showed that burning aluminum particles did not in fact possess such a skin (Ref. 7 and 8). Rather, the oxide or other product formed a globule subsequent to the ignition and grew nonsymmetrically, producing a bilobate droplet. Although convincing, this low-power (about 60X) optical microscope examination revealed only the gross features of the droplet, and it was not until samples were examined with the SEM that the complex structure of the bilobate geometry became known. Figure 18 shows an example of a photomicrograph generated by each technique.

Significant detailed changes in the droplet geometry, which affect the mode of termination of droplet combustion, have been observed. The accumulation of

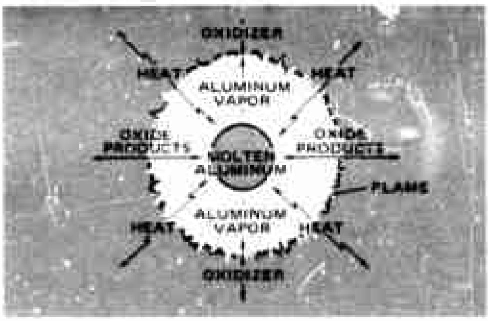


FIG. 17. Simplified Vapor-Transport Combustion Model for Metal Droplet Burning.

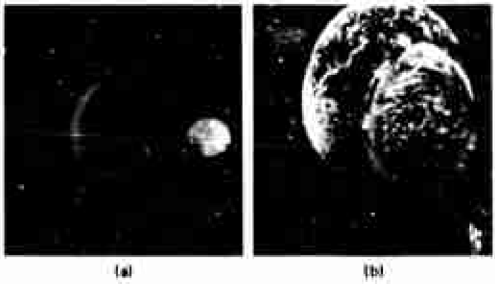

(a) (b)

FIG. 18. Comparison of Photomicrographic Techniques for Nominal 460-μ Aluminum Particles Quenched While Burning in Ambient Air. (a) Taken by optical microscope with long bellows and 32-mm lens; (b) taken by SEM.

product on the droplet prior to fragmentation may be seen in Fig. 19a, b, c, which is a composite of SEM photographs showing droplet evolution. The oxide globule on the droplet, formerly thought to be lens-shaped, is now seen to be a fumarole (Fig. 19b). Observations by SEM of changes in this fumarole-cap on numerous samples quenched after various burning times have assisted us in interpreting the processes leading to inefficient combustion and fragmentation of burning droplets (Ref. 8).


(a) (b) (c)

FIG. 19. Evolution of Burning Aluminum Droplet.

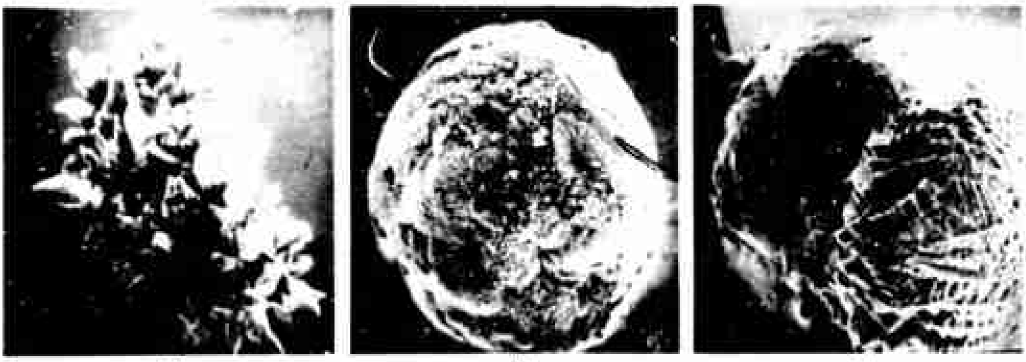

(a) (b) (c)

FIG. 20. Evolution of Beryllium Droplet Burning in 20/80 Oxygen/Argon.

Beryllium. Although beryllium appears to be a useful propellant ingredient, we lack knowledge of the combustion of this metal, primarily because of handling problems associated with the toxicity of the combustion products. Beryllium is unique among the metals used as fuels in rocket propulsion. The most significant property is that the melting point (2820°K) of the product oxide (BeO) is higher than the boiling point (2757°K) of the metal. This is important to the metal burning rate and mechanism, because it creates the possibility of oxide encapsulation and subsequent freezing, which will result in the termination of vapor-phase combustion. Few single-particle beryllium combustion studies have been performed to date, and prior to our recent investigation using the SEM (Ref. 9), no useful photographs of quenched beryllium particles existed.

