Performance of Solid Propellants Containing Metal Additives

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Test firings of solid propellant research rockets were made to study effects of propellant composition, pressure, and engine size on the exhaust oxide particle size, and on the composition of the solid exhaust products. The experimental results of this work and those reported by others were analyzed collectively to provide a reasonable description of the aluminum combustion and oxide condensation processes in solid propellant rocket motors. Combustion of aluminum was found to occur in the vapor phase, and was essentially complete in the engines studied although some combustion took place in the nozzle. The experimental results indicate that condensation of the oxide vapor can be described by first-order chemical kinetics. Further particle growth by agglomeration appears likely. The effect of two phase flow was found to be significant in the motors tested and reached a maximum in motors of a certain size. In motors where this loss is large, significant improvement in delivered performance can be realized by reducing the aluminum content.

I. Introduction

ALUMINUM has been added to solid propellants to improve performance and to suppress high-frequency combustion instability. Although the measured specific impulse of such propellant is higher than that of the base propellant without aluminum, the specific impulse efficiency of the aluminized propellant is lower. The lower efficiency is largely due to the presence of condensed aluminum oxide in the exhaust. However, there are instances where incomplete combustion of the metal may be the major source of performance loss. Examples would include metals other than aluminum, oxidation by agents other than oxygen, highly metallized solids such as is considered for hybrid rockets, or very small engines.

A study of the factors governing completeness of aluminum combustion in a motor, and those governing the condensed phase particle size, is discussed in this paper. Brief discussions of selected works on gas-particle flow systems and on combustion of metals are included because of their pertinence to the subject matter. It is shown that information regarding the nature of the metal combustion and oxide condensation processes in a motor can be derived from the results of motor testing. Thus, the contributions to performance loss due to two phase flow effects and due to incomplete metal combustion can be deduced. These data provide the starting point for improving the efficiency of motors using metallized propellant. The efficiency of very large boosters is considered in the light of the results obtained.

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II. Gas-Particle Flow Systems

A number of papers pertaining to the gasdynamics of a two phase system have appeared in the recent literature. The chief application has been to the flow field of exhaust nozzles of rockets containing a propellant to which aluminum has been added. These papers have been discussed in a survey article by Hoglund.[1] It was shown that a significant performance loss in these rocket engines occurs in the nozzle: the condensed particles can do no expansion work, the exhausting condensed phase is found to retain some of the energy of combustion as thermal energy which would otherwise be converted to propulsive energy of the gas, and a momentum loss results from the drag force which the gas continuously exerts on the condensed oxide particles in accelerating them through the nozzle.

The magnitude of this performance loss was calculated by considering particles of typical size[2] in the theoretical treatments developed by Kliegel.[3, 4]

Brown[5] was able to predict nozzle efficiency based on theoretically determined thermal and velocity lags; however, the test firings of Kliegel and Nickerson[6] revealed the actual performance loss attributed to lags to be considerably smaller than predicted in each instance. Brown was not successful in obtaining experimental verification of the theoretical velocity lag. Excellent verification of the thermal lags was obtained by Carlson,[7] who used inert solid particles of known size in the propellant taking care that each particle would retain its identity throughout the flow. The excellent agreement might cautiously be taken as evidence of the validity of the values of the heat transfer and drag coefficients used in the interphase equations. These coefficients have not been considered to be known with certainty.

There are several possible causes for discrepancy between theory and experiment. If there is appreciable combustion, condensation, or agglomeration in the nozzle,[8] the particle mass fraction and mean particle size would increase continually along the axis of the nozzle. Calculations based on the size of collected exhaust particles, and on the mass fraction assuming complete combustion and condensation in the chamber, can give pessimistic results such as obtained by Kliegel.[6] The discrepancy between theory and experiment can also be due to the assumptions of the theory, the values of the heat transfer and drag coefficients, inaccurate calculations of the other sources of performance loss, or optimistic values of the theoretical specific impulse.

Parametric results of the two phase flow calculations suggest a number of ways to reduce the thermal and velocity lags in a conventional axisymmetric nozzle. Some of the approaches involve modification of the nozzle, but are limited by practical design considerations. One suggestion of practical interest is to reduce the velocity and temperature gradients in the throat region by decreasing the nozzle convergent angle and increasing the throat radius of curvature.[9] Other approaches involve modification of the propellant such as reducing the metal concentration from the theoretical optimum. A more effective approach would be to reduce the particle size of the metal oxide. The first step in implementing this approach is to acquire knowledge of the metal combustion process in a motor and an understanding of the factors that influence the condensation and agglomeration of the oxide product.

III. Combustion of Metals

The combustion of metals exerts a second influence on specific impulse efficiency, namely, the loss resulting from incomplete combustion. Whether or not a metal will burn in the vapor phase in a rocket motor is an important consideration. Compared with vapor phase combustion, surface burning was described as a slow process.[10]

The possible combustion characteristics of a given metal have been inferred from observation of the combustion of metal particles in burner flames or of electrically heated metal strands. The burning process also depends on certain properties of the metal and its oxide. Attempts at correlating such information with combustion in a rocket motor have been made by observation of a deflagrating propellant slab or strand in a window bomb. Data from actual rocket motors have been limited.

