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ALUMINUM DROPLET COMBUSTION: RATES AND MECHANISMS IN WET AND DRY OXIDIZERS

Jack L. Prentice

Naval Weapons Center
China Lake, California

April 1974

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ABSTRACT

This report describes quantitative single aluminum droplet combustion studies in a variety of gaseous oxidizers including CO_2 and water vapor. A laser ignition technique was employed which has a demonstrated ability to yield metal droplet burning data of very low scatter. This study reveals that aluminum droplets burn much faster in wet CO_2/O_2 than in any of the other gaseous systems studied (N_2/O_2, Ar/O_2). Droplet explosions are found to be characteristic in wet gases and the resultant combustion debris is shown to be both chemically and physically complex. Condensed phase reactions occurring on the droplet surface yield substoichiometric Al-O-C or Al-O-N intermediates prior to the gas-driven droplet explosion. A discussion of droplet burning models is included and the faulty assumptions underpinning them are identified. Based on experimental findings, an outline is given of the direction modeling must take to accurately describe Al droplet combustion.

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FOREWORD

This report covers research performed under ORDTASK UF 31-323-303 and in-house Independent Research funding during the period 1 May 1972 through 30 April 1973. This task was carried out in the Aerothermochemistry Division of the Research Department under the direction of Mr. Jack L. Prentice as Principal Investigator.

This report is transmitted for information only. It does not represent the official view or the final judgment of the Naval Weapons Center.

Released by
E. W. PRICE, *Head*
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Under authority of
HUGH W. HUNTER, *Head*
Research Department

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1. INTRODUCTION

In terms of sheer tonnage used aluminum powder has no peer as a fuel additive to solid rocket propellants. Aluminum combustion has been a much studied subject, and yet, quantitative droplet burning data is still relatively scarce. This study is an attempt to add to the data base while simultaneously examining two questions of considerable import to rocket ballisticians: (1) in quantitative terms, what are the effects of CO_2 and water vapor on Al droplet burning, and (2) what is the nature and state of subdivision of product from aluminum burning as a function of environmental variables. The latter question has relevance to the issue of acoustic damping of combustion instability. The efficacy of particulate damping of solid rocket combustion instability is one of the most intensely studied areas of solid propellant combustion at present.

The modeling of metal droplet burning, and aluminum burning in particular, is currently in a rather retarded state due to a series of fallacious assumptions upon which the present model is founded. In this paper we expect to identify the faulty assumptions and point the direction which a proper solution must take.

This study examines quantitatively the combustion of single laser-ignited aluminum droplets burning in a variety of oxidizing gases including carbon dioxide, nitrogen-oxygen, argon-oxygen, carbon dioxide-oxygen and all of the foregoing gases saturated with water vapor.

2. EXPERIMENTAL METHODS

2.1 LASER IGNITION TECHNIQUE

The single particle lsser ignition technique in use in this laboratory was developed in cooperation with scientists at the Ssndia Laboratories in 1967 (Ref. 1). In the interim it has become the preferred technique to be used when qusntitative single metal droplet combustion research is contemplated. The technique, or variations thereof, has been used to study the combustion of zirconium (Ref. 2), boron (Ref. 3), beryllium (Refs. 4, 5), aluminum (Ref. 6), snd magnesium (Ref. 7). Figure 1 shows our appsratus in schematic form.

A typical experiment is described briefly below. A very smali Al disc is placed at the intersection of a set of fine cross-wires (12.5 μm Al) which are supported on a C-shaped metal holder. The specimen holder is housed in a rectangulsr heavy-wall stainless steel reaction vessel which has Pyrex windows on the front and back. The

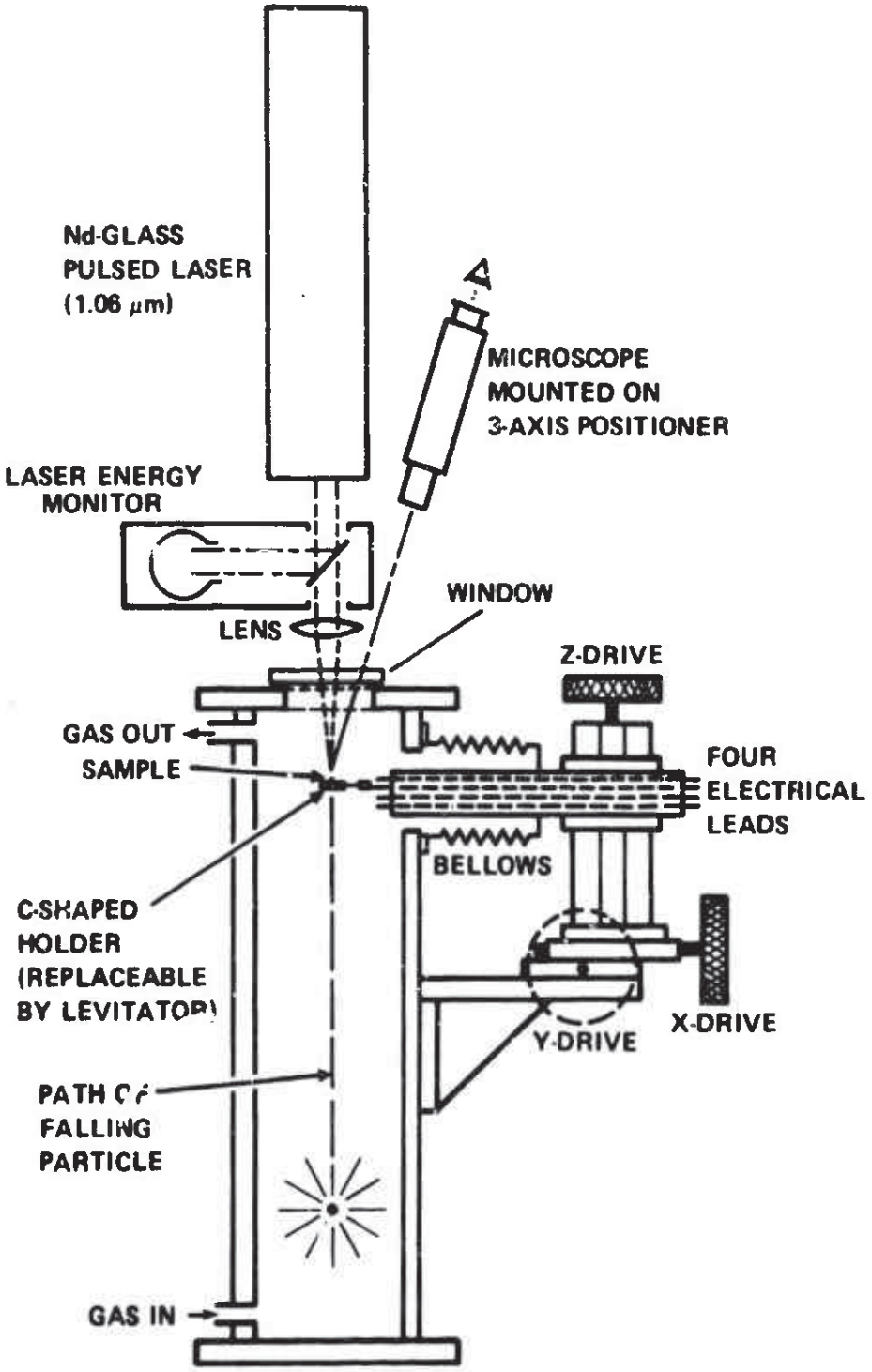

FIG. 1. Single Particle Laser Ignition Apparatus.

sample holder is articulated by means of a 3-axis manipulator operating through a stainless steel bellows attached to the reactor wall. An Al disc is placed on the cross-hairs and positioned at the laser focus, the atmosphere in the vessel adjusted to the desired composition and pressure, and the laser fired remotely to ignite the particle. The droplet burns in free-fall and characteristic burning parameters are measured photographically and photometrically. Droplet radiation is measured with an RCA 7102 photomultiplier viewing the combustion through a narrow band-pass filter with peak transmission at 8100 $\pm$ 50 Å. Burning times are measured from oscilloscope records of the photomultiplier intensity-time trace. Still plate track photographs of the burning droplet are made simultaneously.

2.2 MATERIALS

Tank oxygen (aviator's breathing, 99.5%) and water-pumped argon or nitrogen or technical grade carbon dioxide were mixed as required for these experiments in a gas blender. When experiments in dry gases were to be performed the mixtures were passed through a drying train containing silica gel and molecular sieve immediately prior to use. For wet gas experiments the gases were passed through tandem water saturators prior to use.

The aluminum used in this study (Mirro Aluminum Company, 99.5%) was in the form of foils 17 μm thick. These foils were cut into discs of various diameters in a miniature precision punch press fabricated for the purpose. By changing punch sizes discs were produced whose room temperature volume - equivalent corresponded to spheres of 250, 279, 307, 339, 369, and 400 μm.