The power of the SEM as a diagnostic tool, when used in conjunction with other sources of data, may be illustrated by citing a few major advances in the knowledge of beryllium combustion obtained by application of the SEM to what was an exploratory series of experiments.

A series of SEM micrographs is presented in Fig. 20a, b, c, showing the evolution of droplets formed from xenon-flash-ignited beryllium foils, with extensive growth of hexagonal BeO needles from the surface of the spongy, still-unmolten metal. The specimens indicate that the droplet temperature rises sufficiently to melt the encapsulating oxide, but that heat loss through radiation to the cold environment is sufficient to cause freezing of the oxide, which terminates combustion prematurely. Development of BeO needles and subsequent encapsulation of burning beryllium droplets had not been seen before this SEM investigation.

The effect of water on the metal combustion in the rocket motor environment is significant. Water, present as a combustion by-product, is postulated to affect the beryllium combustion according to the following:

$$BeO_{(s)} + H_2O_{(gas)} \rightleftarrows Be(OH)_{2(gas)}$$

In a dry environment, beryllium droplets become encapsulated with oxide, with subsequent freezing and quenching of the combustion. The process in Eq. 2 would be advantageous from the standpoint of removing the encapsulating oxide and improving the combustion efficiency of the metal.

The effect of water is shown in Fig. 21, which compares two flash-ignited beryllium particles burned in mixtures of 20% oxygen in argon and quenched after equal burning times. One atmosphere contained no water, and the other was saturated with water vapor at 28°C. These micrographs demonstrate conclusively that oxide is transported from the surface of the burning droplet in the presence of water, probably by means of the reaction in Eq. 2.

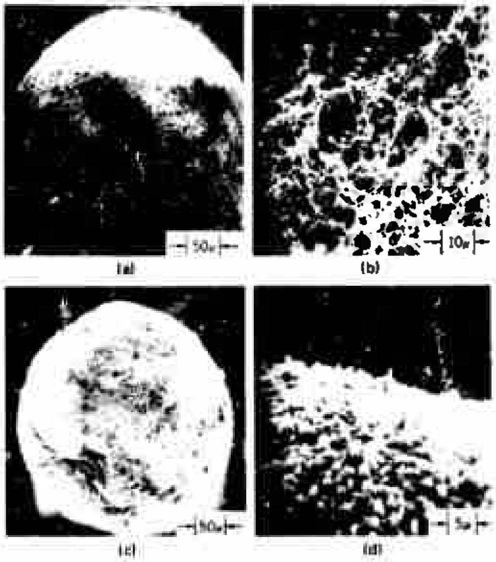


FIG. 21. Comparison of Droplets Showing the Effect of Water on the Combustion of Xenon-Flash-Ignited Beryllium Particles Burning in 20/80 Oxygen/Argon. (a, b) Particle burned in atmosphere saturated with water vapor, (c, d) particle burned in dry gas.

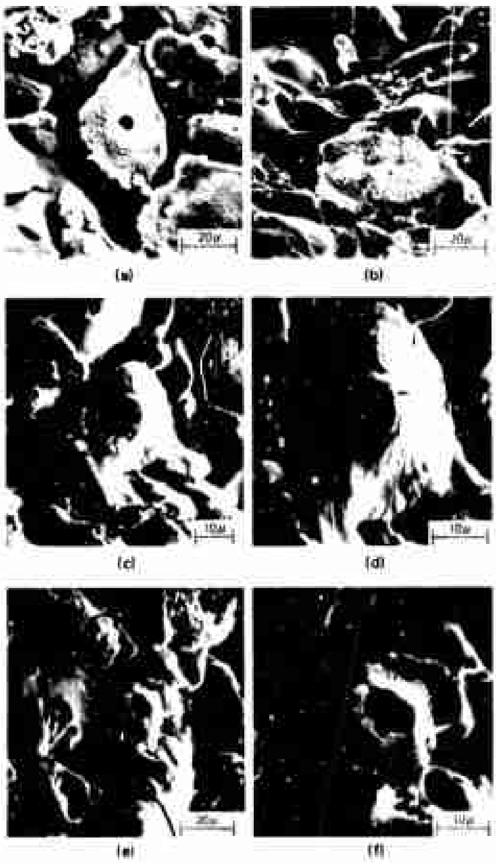


*FIG. 22. **Ammonium-Perchlorate/Polyurethane Propellant Quenched** at 100 psia (a, b) and at 200 psia (c, d, e, f).*