From energy considerations, Glassman[11] postulated that, if the boiling point of the metal oxide is higher than that of the metal, combustion takes place in the vapor phase; otherwise it is a surface process. This hypothesis was supported by the experiments of Coffin[12] with magnesium, and Talley[13] with boron.

The experiments of Fassel et al.[14] with aluminum-magnesium alloys, of Wood[15] with a number of metals, and of Gordon[10] with a number of metals and metal compounds, indicated that the oxide boiling point being higher than the metal boiling point is a necessary although not sufficient condition for vapor phase combustion. Gordon[10] then classified the metal combustion process in more detail from physical considerations. Brzustowski and Glassman[16] extended these categories in a complete coverage of metals of interest to collectively explain the observed phenomena cited in Ref. 10–16. Basically, for metals whose boiling points are lower than that of their oxides, the combustion process will depend upon the degree of surface oxidation that can occur prior to ignition and upon the rate of heat transfer across this oxide layer during burning.[16] The work with aluminum, titanium, and zirconium has shown that environment and metal particle size will influence these factors.[10, 14–18] The environment produced by deflagrating solid propellants seems to foster vapor phase combustion for aluminum.[15, 17, 18] Although titanium and zirconium exhibited vapor phase combustion in burner tests,[10] indicating the metal boiling points to be lower than the oxide boiling points, these metals appeared to burn by a surface process in deflagrating propellant.[15] Magnesium was always observed to burn in the vapor phase.

Combustion efficiency of metals in a rocket motor also depends upon the ease of ignition. Friedman and Maĉek[19] observed the ignition time for an aluminum particle to follow a "d^2 law" and showed the oxygen concentration to have a small effect on the ignition temperature limit. Wood[15] observed that large aluminum particles do not ignite as close to the propellant surface as do small particles, but that the large particles would ignite sooner in the presence of small particles. Gordon[10] found that increasing the concentration of aluminum particles passing through a burner flame facilitated ignition and the establishment of vapor-phase combustion; at low concentrations, ignition was difficult and combustion was by a surface process. These observations were explained by improved radiant energy conservation between particles; Glassman[11] reported that the emissive radiant energy of the metal flame zone is very high. However, a high concentration of small particles may result in agglomeration of metal droplets at the propellant surface[17] which will bring about larger particles and smaller effective burning area.

Beryllium falls in the same category as aluminum,[10, 16] yet Gordon observed that beryllium particles would not ignite when passing through the burner flame. Maĉek[20] succeeded in igniting beryllium particles at very high temperatures (near the oxide melting point) and observed an appreciable effect of oxidizer concentration. Apparently, the effects of surface oxidation are more severe in the case of beryllium which is noteworthy in view of the performance potential of beryllium. The work of Fassel et al.[14] implies that rapidity of ignition and burning can be accomplished by alloying or mixing with a volatile metal; however, one must be aware of any resulting change in theoretical specific impulse.

The research to date has been chiefly concerned with the oxidation of metals by oxygen, and it should be kept in mind that the foregoing discussion pertains only to that. Extensive study of metal combustion is rather recent. With the growth of propellant technology, it has become of interest to study metal combustion in atmospheres containing oxidizers other than oxygen.[21]

IV. Experimental Program

The foregoing discussion indicates that the understanding of the factors affecting the performance of metal containing propellants requires knowledge of the metal combustion and oxide condensation processes in a rocket motor. An experimental program was carried out to confirm and extend the limited available data for the case of aluminized propellant. Particular emphasis was placed on experiments that would yield results to elucidate these processes.

Three motors were used, referred to as motor 1, motor 2, and motor 3. They are, respectively, 2 in. diam × 6 in. long, 5 in. diam × 20 in. long, and 10 in. diam × 40 in. long. They contain, respectively, about 1, 15, and 100 lb of aluminized polyurethane-type propellant. The exhaust product composition or exhaust particle size distribution, pressure, and specific impulse were determined for each firing. The effects of residence time, pressure, aluminum concentration, and aluminum particle size were investigated.

Particle Size Determination

A number of techniques for determining the size distribution of microscopic droplets have evolved from studies of fog, aerosol sprays, and fuel injectors.[22] Size determinations of the aluminum oxide particles have been made by sampling the residue on the walls of a settling chamber, or by placing wetted plates in the exhaust stream. The samples were then examined under a microscope. Brown and McCarty[2] also used a photographic technique based on optical absorption by the hot particles.

In the present work, the possibility of using the light-scattering technique developed by Dobbins,[23, 24] for determining the Sauter (volume-to-surface) mean diameter, was investigated. However, the opaqueness of the exhaust stream, even at low concentrations of aluminum, made such a technique impractical.‡ For simplicity, sampling was done by means of wetted plates attached to moveable cross-members in a plane perpendicular to the motor axis. The plates are coated with a polypropylene glycol diol. After the firing, the residues are scraped off into jars containing the diol. Samples are placed

‡ This problem is currently under study by Dobbins at Brown University.