3.0 SINGLE PARTICLE COMBUSTION

3.1 BURNING IN DRY GASES

Given the absence of systematic quantitative aluminum droplet burning data in the literature we decided to burn the droplets in dry gases first in order to establish a data base for later comparison. First experiments burned Al droplets in dried mixtures of Ar/O_2. Figure 2 shows a plot of droplet burning time vs oxygen mole fraction for several different original particle sizes. Figure 3 shows a plot of droplet burning time as a function of original diameter for several different oxygen concentrations.

In Fig. 4 we show a plot of droplet burning time vs original particle diameter for several oxygen concentrations in N_2/O_2 mixtures. Comparing the data in Fig. 3 and 4, we can see that a particle size

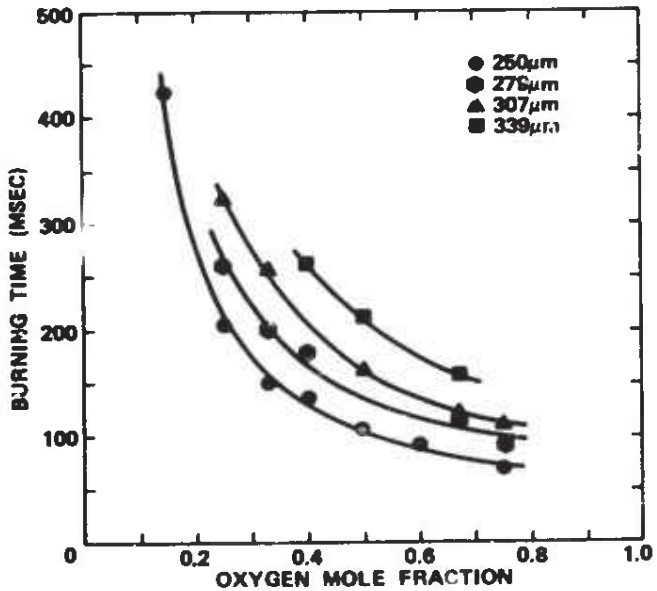

Fig. 2. 250 μm Aluminum Droplets Burning in O_2/Ar and O_2/N_2 Mixtures at 700 ± 7 Torr. (Dry).

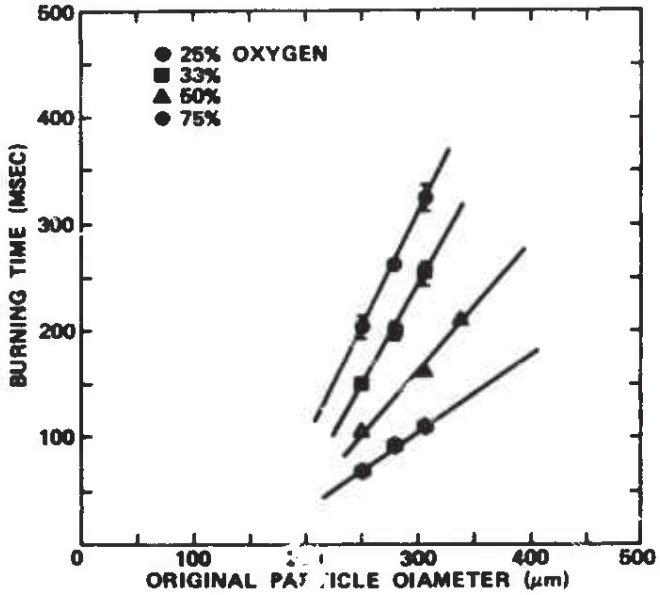

Fig. 3. Aluminum Droplets Burning in O_2/Nitrogen Mixtures at 700 ± 7 Torr.

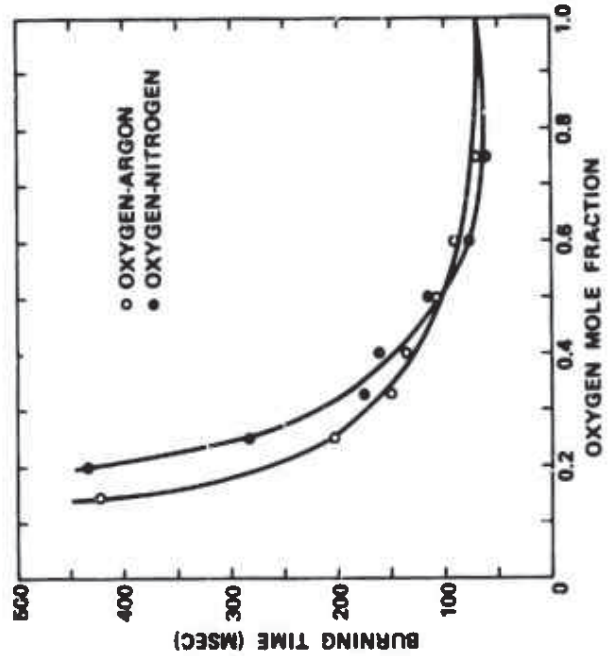

Fig. 5. Aluminum Droplets Burning in O_2/Ar Mixtures at 700 ± 7 Torr.

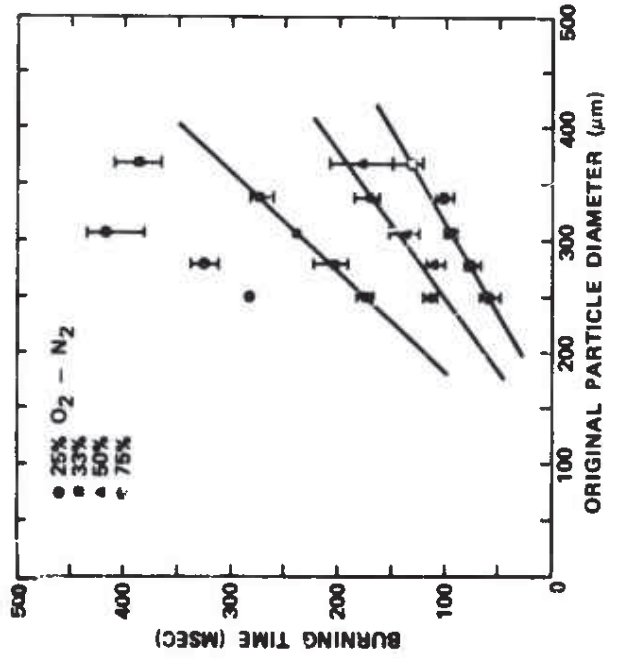

Fig. 4. Aluminum Droplets Burning in O_2/Argon Mixtures at 700 ± 7 Torr.

effect exists with large particles burning faster in N_2/O_2 and small particles burning faster in Ar/O_2. Figure 5 compares the burning time vs oxygen mole fraction for 250 μm Al droplets burning in N_2/O_2 and Ar/O_2 mixtures. Note that at oxygen mole fractions less than 0.5 the metal burns faster in Ar/O_2 but above that oxygen concentration a reversal of roles occurs. This difference is not appreciable but is repeatable throughout the series of particle sizes studied.

Figure 6 compares representative track photographs and photomultiplier emission traces from aluminum droplets burned in "wet" and dry mixtures of the gases cited earlier. Water-saturated gases are shown on the left and dried gases on the right. The top row (A-D) shows specimens burned in N_2/O_2. The middle row (E-H) shows specimens burned in Ar/O_2. The bottom row shows Al burning in wet CO_2/O_2 (J,K) while the other specimens (L,M) represent Al burning in dry CO_2.

There is little difference to be seen between the wet and dry N_2/O_2. Recognition should be accorded, however, to the droplet explosion in both cases. $Argon/O_2$, on the other hand, is quite another matter. In the dry gas case (Fig. 3,H) no product accumulates on the droplet, the only product is smoke (∿ 1 μm) and the droplet burns away symmetrically to zero. In the wet Ar/O_2 case the droplet becomes encapsulated with oxide and the vapor phase flame is seen to collapse onto the particle late in burning. The products from such droplet burning include the usual 1 μm smoke and a single large oxide sphere whose diameter varies from 0.75 - 0.85 d_o. The quenching and rekindling of the lower portion of the track in (E) is the "spearpointing" which is characteristic of the thermal quench of a refractory sphere.

The photos shown in J, K, show a specimen burned in wet CO_2/O_2 and reveal vigorous burning and violent fragmentation of the droplet. Items (L,M) show an Al droplet burning in pure dry CO_2. While it is possible to ignite Al particles in CO_2 (either wet or dry) the droplets will not burn to completion in the cold gas of these experiments.

