Engineering Notes

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Combustion of Ammonium Perchlorate-Aluminum Mixtures

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Introduction

THE first study of the combustion of ammonium perchlorate (AP)-aluminum (Al) mixture was carried out by Romodanova and Pokhil,[1] who were interested in studying the effect of catalysts on AP-A1 systems. They experimented only with stoichiometric compositions using AP of particle size $<100\mu$ and Al of particle size $\leq 1\mu$ and pelletized the charges of 5 mm diameter to maximum density. The burning rate of AP-A1 composite (A1 content being 27.7%) without any catalyst, was found to be around 85 mm/s at 60 kgf/cm^2 pressure of nitrogen. Later, Cohen Nir[2] undertook a detailed study of the combustion of AP-A1 system as a function of pressure for 10%, 20% and 25% Al in the system. The particle size of AP was 55-80 μ and the Al particle size was not indicated. His data revealed for AP-Al pellets at 60 atm of nitrogen, an increase in the burning rate from 8.5 mm/s for pure AP to 10 mm/s for 10% Al composite. Above 10% Al content, the burning rate decreased, e.g., 7.5 mm/s for 20% Al. Above 25% Al content, the burning rate could not be obtained since the metal did not ignite even at 90 atm. Thus, a contradiction exists not only regarding the optimum AP-A1 ratio to obtain the maximum burning rate, but also whether the AP-A1 system containing more than 25% Al can burn at all.

Although the heat of combustion of a system is not the only parameter to influence the burning rate, it is nevertheless an important factor and, under favorable conditions, should predict the variation of burning rate with the composition of pellets. The objective of the present work is to throw some light on the above-mentioned controversy and to obtain burning rate data on aluminum-rich mixtures of AP-A1 around 60%:40%.

Experimental

The ammonium perchlorate used was reagent grade material from Hopkin and Williams Limited, England; the aluminum used was laboratory reagent grade material fine powder from Sarabhai M. Chemicals Limited, Baroda. In one set, the average particle sizes of AP and Al were found to be 11μ and 18μ, respectively, and in the other set, AP particle size was 11μ and that of Al particles was 37 to 45μ in diameter.

The powders were thoroughly mixed in the desired ratio and a pellet was made using a hydraulic press. A predetermined pressure was applied on a fixed weight, i.e., on 20 g of the sample to make a 5 cm diam pellet. For all the pellets, the pressure was maintained in an identical manner and the desired pressure maintained for a few seconds. Applied pressure in the present set of experiments on the pellet was 1500 kg/cm^2 with an uncertainty of 10 kg/cm^2.

Strands of dimensions ($L \times 5 \times 5$ mm, where L varied from 28 to 40 mm) were made from the cylindrical pellet. A strand burner was used to find the burning rates. Inhibited strands were taken in the present set of experiments, at a constant pressure of 60 atm N_2 in the strand burner, to find the burning rates.

Prior to obtaining the burning rate data on composites, burning rate measurements on pure AP strands were carried out as a function of the pelletizing pressure. The results are presented in Table 1 and are qualitatively agreeing with the results of Boggs and Zurn[3] for pure AP pellets.

Results and Discussion

The calculated values of heat of combustion with varying concentration of Al are presented in Fig. 1. The stoichiometric equation used for the preceding calculations is:

$$2.0\,NH_4ClO_4 + 3\tfrac{1}{3}\,Al$$

$$\rightarrow 2.0\,HCl + 3.0\,H_2O + N_2 + 1\tfrac{2}{3}\,Al_2O_3$$

The heat of combustion is 2.39 kcal/g. The standard values[4] of heats of formation of AP, H_2O (1), HC1 were considered to be 69.30, 68.32, and 22.06 kcal/mole, respectively. The heat of formation of Al_2O_3 was considered as 400 kcal/mole. From the preceding values, ΔH values for combustion were calculated for 2%, 5%, 10%, 27.7%, and 40% Al compositions.

As expected, the heat of combustion is seen to increase as Al concentration increases to stoichiometric composition, after which it decreases.