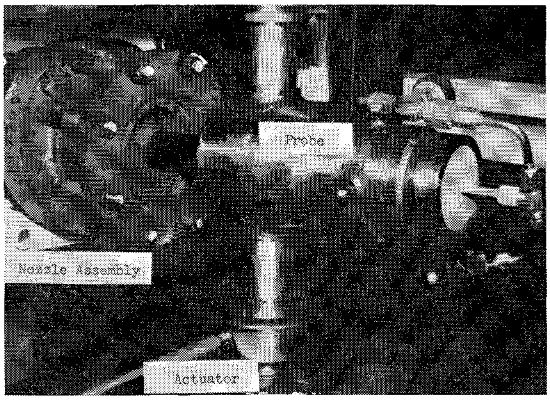

Fig. 1 SRI probe and actuator.

on slides and examined under an electron microscope. The volume mean diameter is calculated from the size distribution.

The chief arguments against this technique are the validity of representation of the sample and the discrimination against smaller particles. Validity of representation can be improved by comparing a number of samples. Sehgal[25] avoided the discrimination argument by firing motors into a chamber, but did not report particle sizes smaller than those found by Brown and McCarty by direct sampling. In addition, the absence of small particles does not significantly affect the volume (or mass) mean diameter, which is heavily weighted toward the larger particles. This mean diameter, which is the diameter of the particle whose volume is equal to the average of the particle volumes in the distribution, is considered because the condensation process is a transfer of mass from one phase to another, and for ease of comparison with previous works.

Composition of Solid Exhaust Products

The concentrations of aluminum and aluminum oxide in the rocket exhaust were determined by chemical analysis of solid exhaust products collected with a sampling probe (Fig. 1) developed by the Stanford Research Institute.[26] Samples of exhaust products are obtained by a hydraulically actuated swinging motion of the probe through the rocket exhaust. The probe chamber is initially maintained at a vacuum by a check valve that is opened by the exhaust dynamic pressure; material is trapped only when the traversing probe is parallel to the axis of the rocket exhaust, and the probe sample will consist of exhaust products only. The apparatus is equipped with a position indicator and pressure transducer such that the sampling time and position are recorded. The details of the chemical analysis procedure are beyond the scope of this paper and are presented in Ref. 26. As the probe interferes with the gas stream, no attempt was made to simultaneously collect samples for particle size distribution and for chemical analysis.

V. Discussion of Results

A. Exhaust Particle Size

1. *Effect of aluminum particle size*

Figure 2 shows the invariance of the exhaust particle size with respect to the size of the aluminum particles in the propellant and extends the results of the previous investigations over a wider range. This result confirms that the vapor phase combustion model for aluminum particles is applicable in a rocket motor. The aluminum oxide particle size will therefore depend upon the factors that influence the rates of oxidation, nucleation, and condensation. Agglomeration of the condensed particles may also occur. The apparent effect of motor size shown on Fig. 2 will be discussed subsequently.

2. *Effect of pressure and residence time*

Sehgal[25] observed a direct linear relationship between volume mean diameter and the logarithm of pressure over a range from 75 to 1000 psi. Sehgal's motor was the same as motor 2 used in this study, except that it was 6 in. long rather than 20 in. long; the propellants used are also essentially the same. Good agreement with Sehgal's result was obtained at 1000 psi (see Fig. 3), and the pure pressure effect was not pursued further with conventional propellant. It is interesting to note that, for a given mixture of perfect gases at constant temperature, the logarithm of pressure determines the chemical potential (driving force) for condensation of the components.[27] On the basis of this concept and a number of simplifying assumptions, the linear relation observed by Sehgal was derived.[37] However, additional factors give much more weight to an approach based on chemical kinetics of condensation as discussed below.

Figure 3 shows the influence of mean residence time on the exhaust particle size. The data of this work, indicated by the solid curve and dark circles, came from experiments in which only the residence time was varied by changing motor size. The other points are data from Sehgal's pressure study. In his study, the pressure was varied by changing the throat size only; the residence time was thereby changed simultaneously. Thus, each of his measurements corresponds to a point on the diameter versus residence time curve for the particular pressure as represented by the dashed curves. These curves are drawn

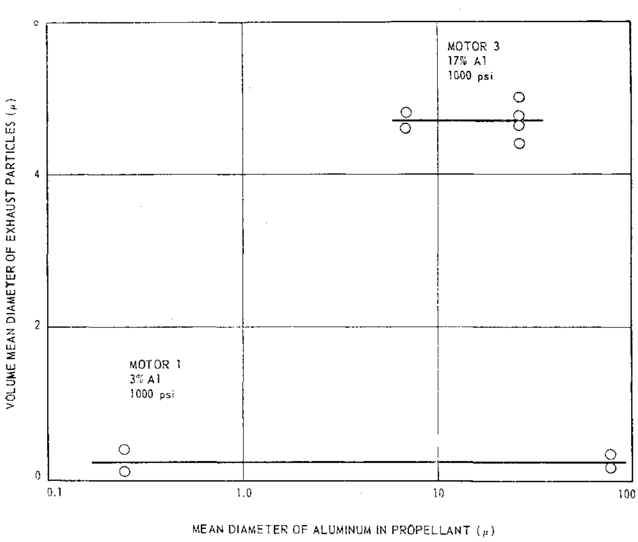

Fig 2. Effect of aluminum particle size on exhaust partical size.