To recapitulate the revelations of this series of burning droplets shown in Fig. 6 we see that little difference exists between wet and dry N_2/O_2. Asymmetric burning and explosion of the droplets is common to both cases. For the case of Ar/O_2 no product accumulates on the surface in dry gas, while complete encapsulation occurs if the gas is saturated with water vapor. A large oxide sphere is the most significant product when burning in wet Ar/O_2. Al droplets burned in wet CO_2/O_2 seem to burn more vigorously and explode a good deal more violently than in the other gases studied. The oxide(s) formed on Al droplets burning in wet gases differ from that found in our former experience of aluminum burning in dry air, for example. The oxides formed in the presence of water vapor are transparent where the other is opaque α - alumina and this newer oxide wets the metal droplets where α - alumina does not.

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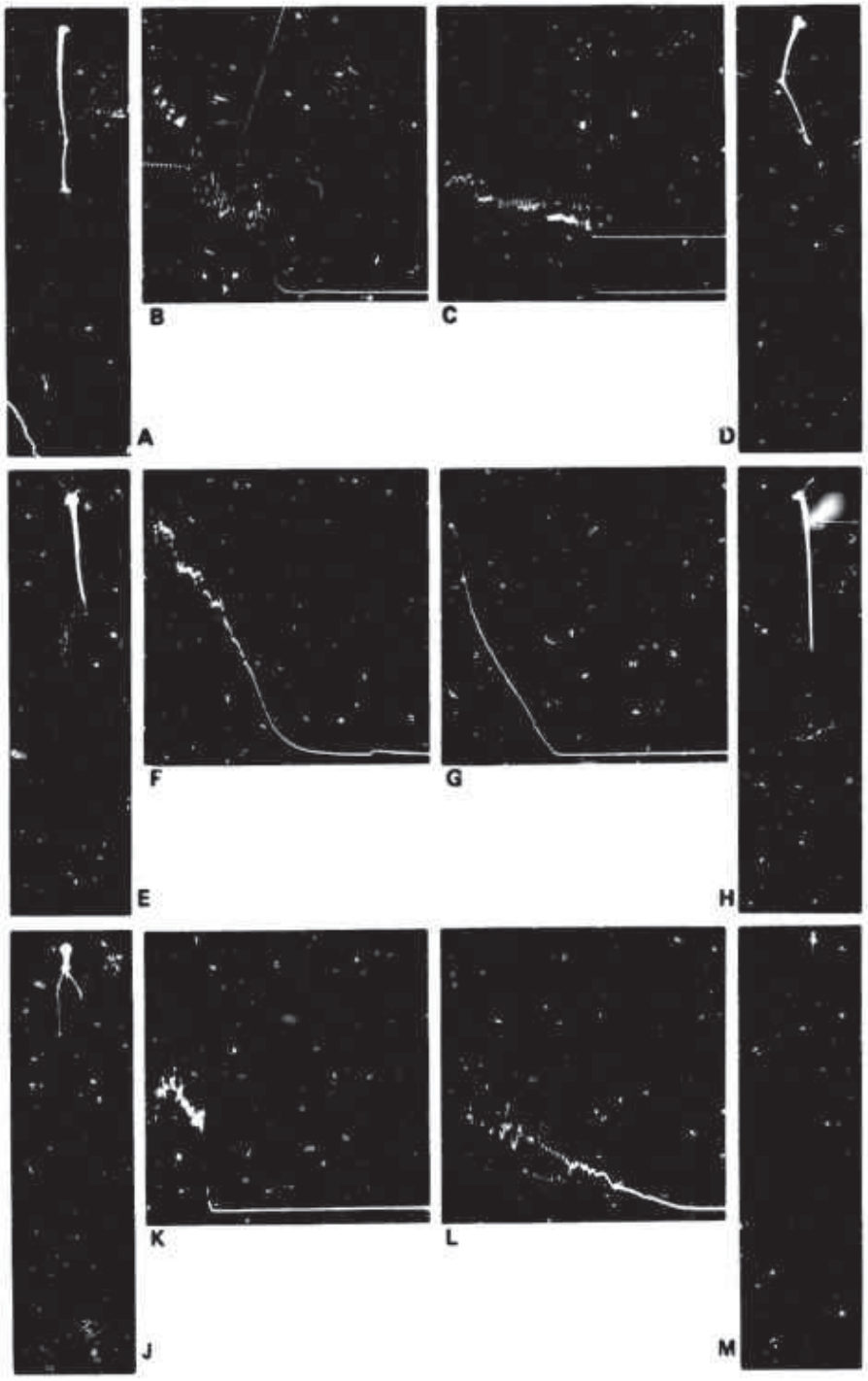

Fig. 6. Still Plate Track Photos and Photomultiplier Emission Traces of Aluminum Droplets Burning in Various Oxidizing Gases. Left hand column shows droplets burned in gases saturated with water vapor, right hand column shows burning in dried gases. Top row (A-D) droplets burned in N_2/O_2. Middle row (E-H) droplets burned in Ar/O_2. Bottom row (J, K) "wet" CO_2/O_2 and bottom right (L,M) dried CO_2.

High speed motion pictures indicate that droplets burning in water vapor-saturated mixtures of N_2/O_2, Ar/O_2 and CO_2/O_2 will fragment. Those burned in wet Ar/O_2 fragment about 15% of the time while the others fragment all the time.

3.2 BURNING IN WET GASES

Having established a data base for the burning in dry gases we turned to a quantitative determination of droplet burning time in wet gases. Figure 7 compares droplet burning time as a function of particle diameter for wet and dry N_2/O_2. It can be seen that Al droplets burn slightly faster in the wet gas.

Figure 8 compares droplet burning time as a function of d_o for wet and dry Ar/O_2. The banded area enclosed by the open circle curves represents an area of ambiguity in the determination of droplet burning time in wet Ar/O_2. This area of uncertainty is bounded on one extreme by the collapse of the vapor phase reaction (Fig. 6E) and on the other by the onset of spearpoint. It is certain that the burning is completed by the time of spearpoint but it is not clear that burning terminates with collapse of the vapor phase flame, although we believe that termination is very close if not identical to $t_{collapse}$. Recall that in this case the droplet becomes completely encapsulated with oxide and produces a large sphere of oxide as the end product. It appears that the metal also burns slightly faster in the wet situation for Ar/O_2.

Figure 9 compares burning time as a function of d_o for wet and dry CO_2/O_2 mixtures. Here also, as in the N_2/O_2 and Ar/O_2 cases, the metal burns faster in the wet gas. Experiments performed in water vapor-saturated CO_2/O_2 mixtures explode at all O_2 mole fractions greater than 0.25. The aluminum droplets do everything much more vigorously in wet CO_2/O_2 than in all other gases tried. The droplets spin violently and exhibit multiple eruptions of gas and often condensed phase debris prior to terminal fragmentation. If the droplet fails to explode ($X_{O_2} \leq 0.25$) there results an oxide sphere of diameter $\sim 0.75 d_o$. In all other cases (explosion) there is a shower of debris with particle sizes ranging from $0.2 - 0.8 d_o$.

In Fig. 10 we have plotted the mean time-to-erupt vs d_o for the major eruption preceeding the terminal fragmentation in wet CO_2/O_2 for several O_2 concentrations. In Fig. 11 can be seen the time-to-burnout or extinction plotted as a function of d_o for various mixtures of wet CO_2/O_2 It should be reemphasized here that for $X_{O_2} \leq 0.25$ the droplets do not explode but yield a large oxide sphere. For the other two cases shown ($X_{O_2} = 0.5$ and 0.75) the droplets explode violently. In all cases the droplets are encapsulated with oxide.

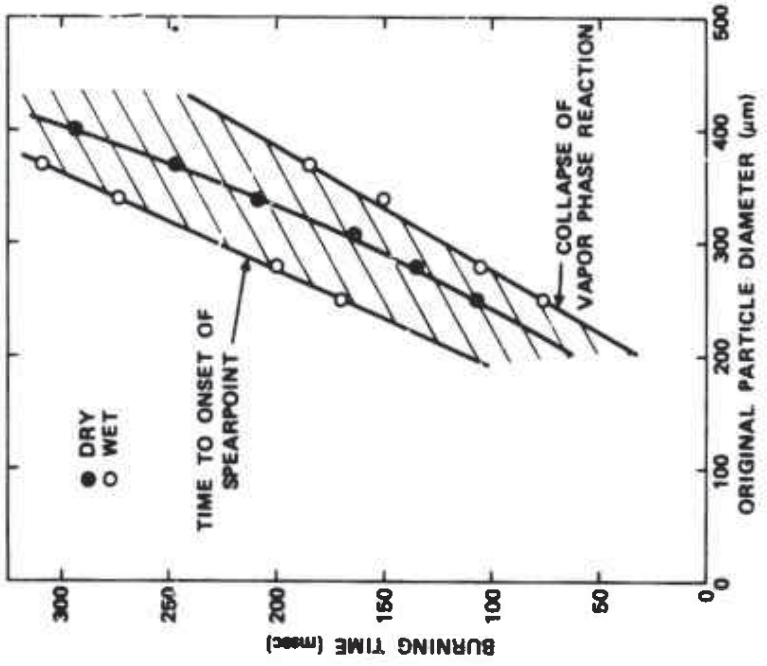

Fig. 8. Aluminum Droplets Burned in Dry and Water-Saturated Mixtures of 50/50 O_2/Ar at 700 ± Torr.