SURFACE STRUCTURE OF COMPOSITE SOLID PROPELLANTS

In order to predict quantitatively the combustion behavior of solid propellants, it is necessary to reduce the description of this behavior to a set of relations that are amenable to mathematical expression. The surface structure of a burning solid propellant must be considered when attempting to model the propellant combustion mathematically. The majority of models proposed for steady and nonsteady combustion of solid propellants treat the burning surface as a dry, planar, homogeneous entity with one simple Arrhenius expression describing the kinetics of the processes over the entire surface. For composite propellants, this obviously is not the case. One reason for such simplification is that the complex reality can be reduced to a more tractable mathematical representation. Another reason is that detailed information defining the structure of the surface accurately enough to construct such a model is not available. Because of the latter reason, we initiated an experimental investigation to provide a better understanding of the physical nature of the surface and to determine, if possible, the extent of heterogeneous or subsurface reactions. In this study, burning propellant samples were quenched and then examined with a SEM to infer the structure of the burning surface prior to quench.

The unmetallized propellants tested consisted of a crystalline oxidizer and either polyurethane or carboxyl-terminated polybutadiene (CTPB) binder. The propellants were formulated with oxidizer particles of one size, unimodally distributed, or oxidizer particles of two sizes, bimodally distributed, 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. 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, plated with a gold/palladium alloy of a few angstroms thickness, and examined and photographed with the SEM.

Results typical of this study are shown in Fig. 22-25. Figure 22 presents SEM micrographs of samples consisting of ammonium perchlorate and a polyurethane binder that were burned and quenched at 100 psia (Fig. 22a, b) and 200 psia (Fig. 22c, d, e, f). Inspection of the photographs reveals that at low pressures the pyrolysis rate of ammonium perchlorate was lower than that of the polyurethane binder, thus confirming the observation reported by Bastress (Ref. 16) that the ammonium perchlorate protrudes above the binder at low pressures. Also, the smooth appearance of the binder suggests that it was molten during burning. It is of interest to note that all of the views shown in Fig. 22 indicate definite undercutting of the binder at the binder/oxidizer-particle boundary. Such undercutting illustrates the error of using one space coordinate to try to describe the combustion. Figure 23 illustrates the effects of pressure on the surface structure. The photographs on the left (Fig. 23a, c, e) are of samples obtained at 100 psia; those on the right (Fig. 23b, d, f) were obtained at 800 psia. Both sets of samples conclusively demonstrate that the binder was molten prior to quench. At the lower pressure, the ammonium perchlorate crystals protrude above the binder surface, and undercutting is again noted. At the higher pressure, the crystals are recessed below the binder surface, to the extent that the molten binder has apparently flowed into the recesses and covered the crystal surfaces (possibly during extinguishment). This phenomenon provides an explanation of why some polyurethane propellants do not sustain combustion at pressures above approximately 800 psia, as previously reported in Ref. 10. As the pressure is increased, the regression rate of the ammonium perchlorate eventually becomes greater than that of the binder, and the molten binder then

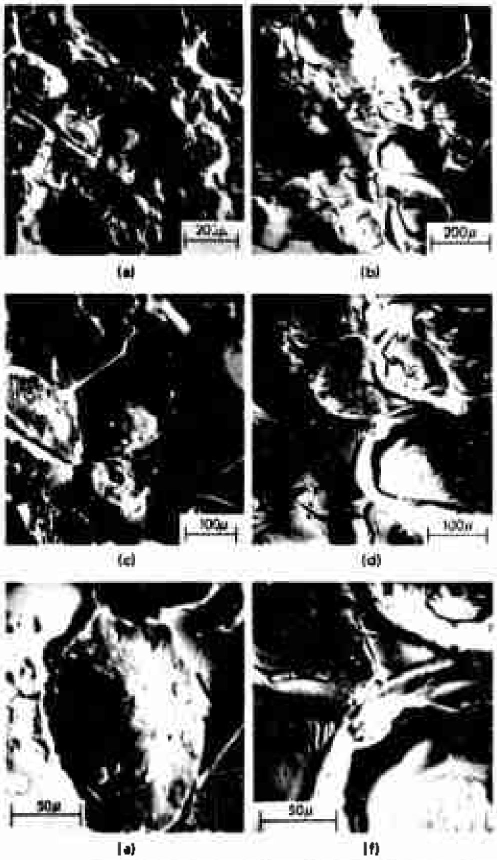


FIG. 23. Ammonium-Perchlorate/Polyurethane Propellant Quenched at 100 psia (a, c, e) and at 300 psia (b, d, f). Note the difference of position of oxidizer relative to binder for the two cases.