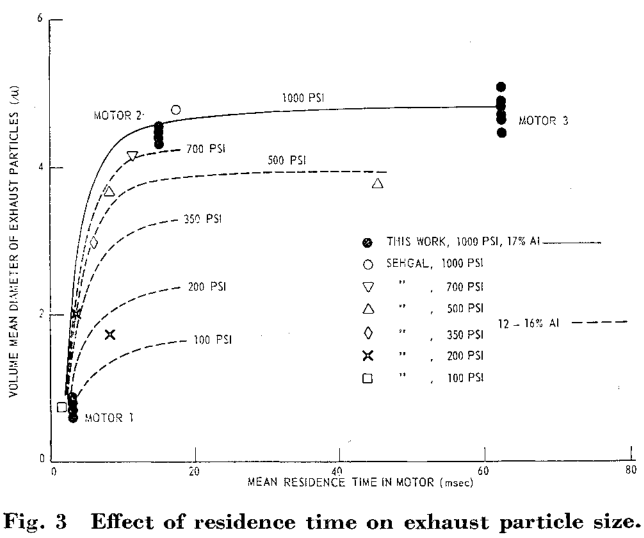

Fig. 3 Effect of residence time on exhaust particle size.

from theoretical considerations discussed below and therefore are approximate representations of the limited experimental data. Subsequent to the pressure study reported in Ref. 25, Sehgal examined the residence time effect at 500 psi[28]; this additional point is included. His study of the residence time effect at 200 psi was limited, but it can be seen why Sehgal reported no effect of residence time at a given pressure. Brown and McCarty also reported no effect of residence time, probably for the same reason; they did, however, report that particles collected in the combustion chamber were considerably smaller than those in the exhaust stream.

The formation of Al_2O_3 particles is not the result of condensation in the usual sense. Al_2O_3 does not exist in the vapor phase. What probably occurs is that aluminum burns to suboxides in the vapor phase, which can then react with various oxidizing species to form condensed Al_2O_3.[29] Present knowledge does not yet permit the writing of definite and balanced chemical equations. However, from consideration of chemical kinetics, it was believed possible that the rate of growth of condensed phase mass could be of exponential form. For example, assume that the rate controlling step is a second-order reaction of the form

$$A + B \xrightarrow{k_f} C + E \tag{1}$$

A represents the metal or a suboxide, and B is an oxidizing species. C is either suboxide or liquid Al_2O_3, depending on the rate-limiting step, and E may be an additional product or zero. Letting y be the moles of C formed per unit volume, the change in y is given by

$$(1 - y/A_0)/(1 - y/B_0) = \exp[-k_f(B_0 - A_0)t] \tag{2}$$

A_0 and B_0 are the initial moles of A and B, per unit volume, and are therefore proportional to pressure. Note that y can be taken proportional to the cube of the particle diameter. From equilibrium considerations, it can be assumed that $B_0 \gg A_0$, making the reaction first-order bimolecular. Then in terms of particle diameter and pressure, Eq. (2) takes the form

$$D^3 = aP[1 - \exp(-bk_fPt)] \tag{3}$$

where a and b are constants. Therefore, the particle growth rate would be of the exponential form

$$\ln(dD^3/dt) = n - mt \tag{4}$$

Accordingly, Fig. 4 was plotted as shown. The growth rates were derived from the curve drawn in Fig. 3 for 1000 psi. These growth rates are reasonably well fitted by a straight

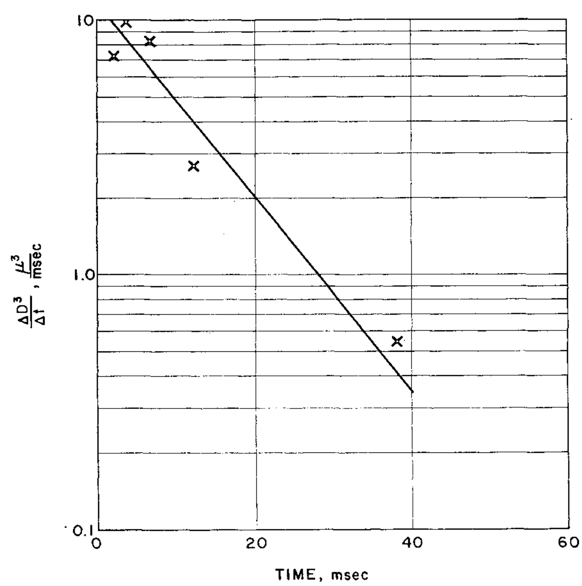

Fig. 4 Oxide particle growth rates.