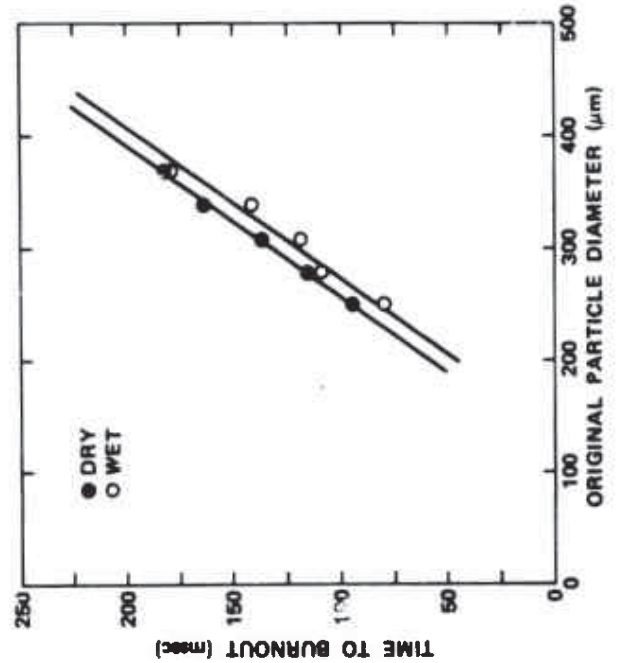

Fig. 7. Aluminum Droplets Burned in Dry and Water-Saturated Mixtures of 50/50 O_2/N_2 at 700 ± 7 Torr.

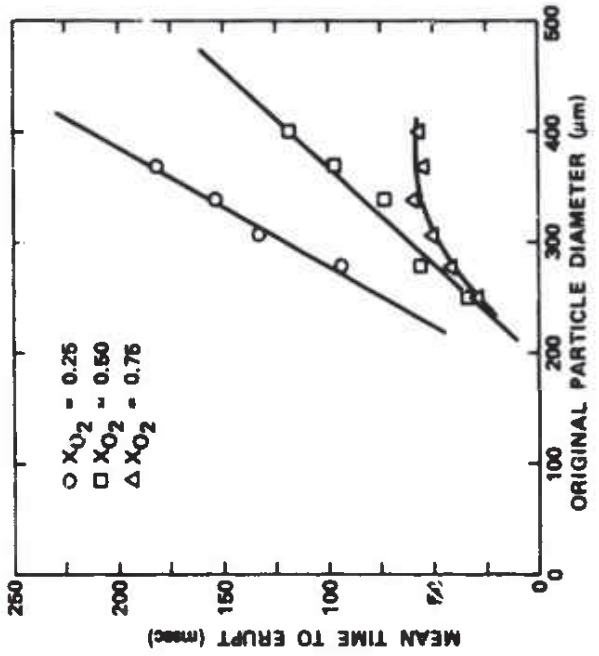

Fig. 10. Al Droplets Burning in CO_2/O_2 Mixtures Saturated with Water Vapor at 700 ± 7 Torr.

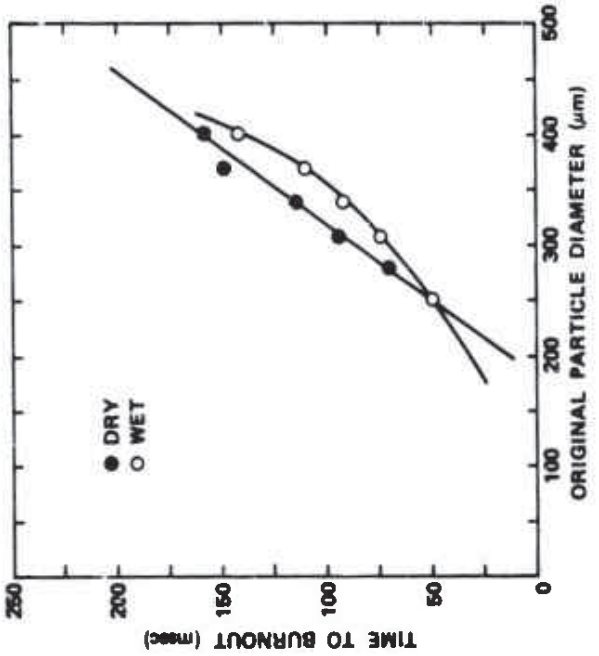

Fig. 9. Al Droplets Burned in CO_2/O_2 Mixtures Saturated with Water Vapor at 700 ± Torr.

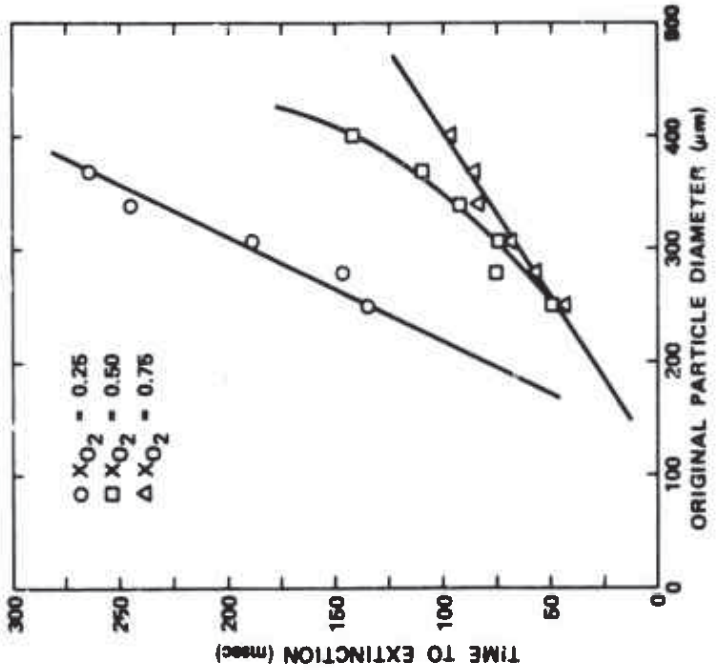

Fig. 11. Al Droplets Burning in CO_2/O_2 Mixtures Saturated with Water Vapor at 700 ± 7 Torr.

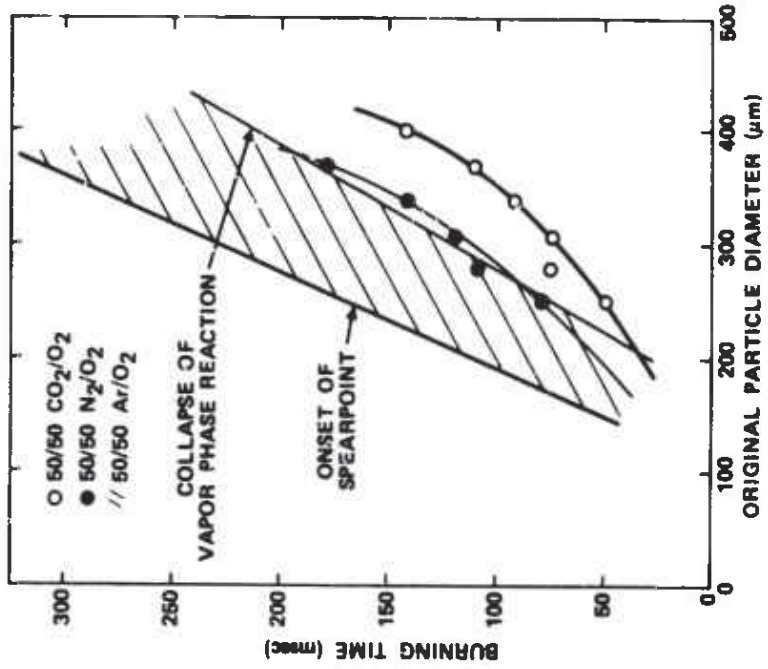

Fig. 12 Aluminum Droplets Burned in Various Gas Mixtures Saturated with Water Vapor at 700 ± 7 Torr.

Comparison of the burning in all three of these wet gas mixtures can be seen in the plot shown in Fig. 12. In this plot we have again shown the area of ambiguity for the case of wet Ar/O_2 with the same boundaries as before. Note that Al droplets burn significantly faster in wet CO_2/O_2 than in the other two gases.