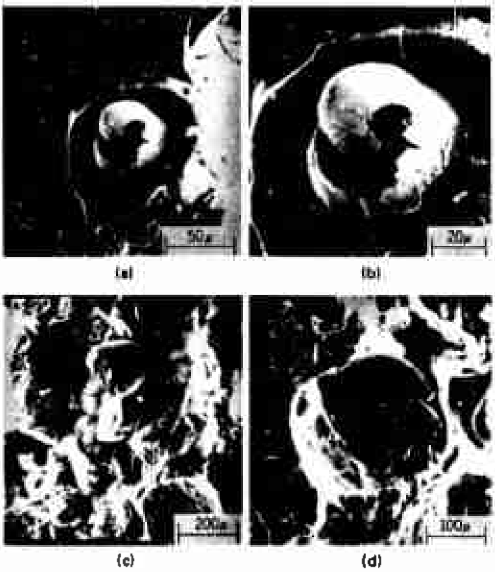


FIG. 24 Quenched Ammonium-Perchlorate/Polyurethane Propellant.

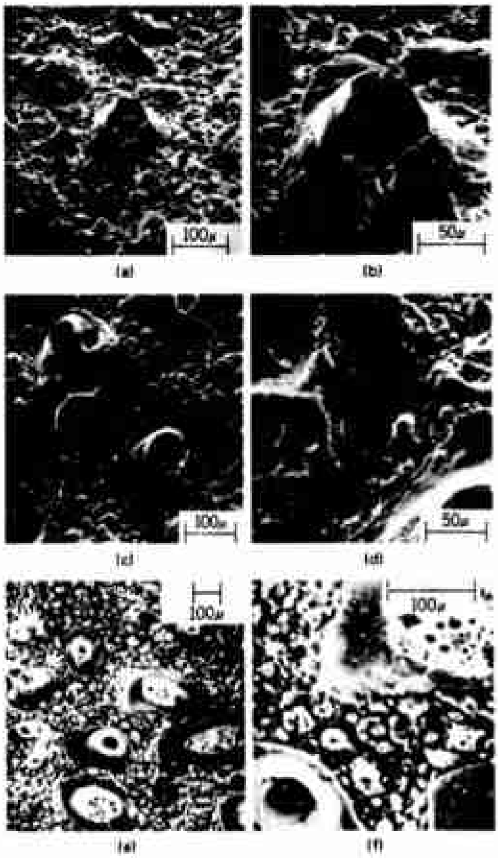
flows over the ammonium perchlorate crystals inhibiting their combustion and causing extinguishment.

Earlier we showed that, under certain conditions, ammonium perchlorate crystals have a surface melt. Prior to the SEM studies described herein, there had been considerable controversy surrounding the question of whether these crystals in the propellant matrix melted or sublimed during combustion. The SEM permitted us to make a detailed examination of quenched propellant samples, which showed that the ammonium perchlorate in a burning propellant is molten (Fig. 24 and 25). The bubble formation shown in Fig.

24 is similar to the structure seen in Fig. 8, which was interpreted as evidence that the surface of the ammonium perchlorate consists of a thin molten layer. Gases formed from the decomposition of the crystals within the molten layer expanded during rapid depressurization, causing the bubble formation as the melt froze. Indeed, it would be difficult to explain the bubble-like structure without assuming the existence of a liquid state. Similar structures are evident in Fig. 22 and 25, as well as in the majority of the samples studied. The volcano-like structure seen in Fig. 22a, e, f and Fig. 25 and the vented structure shown in Fig. 22c, d also indicate that condensed-phase subsurface reactions have taken place within the crystal prior to quench. These structures are in agreement with those observed when pure single crystals of ammonium perchlorate are burned, quenched, and examined.