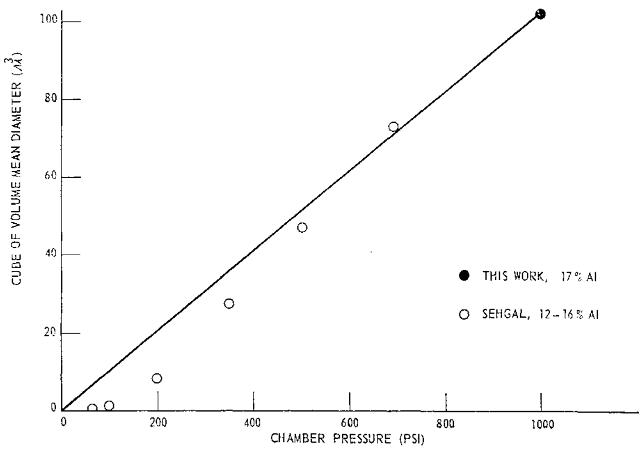

Fig. 5 Effect of pressure on the limiting diameter.

line. The slope of this line m would yield the reaction rate constant if the initial concentrations of the reacting species were known.

The logarithmic dependency of the rate of growth on time indicates the existence of a limiting, or equilibrium, diameter. An exponential law is also consistent with the physical consideration that the oxide vapor is not in infinite supply. Letting $t \rightarrow \infty$ in Eq. (3), a limiting diameter of 5 μ is obtained for the constants (m and n) derived from Fig. 4. The particle size from motor 3 was 4.7 μ; condensation is, therefore, essentially complete. It appears that agglomeration plays an insignificant role during the period of rapid condensation.

Equation (3) also shows that the limiting particle mass is proportional to pressure. Figure 5 shows experimental verification of this relation. Sehgal's points at lower pressures are believed to fall below the line because the limiting diameters were not yet reached for the residence times corresponding to these pressures. Finally, Eq. (3) indicates that the time required to reach a given fraction of the "limiting" diameter is inversely proportional to pressure. Data are as yet not available to verify this relation, but the curves in Fig. 3 have been drawn accordingly.

3. *Effect of aluminum concentration*

Figure 6 shows the effect of aluminum concentration on the exhaust particle size, at constant residence time and pressure. These data are consistent with Sehgal's observation[25] that the exhaust particle size is essentially independent of aluminum

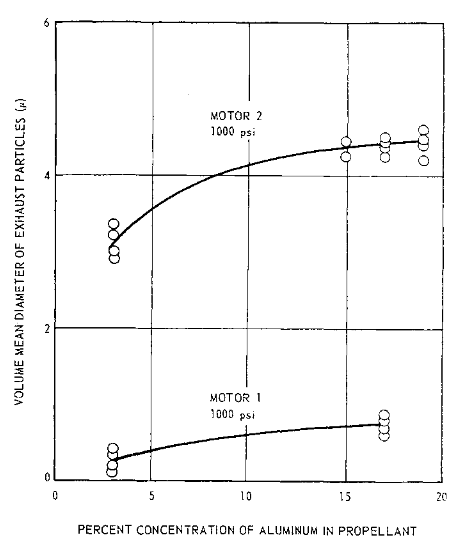

Fig. 6 Effect of aluminum concentration on exhaust particle size.

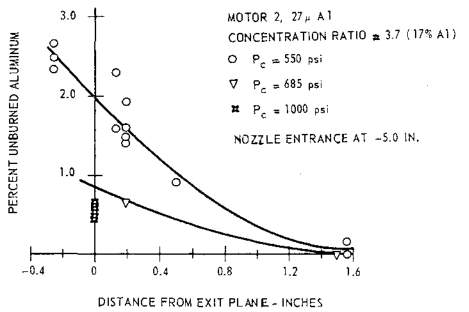

Fig. 7 Effect of trapping distance and pressure on completeness of metal combustion.

concentration between weight fractions of 12 and 16%. At lower concentrations, however, lowering the aluminum content does result in a decrease in exhaust particle size.

According to Eq. (3), the limiting mass of the oxide particle is proportional to aluminum concentration, upon which the constant a depends. Lowering the aluminum concentration reduces the particle growth rate as well. Letting $t \rightarrow \infty$ in Eq. (3), it is calculated that the ratio of the limiting diameters for the 15% aluminum to that for the 3% aluminum should be 1.60 in motor 2. Experimentally, this ratio was found to be 1.44. Note, however, in motor 2, the residence time is not quite adequate to achieve the limiting diameter, so it is not surprising that the experimental value is a bit lower than theoretical.

No increase in particle size with aluminum concentration was observed between 15 and 19% aluminum, possibly because the change in concentration was relatively small. With increasing aluminum concentrations, an underoxidized condition would eventually be encountered; particle size would be limited because incomplete combustion would limit the suboxide vapor concentration.