3.3 NATURE OF COMBUSTION DEBRIS

Returning to the matter of particulate damping of combustion instability, it is important to know the nature and state of subdivision of the oxide product as a function of the environmental variables. We have pointed out earlier that Al droplets will not burn to completion in either wet or dry CO_2 in these cold gas experiments. The combustion in wet CO_2 is nearly complete but the residue of combustion is a metal sphere almost completely encapsulated with clear-to-transluscent oxide and usually one other shed sphere of an opaque oxide. Figure 13 shows the data resulting from these burns as a plot of debris diameter vs d_o. Two spheres result from each droplet burned: the encapsulated remains of the original and a smaller opaque oxide sphere.

Debris from these droplet burning experiments can be complex, particularly if droplet explosion occurs. That aapect of the burning is treated a little later, but for the moment we wish to consider cases where only a single large sphere of oxide results from the burning of a given droplet. Figure 14 summarizes the available data for the case of single sphere formation (ignoring for the moment the associated smoke formation). In this example we plot the diameter of the debris spheres as a function of d_o for two different gaseous systems, namely, Ar/O_2 and CO_2/O_2. It was intended to use the data for 50/50 mixtures of both of these systems so the data would relate directly to the data shown in Fig. 12. However, as noted previously, droplets burned in mixtures of wet CO_2/O_2 in which $X_{O_2} \geq 0.25$ all explode violently yielding showers of mixed balloons and solid spheres of various sizes.

In all of the droplet burning reported so far, only those droplets burned in dry Ar/O_2 or wet Ar/O_2 of O_2 mole fraction ≤ 0.25 do not explode. Aluminum droplets burned in wet Ar/O_2 only explode about 15% of the time but that is deemed significant.

Another question of considerable import has to do with what fraction of the original Al metal in a given droplet ultimately appears as smoke and what fraction in the large residue globules or spheres. Accordingly, the data of Fig. 14 was manipulated to yield (for the Ar/O_2 case) the weight fraction of original Al appearing in the final oxide sphere as a function of d_o. In this exercise, shown in Fig. 15, the oxide was

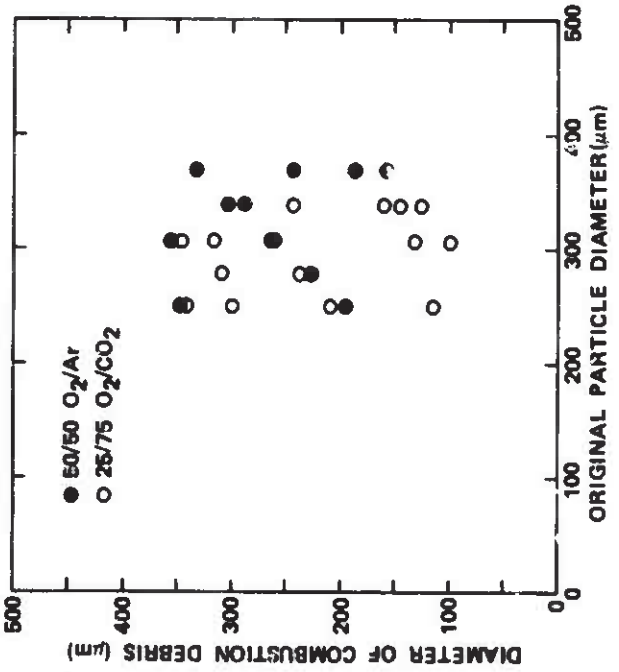

Fig. 14. Comparison of Spherical Oxide Residue (Single Large Sphere) from Combustion in Wet Gases. Each data point represents a separate experiment. (Pressure: 700 ± 7 Torr.)

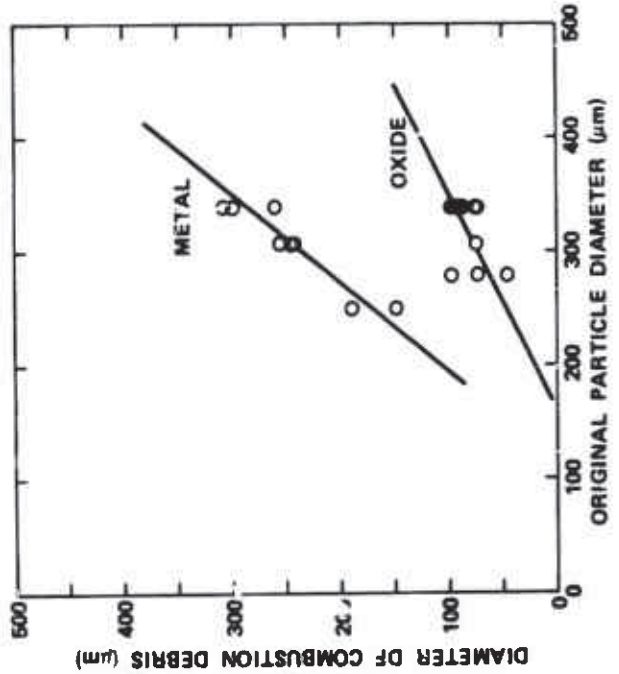

Fig. 13. Aluminum Droplets Burning in Pure CO_2 Saturated with Water Vapor at 700 ± 7 Torr.

assumed to be α - alumina and the appropriate density used to calculate the quantity of metal in the oxide sphere. When the same technique was applied to the spheres from the CO_2/O_2 burning, values of W/W_o ranging from 0.3 - 1.3 were found, indicating an erroneous choice of density, thus leading to the conclusion that not α - alumina but some non-stoichiometric Al-O-C species was, in fact, the product. Interim X-ray analyses have confirmed this fact. At least two aluminum oxycarbides are known (Ref. 8).

3.4 EFFECT OF WATER VAPOR ON COLOR TEMPERATURE

Previous investigators (Ref. 9) have reported a reduction of the color temperature of burning Al droplets when significant water vapor was present, usually of the order of 15 - 18%. We find this to be the case also, but the effect appears at a much lower water concentration (∿1.8%). In Figs. 16 and 17 we show the effect of water vapor on the radiant emission intensity for droplets burned in N_2/O_2 and Ar/O_2. Figure 18 shows the effect of oxygen mole fraction on radiant emission intensity for droplets burned in wet CO_2/O_2. And finally, Fig. 19 compares the radiant emission intensity for Al droplets burned in water-saturated 50/50 mixtures of all three gaseous systems studied. Note particularly that the intensity of burning, measured photometrically, is appreciably greater for CO_2/O_2 than either of the other two systems, which is consistent with the track photos of Fig. 6 and the burning time data in Fig. 12.

3.5 SUMMARY OF BURNING GEOMETRIES

In summarizing our experience with respect to the geometry of burning aluminum droplets, their ultimate fate, and the debris from combustion, we have condensed those findings into the schematic in Fig. 20. The salient features to be derived from this portrayal are as follows. Except for the dry Ar/O_2 case, product accumulation on the parent droplet is characteristic. In N_2/O_2 this accumulsation is globular, in all the other systems encapsulation occurs. In all examples except dry Ar/O_2 condensed phase reactions occur on the droplet yielding multiple eruptions of gas and/or liquid material during burning. In all cases except dry Ar/O_2 explosion of the droplets is the characteristic terminal event. The oxides formed on the droplet differ between the "wet" and dry gases. The condensed phase chemistry is complex, yielding substoichiometric Al-O-C or Al-O-N species. Water vspor modifies both the chemical and physical properties of the surface oxide allowing, in some cases, complete encapsulation of the burning droplet. Combustion debris is both chemicslly and physically complex. Droplet explosions yield a shower of material which is often difficult to retrieve quantitatively. Recovery, counting, cataloging, snd sizing under such circumstances are difficult and are not always possible to accomplish. Thus, a statistically viable sample is not yet in hand. (c.f. summary in Fig. 20 and Appendix A).

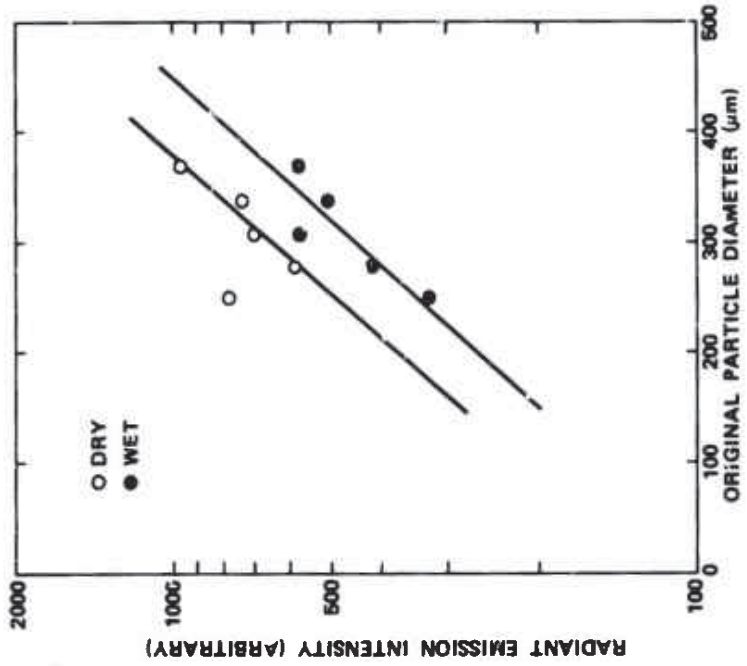

Fig. 16. Aluminum Droplets Burning in Dry and Water-Saturated Mixtures of 50/50 O_2/Ar at 700 ± 7 Torr.