By mechanically stressing the quenched samples, it was possible to break the ammonium perchlorate/binder bond, releasing the crystals as seen in Fig. 24. Examination of the displaced crystals shown in Fig. 24e and one of the craters left undisturbed in the binder, shown in Fig. 24d, shows no indication of subsurface or interfacial reaction between the ammonium perchlorate and the binder.

In order to explore the effect of binder type on the surface structure, a propellant containing a CTPB binder was tested. Results from these tests at 600 psia are shown in Fig. 25. The micrographs indicate that the surface of the ammonium perchlorate crystals was molten and that subsurface reactions in the molten phase of the amonium perchlorate resulted in gas liberation within the molten phase. The micrographs seen in Fig. 25d, f seem to indicate that interfacial reactions were not present at the binder/oxidizer interface at this pressure. No undermining was observed on samples obtained at other pressures, indicating a lack of interfacial reactions with the CTPB samples. Also,



(a) (b)

(c) (d)

(e) (f)

FIG. 25. Ammonium-Perchlorate/CTPB Propellant Quenched at 600 psia.

there is no indication of the CTPB binder melting, as there was with the polyurethane binder (that is, the binder does not have a smooth appearance or the "cracked-mud" appearance seen in Fig. 23).

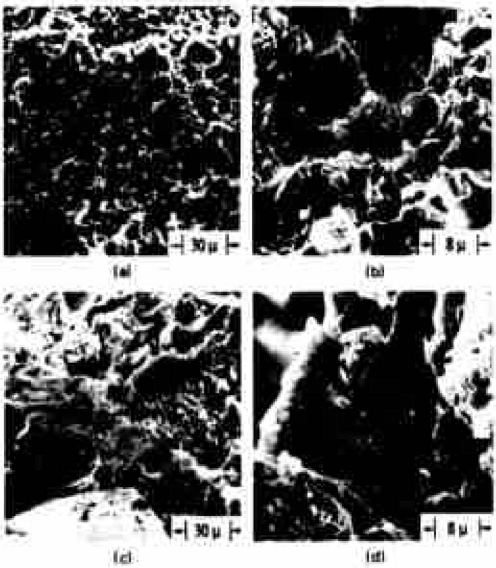


FIG. 26. Quenched Samples of Cyclotetramethylenetetranitramine/ Polyurethane Propellant.

Just as different binder types behave differently during combustion, so do different oxidizers. Figure 26 presents photomicrographs of a research propellant that contained polyurethane binder and HMX

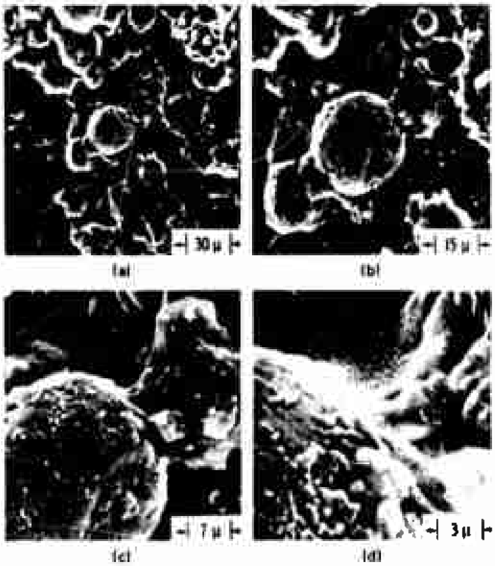


FIG. 27. Bridges Between Aluminum Particles on Quenched Surface of Propellant.

(cyclotetramethylenetetranitramine). The HMX behaved differently than the ammonium perchlorate in that it seemed to have reacted beneath the surface of the propellant. The melting point of HMX is about 280°C (compared with about 600°C for ammonium perchlorate), and therefore it is to be expected that HMX might melt beneath the surface of the propellant (while ammonium perchlorate would not). This may be seen in Fig. 26c, d. Figure 26d is a profile of a cleaved sample showing the depth to which the oxidizer will react.

The addition of aluminum to the propellant mixture introduces further complexity due to agglomeration. Quenched samples of aluminized propellant were obtained using the technique described earlier. The topology of the quenched surface was so irregular that high-magnification optical microscopy was unsatisfactory.