4. *Effect of sampling position*

According to the discussion by Brown and McCarty,[2] sampling position should exert no influence on the exhaust particle size. Several firings were made to confirm this notion. Samples for motor 1 were taken at 10 and 15 ft (80 and 120 exit diameters); samples for motor 2 were taken at 15 and 30 ft (60 and 120 exit diameters); samples for motor 3 were taken at 30 and 60 ft (60 and 120 exit diameters). In each case there was no noteworthy effect on the exhaust particle size distribution. A sample for motor 3 collected at 10 ft (20 exit diameters) consisted of a molten layer of oxide; apparently, such a distance was well within the supersonic jet cone.[30]

On firings where five sampling plates were attached at various positions on the crossbar, no effect of radial position on size distribution was perceived. However, a weakness of the experiment is that the angle subtended by the crossbar (as measured from the nozzle throat) was much smaller than the nozzle divergence angle.

Photomicrographs of the samples showed that the particles are spherical, as has been observed by others.[2, 25] Further analysis showed them to be solid.

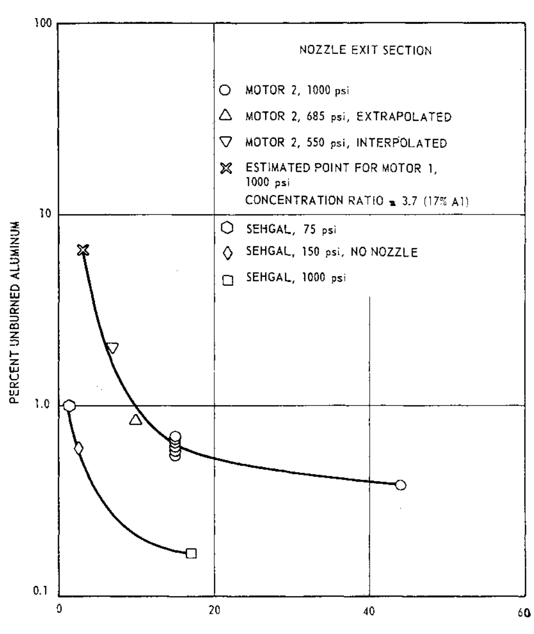

Fig. 8 Effect of residence time on completeness of metal combustion.

5. *Work with double-base propellants*

Brown and McCarty[2] observed no effects of aluminum particle size, aluminum concentration, pressure, or residence time on the size of the exhaust particles from aluminized double-base propellants. Although the ranges of these independent variables were not as extensive as in this work, their observations are consistent with the results of this work within the common range.

Motor firings at 350 psi, which corresponded to mean residence times of about 4 and 6 msec for their two motors, yielded mass mean diameters of about 2.3 μ.[31] Firings at 1000 psi, which corresponded to mean residence times of about 8 and 11 msec, also gave mass mean diameters of about 2.3 μ. If these points were plotted in Fig. 3, the data for 350 psi would be observed to closely straddle the dashed line corresponding to 350 psi; however, the data for 1000 psi would be somewhat removed from the 1000 psi line. Particles collected in the combustion chamber at low residence time were submicron, an observation consistent with Fig. 3 regardless of pressure.

From these results it would appear that, in the case of double-base propellants, the limiting diameter is lower than that observed for the composite propellants, and this limiting diameter is unaffected by pressure. Also, the initial particle growth rate appears to be higher for the double-base propellant. The high growth rate and low limiting diameter could have conceivably rendered any pressure effect difficult to detect.

In the light of the kinetics of particle growth, these results with double-base propellant need not be considered inconsistent with the data from composite propellants. The reaction mechanism for particle growth, and therefore the reaction kinetics associated with double-base propellant, need not be the same as for the ammonium perchlorate composite propellant. That the limiting diameter was smaller for the double-base propellant would indicate, assuming completeness of condensation, that a greater number of condensation nuclei were initially formed. The lower limiting diameter would render the double-base propellant attractive from the point of view of minimizing two phase flow loss.

B. Completeness of Metal Combustion

1. *Effect of pressure and residence time*

Samples of solid exhaust products were collected from motors operating at various pressures. Collections were made at various stations from the nozzle exit plane. The percentage of the original aluminum which is unburned was determined from the concentrations of Al and Al_2O_3 in each sample. The results are shown in Fig. 7. Although there is a large scatter in the data, the trends are quite clear. It is seen that metal combustion occurs in the nozzle and continues for a certain distance downstream of the nozzle exit plane. There also appears to be a pressure effect. In any case, completeness of metal combustion in motor 2 is such that the associated loss in specific impulse is about 0.1% at 1000 psi.

Figure 8 shows the effect of residence time on the completeness of metal combustion. The points denoted by circles are the only ones derived from an experiment in which all operating variables except the residence time were kept constant. This was accomplished by placing a grain 10 in. long in the forward end of the 20-in.-long motor (motor 2). Points at 550 and 685 psi, with exit plane aluminum concentration estimated from Fig. 7, are included in Fig. 8. As in the case of aluminum oxide particle growth discussed earlier, completeness of combustion depends on pressure as well as residence time. Unfortunately, there is insufficient data here to separate these effects. Figure 8 indicates that experiments should be performed in the region of high residence time, where the curve is flat, and at low pressures. Theoretical support for a pressure effect appears elsewhere[32] in addition to the kinetics discussion presented earlier.