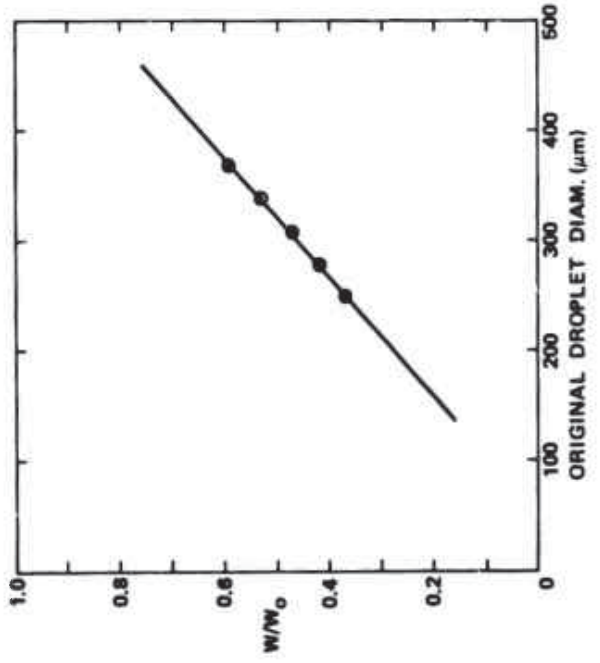

Fig. 15. Aluminum Droplets Burning in Dry and Water-Saturated Mixtures of 50/50 O_2/N_2 at 700 ± 7 Torr.

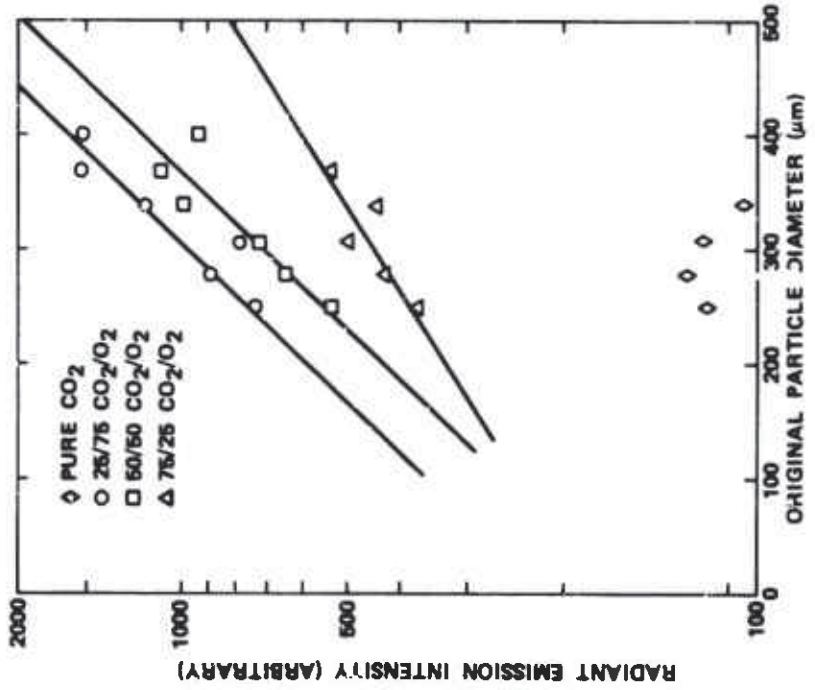

FIG. 18 Aluminum Droplets Burning in Various Gas Mixtures saturated with Water Vapor at 700 ± 7 Torr

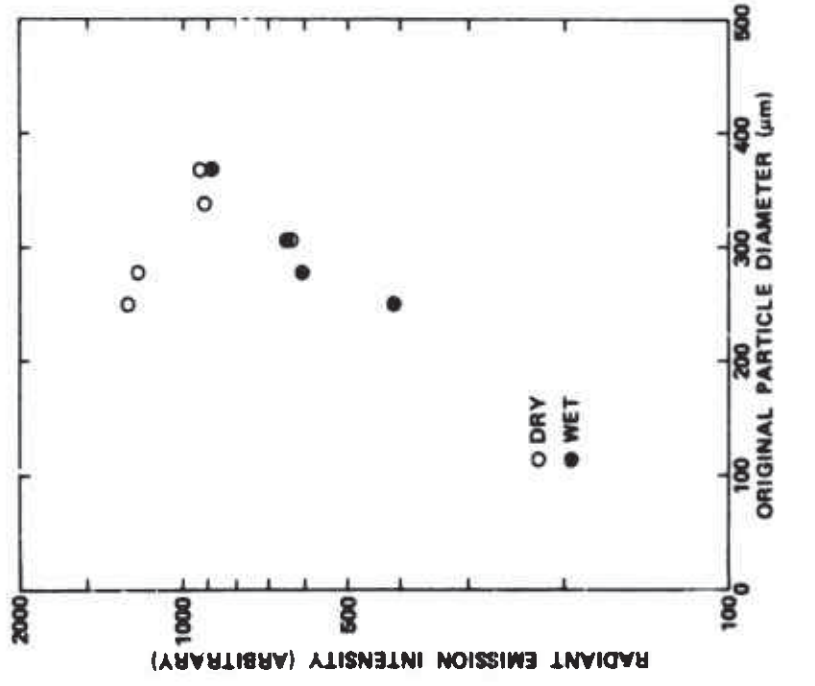

FIG. 17 Aluminum Droplets Burning in Various Mixtures of CO_2/O_2 Saturated with Water Vapor at 700 ± 7 Torr

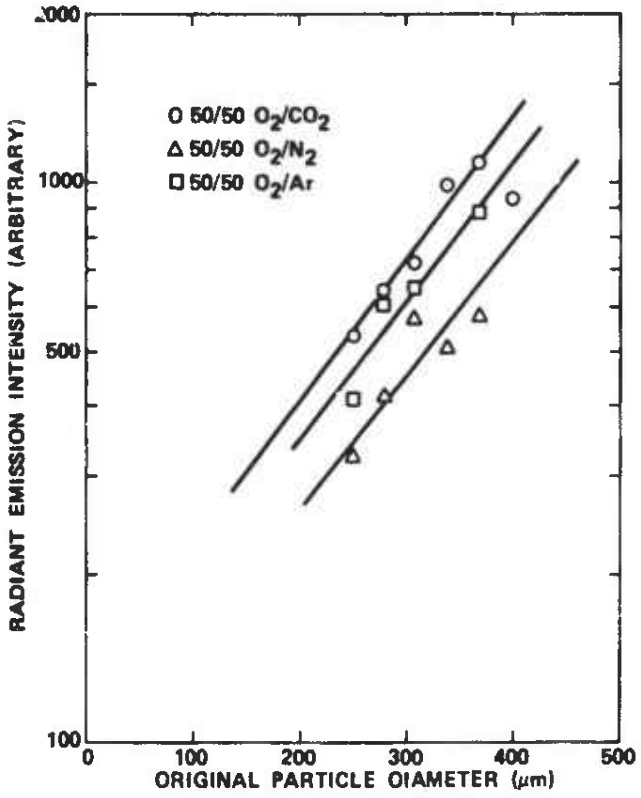

Fig. 19. Comparison of the Radiant Emission Intensity of Burning for the Three Gaseous Systems Studied (Pressure: 700 ± 7 Torr).

4. DISCUSSION

4.1 MODELING OF METAL DROPLET BURNING

Modeling of metal droplet burning, and particularly aluminum burning, suffers from several deficiencies attributable largely to attempts to extrapolate experience with hydrocarbons to the metal droplet situation. The metal droplet burning model most frequently used can be seen in the schematic shown in Fig. 21. This is a vapor phase diffusion-controlled model and could just as easily be applied to the burning of hexane, for example. Efforts to employ such a model for aluminum droplet burning ignore an enormous amount of experimental fact.