SEM micrographs (FIG. 27a, b, c, d) show that the aluminum particles (original nominal diameter of 15 microns) in the propellant agglomerate by bridging. The higher magnification pictures show vestiges of welded cracks across the bridge.

Figure 28a, b, c, d is another view of the quenched propellant. Again bridging of aluminum particles may be seen. With the large depth of field of the SEM, it is possible to see the aluminum agglomerates on the propellant binder and on ammonium perchlorate particles. Since the agglomeration of metal particles occurs on both the binder and the oxidizer surfaces, the inference is that the temperature and duration of exposure experienced by the particles are more important factors in the agglomeration than is the surrounding chemical environment. This is important because it allows us to perform meaningful laboratory tests of aluminum agglomeration and combustion without undue concern about the choice of oxidizer or binder.

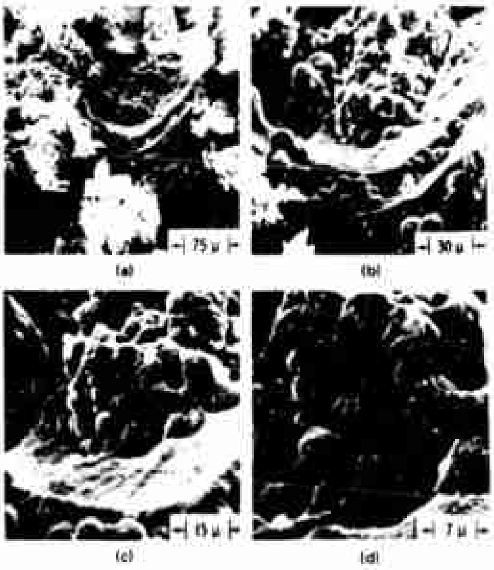


FIG. 28. Bridges Between Aluminum Particles on the Quenched Surface of Oxidizer and Binder of Propellant.

SUMMARY

The SEM has made contributions to several phases of propellant research. We have indicated in a limited way the complex interdisciplinary nature of the problem. In this report, which was prepared for persons not necessarily familiar with combustion research, it is difficult to summarize the large amount of information that we have obtained by using the SEM. Rather than just list the findings, we have chosen to group them under the headings of Phenomena Seen for the First Time, Controversies Resolved, and Hypotheses Originated. Such categorization more closely reflects how the SEM has assisted us in our research. In our application of the SEM to the problems of solid propellant combustion, phenomena that were observed for the first time were often used to resolve controversies concerning existing combustion or agglomeration mechanisms. Alternatively, these new findings often led to a rejection of existing mechanisms and to the hypothesis of new ones.

Phenomena Seen for the First Time

Among the significant phenomena seen for the first time are the following:

- Decomposition sites on ammonium perchlorate crystals, reflecting the growth habit of the crystals
- Reaction sites on ammonium perchlorate crystals during deflagration, reflecting the different energy transfer mechanisms
- Bridging between aluminum particles, the fundamental step in the agglomeration of metal particles
- Growth of beryllium oxide needles on a burning beryllium droplet, indicating growth of oxide from the vapor phase before the metal had melted
- Removal of encapsulating beryllium oxide by water vapor during combustion of beryllium droplets
- Formation of a surface melt on ammonium perchlorate particles within the burnt propellant

Controversies Resolved

Some of the observations that we made allowed us to resolve controversies existing between several hypotheses. Examples:

- At low pressures (less than 2,000 psia), ammonium perchlorate deflagrates with a melt instead of by direct sublimation.
- Fragmentation of burning aluminum particles is caused by overpressure within an oxide globule acting on the droplet surface, rather than by superheating of the droplet itself.
- Interfacial reactions between ammonium perchlorate and binders are not important for the combustion of propellants.

Hypotheses Originated

Results of our work have led to the following hypotheses:

- The deflagration behavior of ammonium perchlorate can be divided in four phenomenological pressure-dependent regimes (Table 1).
- Self-extinguishment of polyurethane propellants at high pressures is caused by the molten binder flowing over and covering the oxidizer.
- Agglomeration of aluminum particles is less dependent on the chemical environment than on the temperature and heating rate.

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13. ABSTRACT

The scanning electron microscope (SEM) has provided data which have been used to infer the physical and thermochemical mechanisms of the following processes: ammonium perchlorate decomposition and deflagration, aluminum combustion, beryllium combustion, aluminum agglomeration, and solid propellant combustion.

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