Sehgal[25] measured completeness of metal combustion by sampling the walls of a tank into which the motor fired. These data are included in Fig. 8, taking the residence time as that in the motor. The similarity and relative positions of the two curves suggest that metal combustion continued in the free jet of Sehgal's motors. Brown and McCarty[2] similarly observed that aluminum combustion was complete in their work with double-base propellant.

Samples were not collected from motors 1 and 3. However, the results from motor 2 (Fig. 8) extrapolated to the mean residence time in motor 3 would indicate that metal combustion is about 99.7% complete in motor 3 at 1000 psi. For the case of motor 1, the loss due to incomplete metal combustion was crudely estimated by subtracting the other sources of loss, theoretically calculated, from the measured specific impulse. The completeness of metal combustion associated with such a loss is included as a point in Fig. 8.

2. *Effect of oxidizer-to-metal concentration ratio*

Changing the oxidizer-to-aluminum concentration ratio in motor 2 produced a significant change in the appearance of the solid exhaust products collected.[26] For a concentration ratio of 3.7 the sample is dark, whereas at a concentration ratio of 7.5 the sample is almost white. The operating pressure was 1000 psi. At the higher concentration ratio, corresponding to an aluminum concentration of 10%, the percent of unburned aluminum was 0.1%. At the lower ratio, corresponding to an aluminum concentration of 17%, the unburned aluminum was 0.6%. Although completeness of aluminum combustion is shown to be a minor consideration in motor 2, it is clear that an improvement is realized by using oxygen-rich mixtures. This can be important in instances where other factors (different metal, low residence time, etc.) may influence the completeness of burning.

C. Two Phase Flow Losses

1. *Effects of oxide particle and motor size*

The results of calculations of the two phase flow loss as a function of particle size for the three motors are shown in Fig. 9. The calculations were made with an extension of the computer program of Glauz[33] to include variable non-Stokes drag coefficient and heat-transfer coefficient. The particle sizes collected from each motor are plotted on the corresponding theoretical curves. It is seen that the losses are 0.5% for motor 1, 5.8% for motor 2, and 5.4% for motor 3.

Apparently, for a series of motors of varying size but geometrically similar, there is a size at which the loss is a maximum. This is the result of the dependency of efficiency on nozzle size and particle size, and of the dependency of particle size on motor size. For a given nozzle size, the efficiency increases with decreasing particle size. Experimentally, particle size decreases with decreasing nozzle (motor) size.

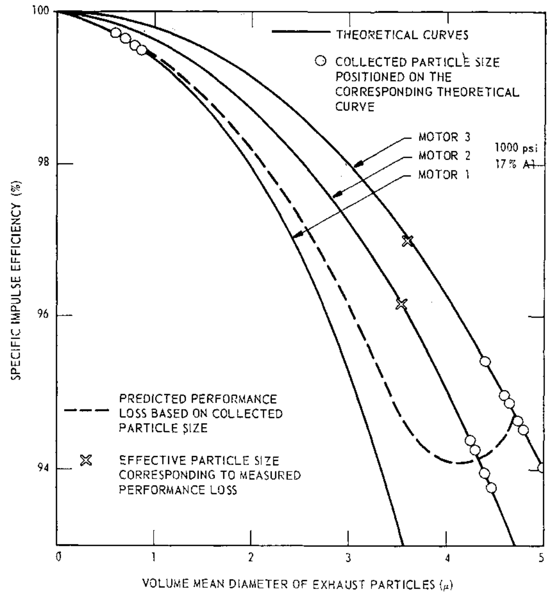

Fig. 9 Performance losses resulting from two phase flow.

Therefore, a point of lowest efficiency would be expected. Because of a lack of intermediate data, it is not certain where this point actually would be. It is also not certain how the dashed line of Fig. 9 would extrapolate to curves for larger motors. If particle growth is limited as suggested by the kinetic model, it would be expected that, for motors of increasing size, performance would improve rapidly. If, however, particle growth does continue by agglomeration, the improvement with increasing motor size would be much more gradual.

Extensive specific impulse measurements at Aerojet-General have resulted in empirical expressions for the specific impulse efficiencies of a given family of propellants, as a function of aluminum content, in motors 2 and 3.[34] By comparing the measured specific impulse efficiencies in these motors with those extrapolated to zero aluminum content (Table 1), the loss due to the presence of aluminum in the propellant can be determined. Neglecting the effects of aluminum on the other sources of performance loss, the two phase flow losses are thereby "measured" to be 3.8% in motor 2 and 3.0% in motor 3. This is, in each case, less than the theoretical values based upon the observed volume mean diameters. There is as yet insufficient data on motor 1 to make a similar estimation of the two phase flow loss. Similar empirical procedures have been studied elsewhere.[31]

An alternate approach to determine the two phase flow loss would be to subtract theoretically calculated values of heat loss, friction loss, etc. from the measured efficiency. The remainder would be attributed to two phase flow, as was done by Kliegel.[6] However, there are uncertainties in the heat-transfer coefficient, the friction factor, and the degree of nonequilibrium expansion. Although limits can be placed on these factors, the range turns out to be such that the measured efficiencies can be accounted for disregarding two phase flow. Nevertheless, assuming shifting equilibrium nozzle flow in motors 2 and 3, and taking the "midpoint" values for heat loss

Table 1 Specific impulse efficiencies[a]

	Motor 1	Motor 2	Motor 3
Measured, 17% Al, 1000 psi	87.2 ± 2.0%	91.5 ± 0.1%	93.8 ± 0.2%
Ref. 34, 0% Al, 1000 psi	...	95.3%	96.8%

[a] Nozzle divergence loss (15° half-angle) is included.

and friction loss in each case, the two phase flow losses are computed to be 4 and 3%, respectively. This agrees with the empirical equations just cited. Performing similar calculations for the case of the large boosters, the two phase flow loss therein can be as high as 3%. Such a loss would be evidence of further particle growth by agglomeration.