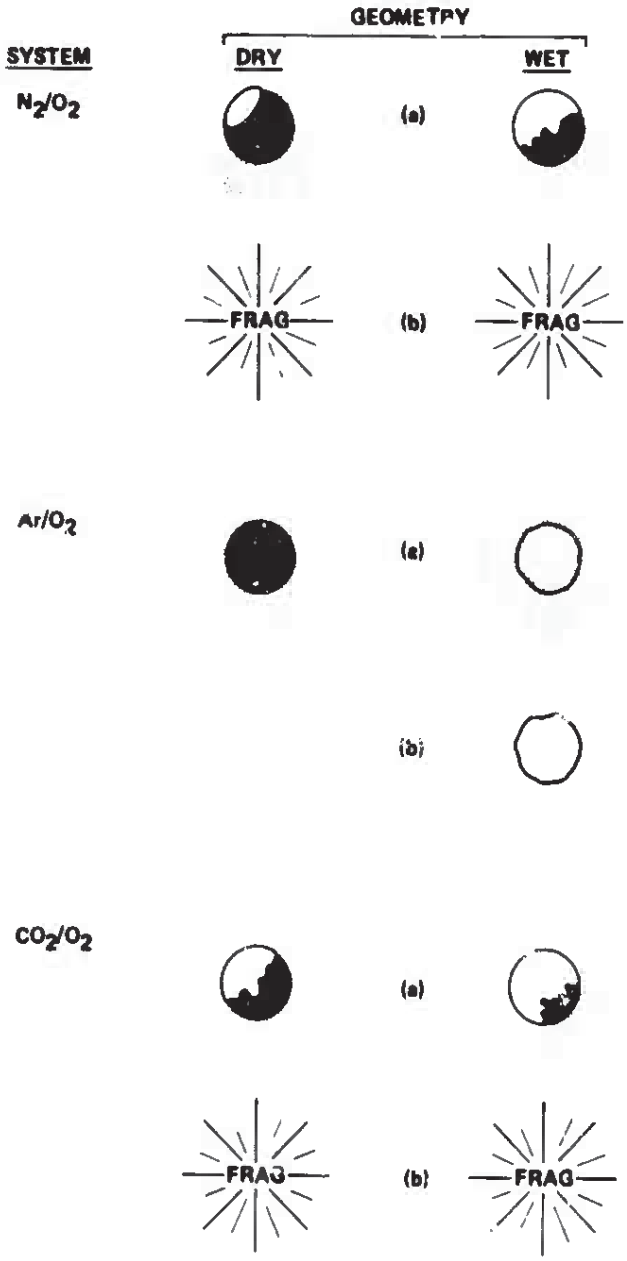

FIG. 20. Summary of Aluminum Droplet Combustion. All (a) represent quasi-steady state, all (b) represent terminal state. (See Appendix A for description of debris.)

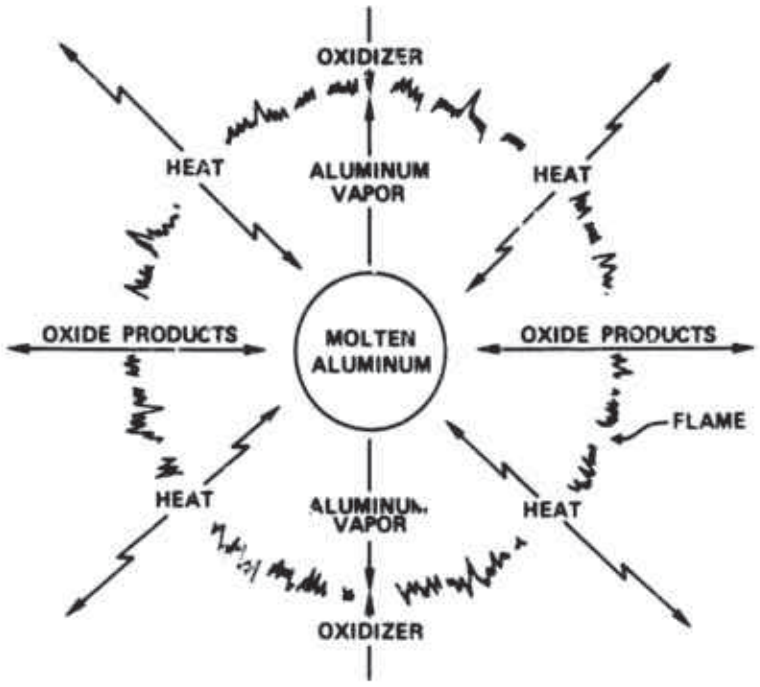

Fig. 21. Schematic of Over-Simplified Burning Model

Much has been made in the literature (Ref. 9 and 10) of a so-called "d^2-law" of droplet burning. This concept grew out of experience (both experimental and theoretical) with simple hydrocarbons where vapor phase diffusion-controlled burning and gaseous products were the norm. To properly appreciate where things have gone awry with the metal droplet modeling it is important to understand the assumptions upon which current modeling efforts are founded.

The so-called "d^2-law" can be derived strictly from geometrical considerations. Consider, for example, a freely vaporizing droplet such as that shown in the schematic in Figure 21. One can write an expression for the rate of mass loss, $\dot{m} = dm/dt$ as follows:

$$\dot{m} = \frac{dm}{dt} = \text{Mass Burning Rate}$$

$$\dot{m} = -\frac{d(4/3\pi r^3 \rho)}{dt}$$

$$\dot{m} = -4\pi r^2 \rho \frac{dr}{dt}$$

$$\frac{\dot{m}}{r} = -4\pi r\rho = -2\pi\rho \frac{d(r^2)}{dt} = -\frac{\pi}{2}\pi\rho \frac{d(d^2)}{dt}$$

$$\frac{d(d^2)}{dt} = \frac{-2}{\pi\rho}\left(\frac{\dot{m}}{r}\right) = \text{Constant for } \left(\frac{\dot{m}}{r}\right) = \text{Constant}$$

$$\text{If } \left(\frac{\dot{m}}{r}\right) = \text{Constant}$$

$$\text{Then } d_o^2 \propto t$$

This description only allows for mass loss, never for accumulation of mass.

That is, the droplet burning time would be proportional to d_o^2 (original diameter) if the ratio $(\dot{m}/r)$ were constant. If $(\dot{m}/r)$ can be shown to be constant for all droplet burning, then it can be said that a "d^2- law" of droplet burning exists. Parenthetically, slight rearrangement of the equations would show that if surface processes were rate-controlling the burn rate exponent n (in d_o^n) would equal 1 instead of the value 2 found for vapor phase diffusion control.

It is now necessary to consider the assumptions made regarding how droplets burn. The theory of hydrocarbon diffusion flames and combustion mechanisms can be found in texts on combustion theory (Ref. 11). Fundamental assumptions usually made in describing gas phase diffusion flames are listed below with checks denoting those which experimental evidence to the contrary leads us to challenge.

Neglect the following:

- Body forces (no natural convection)
- Thermal Diffusion
- Diffuso-thermal effect
- Pressure diffusion
- Bulk viscosity

Assume the following:

√ Steady state - steady flow - low velocity - constant pressure

• All binary diffusion coefficients equal

• Lewis Number = 1

√ Single step irreversible reactions

• No temperature gradient inside the droplet

√ Spherical symmetry

√ No surface or sub-surface reactions

√ No radiant heat transfer

• Infinite reaction rate

Our criticism of the assumptions in question is given below:

Steady State -

No one seriously defends this assumption today. Our work has shown intermittent spinning, jetting (eruption), and fragmentation to be the norm for aluminum droplet burning. Product accumulation on the droplet, condensed phase reactions yielding oxycarbides, oxynitrides and gaseous eruption and balloon formation as intermediate processes destroy the steady-state hypothesis.

Single-Step Irreversible Reactions

The reaction $Al_{(g)} + O_{2(g)} \rightarrow Al_2O_{3(g)}$ is not thermodynamically feasible. It is an easily verifiable fact that the driving force for the reaction comes from condensation of the Al_2O_3 (Ref. 12). AlO is known from spectroscopic analyses of burning droplets to be the dominant gas phase reaction intermediate (Ref. 13 and 14).

Spherical Symmetry -

Our single particle experiments going back 10 years and every cinephotographic study of aluminized propellant combustion reveals that massive droplet asymmetry exists during droplet burning.

No Surface or Sub-Surface Reactions -

The above asymmetry arises from accumulation of product on the droplet and subsequent reactions thereon. The presence of nitrogen, carbon dioxide or water vapor in the environment is able to cause surface reactions to occur, some of which lead to droplet explosion. In the absence of these species (dry Ar/O_2) no product is found to adhere to the droplet surface.

No Radiant Heat Transfer -

Even cursory examination of aluminum droplet burning indicates that the droplet is surrounded by an aerosol of Al_2O_3 smoke which radiates very strongly ($T \sim 3800^{\circ}K$). An ensemble of burning aluminum droplets will produce a radiating cloud in which the combustion will be affected by trapped radiation.