It is believed that the empirical procedure involves less uncertainty than does the technique of calculating the other sources of performance loss at present. Of course, the empirical procedure is not practical for large boosters. Quantitative data showing the effect of aluminum on the other sources of performance loss are required to improve the accuracy of the latter technique. Heat-transfer coefficients have been measured from small motor firings using aluminized propellant and molybdenum nozzles.[35] Friction factors under similar conditions have yet to be determined.

A final point is the question of which mean diameter to use to determine the two phase flow loss from the theoretical relations. The linear mean diameter yields losses of 1.8% in motor 2, and 1.6% in motor 3, which are probably too low. One could argue that the Sauter mean diameter should be used because the volume-to-area ratios of the given particle appear in the interphase energy and momentum equations. However, the Sauter mean diameters are found to be in excess of 6 μ for motors 2 and 3; the corresponding theoretical loss would be greater than the total measured loss for each motor. Based on the expected loss due to lags from the empirical equation, "effective" diameters are included in Fig. 9. For motors 2 and 3, the effective diameters are about equal at 3.6 μ. The measured volume mean diameters shown are 4.3 and 4.7 μ, respectively. In view of the preceding discussion, and the theoretical method of calculating two phase flow loss based on an average diameter, the discrepancies between the two sets of values are not unexpected. Programs taking into consideration the particle size distribution are becoming available.

2. *Effect of aluminum concentration*

It has been noted that aluminum combustion is essentially complete even in small motors such as motor 2. The reduction of performance efficiency upon adding aluminum to a propellant must therefore be attributed to two phase flow. For a given formulation, as the aluminum concentration increases, the theoretical (thermodynamic) specific impulse increases to a maximum at some optimum concentration.[34] At the same time, the I_s efficiency drops off with increasing aluminum concentration. With increasing aluminum content, it is therefore possible to attain a point of maximum measured I_s before the concentration corresponding to maximum theoretical I_s is reached. Experiments have been conducted at Aerojet and elsewhere[31] to demonstrate this point. For example, the propellant containing 17% aluminum was observed to deliver both lower I_s and lower impulse density (ρI_s) than the same propellant but with 10% aluminum in motor 2. The 17% aluminum had the higher theoretical values. Thus, in instances where the two phase flow loss is large, improvements in performance can be realized by reducing the aluminum content.

3. *Effect of pressure*

From the point of view of performance efficiency, lowering the pressure would reduce the two phase flow loss by reducing the exhaust particle size of composite propellants. However, motor operating pressure will be dictated by the mission requirements and over-all design considerations. Low operating pressures may be considered for space applications.

4. *Performance of large boosters*

Although agglomeration is of minor importance in small motors, it is the only process of particle growth beyond the limiting diameter attainable by chemical reaction. Setze[36] has derived an expression for particle growth by collisions based upon kinetic theory. The expression is of the form

$$D^{5/2} - D_0^{5/2} = kt \tag{5}$$

Starting with the value of 4.3 μ for motor 2, Eq. (5) does predict the observed value of 4.7 μ for motor 3. Extrapolating to the residence times of very large boosters, mass mean diameters approaching and exceeding 10 μ would not be surprising. Unfortunately, this has not been confirmed by sampling from a large motor firing. However, the efficiencies exhibited by large motors would indicate, based on two phase flow considerations, that such agglomeration indeed does occur. The observed loss is believed to be primarily due to two phase flow because heat and friction losses become proportionately very small for very large motors. Therefore, it would be expected that reducing the aluminum concentration in large boosters would have benefits similar to that demonstrated in the case of the foregoing motor 2, where the two phase flow loss was also very large.

VI. Conclusions

Aluminum combustion occurs in the vapor phase in solid propellant rocket motors and is essentially complete in motors of *R* and *D* scale. Initial oxide particle growth can be explained by considering the kinetics of condensation by chemical reaction. There is evidence of further particle growth by agglomeration, strongly manifested in large boosters. Where the two phase flow loss is significant, improved performance can be realized by reducing the aluminum content. Lower pressures will promote the formation of smaller particles to reduce two phase flow loss. Different propellants can yield different exhaust particle sizes because the mechanisms of nucleation and condensation kinetics can be different. All other factors being equal, the propellant that yields the smallest particles would be most attractive; this should be a tabulated propellant property. Similar studies for future systems should be undertaken.

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