Further assumptions necessary to show specifically that $(\dot{m}/r)$ = constant are as follows:

√ Surface evaporation an equilibrium process
(i.e., partial press of fuel = equil vapor press.)

√ Droplet remains at its boiling point
(only latent heat need be supplied to sustain.)

- ρD = Constant in vicinity of droplet

- Constant $C_p = 1$
(All species have equal and constant specific heat.)

These last two checked assumptions are placed in equivocal status by the presence of surface reactions (which clearly abound for Al combustion (Ref. 6)).

4.2 BURNING RATE EQUATIONS AND THE SIGNIFICANCE OF THE DIAMETER EXPONENT

Burning rate equations in use are essentially of two kinds, both empirical. An expression of the form

$$t_{burn} = k d_o^{\,n} \qquad (1)$$

used to describe an average burning rate has been used by Belyaev, et. al., (Ref. 15). For burning at high pressures and temperatures using pressed fuel-oxidizer-metal powder specimens those authors found a dependence on oxidizer concentration also and reported their data as fitting the follow ing expression

$$t_{burn} = \frac{0.67\ d_o^{1.5}}{(a_k)^{0.9}} \qquad (2)$$

where a_k represents a composite oxidizer concentration ($CO_2 + H_2O$) reported as a percentage of the burnt gases.

An expression for the instantaneous burning rate such as

$$d^n = d_o^n - \beta t \qquad (3)$$

used by Wilson and Williams (Ref. 10) is of limited usefulness because of the difficulty of performing instantaneous particle burning rate measurements. As a consequence, the value of n the burning rate exponent could not, under their circumstances, be determined unequivocally. Wilson and Williams argue the merits of using the value of n as an indicator of combustion mechanism (i.e., $n = 1$ means surface processes are controlling; $n = 2$ means vapor phase diffusion processes are controlling).

Our data has been plotted according to Eq. (1) and the values of n thus extracted are listed in Table 1. From the table it can be seen that considerable variation exists as a function of environmental composition. If indeed n is a valid criterion by which to judge burning mechanism then the data for dry Ar/O_2 is as close an example to the model in Figure 20 as will ever be found (vapor phase process, no accumulation of product on the droplet). In that case, all values of n are greater than 2. However, the remainder of the data in Table 1 gives cause for concern. It can be seen that for dry N_2/O_2 values of n range from 1.3 to 2.0 as the oxygen mole fraction goes from 0.25 to 0.75. Viewed slightly differently, n goes from 1.3 at low O_2 mole fraction where droplet asymmetry due to accumulation of product (surface reactions) is greatest to $n = 2$ at high oxygen mole fraction where little or no oxide adheres to the droplet and vapor phase processes are dominant. Additionally, examination of the table shows that if one considers a 50/50 formulation of each of the three gas mixtures, each saturated with water vapor (items 5, 10, 13), n for all three cases is seen to be exactly 2.0. Now, we have shown before that all three of these examples are heavily encapsulated with oxide during burning and that all three will explode violently. Fragmentation terminates burning abruptly and fragmentation is caused by condensed phase processes on the droplet.

Table 1.

Comparison of Burning Rate Exponents for Aluminum Droplets Burning in Wet and Dry Gsses.

Item	Gas Mixture	Water Content	Oxygen Mole Fraction	Burn Rate Exponent n
1	O_2/N_2	Dry	0.25	1.3
2	"	"	0.33	1.5
3	"	"	0.50	1.5
4	"	"	0.75	2.0
5	O_2/N_2	Saturated	0.50	2.0
6	O_2/Ar	Dry	0.25	2.3
7	"	"	0.33	2.5
8	"	"	0.50	2.2
9	"	"	0.75	2.3
10	O_2/Ar	Saturated	0.50	2.0[a] 1.6[b]
11	Pure CO_2	Saturated	---	1.4
12	O_2/CO_2	Saturated	0.25	2.0
13	"	"	0.50	2.0
14	"	"	0.75	1.6
15	O_2/CO_2	Dry	0.50	2.5
16*	$CO_2/N_2/O_2$	Saturated	0.15	1.7

[a]Exponent derived from time-to-collapse of vapor phase reaction.
[b]Exponent derived from time-to-spearpoint.
*Representative Rocket Chamber Mixture Ratio (45, 40, 15%).

Further examination of the data in the Table 1 and replotting the data of Fig. 5 according to an equation of the form used by Belyaev, et. al., shows that burning time in our tests is also an inverse function of oxidizer concentration. Our data seems to fit an equation of the form

$$t_{burn} = \frac{kd_o^n}{(X_{O_2})^\beta} \tag{4}$$

The exponent β is 0.97 for dry ar/O_2 and 0.74 for dry N_2/O_2. Since n is seen to be a function of composition as well as oxygen concentration, and to be insensitive to the preaence of massive oxide accumulation on the droplet in which controlling surface processes are often found, it would appear that n is of little or not value as an indicator of combustion mechanism. Before leaving the topic, however, it is interesting to note the agreement between the value of n of Item 11 of Table 1 and the value found by Belyaev, et. al., for conditions of $T \geq 2000^oK$ and $20 \text{ atm} \leq P \leq 50 \text{ atm}$. While possibly fortuitous such agreement lends confidence to the relevance of the results from these single particle tests.

5. SUMMARY AND CONCLUSIONS

A series of quantitative single particle aluminum droplet burning studies has been performed. Aluminum droplets were burned in various oxidizing gases and mixturea of gases. Experiments were done in both dried and water vapor-saturated gasee. The presence of water vapor is found to have a significant effect on the combustion; in some cases altering the burning rate, droplet geometry and burning mechanism. Al droplets burn faster in all the gases examined if they are saturated with water vapor.

The oxide (or oxides) formed on the burning droplet in the presence of water vapor differs from that formed in dry gas. The product formed on the droplet in moist gas will generally be more transparent and actually wets the metal such that complete encapsulation of the droplet is possible. To illustrate, droplets burned in dry Ar/O_2 show no accumulation of product on the surface; those burned in saturated Ar/O_2 become encapsusuleted and yield a large solid sphere of oxide, while those burned in dry N_2/O_2 show product accumulating as a globular deposit on the Al droplet surface (i.e., no encapsulation).

Aluminum droplets were found to fragment in all three gas mixtures (Ar/O_2, N_2/O_2 and CO_2/O_2) if they were saturated with water vapor. Aluminum droplets burn fastest and explode most violently in wet CO_2/O_2.

Debris from these combustion experiments is found to be exceedingly complex as to both structure and subdivision, depending on gaseous environment, whether wet or dry and whether or not explosion occurs. Interim X-ray analyses indicate that the condensed phase chemistry is complex. Intermediates include various non-stoichiometric Al-O-C or Al-O-N species, depending, of course, on the gaseous atmosphere (see Ref. 5 for a more elaborate discussion of the chemistry involved).

Inasmuch as the accumulation of vast quantities of product on the droplet surface radically affects transport properties of the entire system, further systematic studies of the condensed phase processes occurring on the surface of the burning droplets need to be made. Since the high temperature phase diagrams are not known, a high-temperature X-ray examination of the intermediate species (or a splat-quenching technique to freeze high-temperature species) would be beneficial for an adequate elucidation of reaction processes. An inseparable effect of condensed phase chemistry is the resultant state of subdivision of the product. This aspect requires understanding and close control if solid propellant rockets are to perform safely and if they are to perform up to expectations.

It has been shown that there really is no such thing as a "d^2-law" of droplet burning and that the exponent n (in $t_{burn} = kd_o^n$) is of questionable value in determining the burning mechanism (surface or vapor phase control). Further, any metal droplet burning model which ignores the non-steady state product accumulation on the droplet and/or which employs simple gas phase kinetics has little chance to succeed.

APPENDIX A

SUMMARY OF COMBUSTION DEBRIS FROM ALUMINUM DROPLET BURNING

SYSTEM	CONDENSED PHASE PRODUCT	
	DRY	WET (H_2O - sat'd)
N_2/O_2	Smoke (1 - 2 μm) Solid Spheres ($\sim$ 0.2 d_o)	Smoke (1 - 2 μm) Solid Spheres (0.4 - 0.7 d_o) Hollow Spheres (0.2 - 0.8 d_o) 50 μm balloons dominate
A_r/O_2	Smoke (1 - 2 μm) No other product	Smoke (1 - 2 μm) 1 Solid Sphere (0.75 - 0.85 d_o)
CO_2/O_2	Smoke (1 - 2 μm) Solid Spheres (0.2 - 0.4 d_o) Balloons, 40 - 50 μm	Smoke (1 - 2 μm) For $X_{O_2} = 0.25$ 1 Solid Sphere 0.9 - 1.4 d_o For $X_{O_2} > 0.25$ 40 - 50 μm balloons dominate

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