The burning rate of AP-A1 composite strands with varying wt.% of Al are presented in Fig. 2, curve a. The particle sizes of AP and Al are 11μ and 18μ, respectively. This figure is in good agreement with the value of heat-combustion and with the observation of Romodanova and Pokhil[1] that, at stoichiometric composition, AP-A1 composite burns.

Cohen Nir[2] could not study aluminum-rich mixtures (above 25% Al), since the metal did not participate actively in the combustion process. In the present work, the authors

Table 1 Pelletized pressure dependence of AP burning rate

Pelletizing pressure, kg/cm^2	Burning rate, mm/s
1000 ± 10	7.0
1250 ± 10	7.2
1500 ± 10	7.5
1750 ± 10	7.85
2000 ± 10	8.1

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Table 2 Summary of observations during combustion of AP-Al composite pellitized strands

Investigator(s)	Particle sizes, μ AP	Al	Dimensions of the strands/ charges	Observation on combustion of Al particles	Composition at which maximum burning rate obtained
Present work	11	18	$L \times 5$ mm × 5 mm $L = 28$-44mm	Participated up to 40% Al. No experiments conducted for higher Al contents.	Maximum burning rate at 27.7% Al
	11	37-45	"	"	Maximum burning rate at 10% Al
	11	63-75	"	Not participated even at 10% Al	...
	11	90-105	"	"	...
	37-53	90-105	"	"	...
	53-90	90-105	"	"	...
	210-205	210-250	"	"	...
Pokhil et al.,[1] 1970	< 100	≤ 1	5 mm diam cylindrical charge	Al participated	Not known since Pokhil has not studied for other than 27.7% Al
Cohen Nir[2] 1971	55-80	Not indicated	Parallelopipdes 15 mm × 5 mm × 5 mm	Participated up to 25% Al	Maximum burning burning rate at10% Al

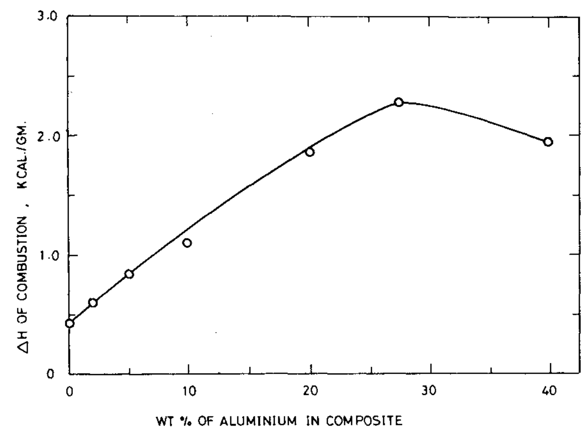

Fig. 1 **ΔH of combustion obtained from theoretical calculations for the AP-Al composite pellets.**

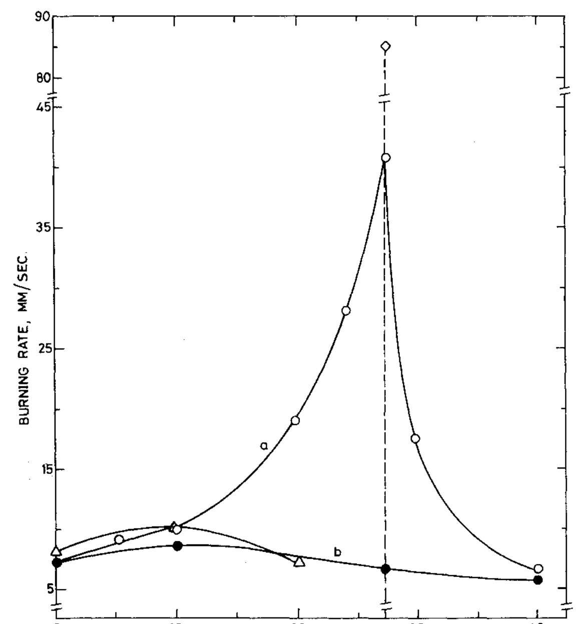

Fig. 2 **Burning rates of AP-Al composite pelletized strands in nitrogen at 60 atm: ○ = AP-11μ, Al-18μ; ● = AP-11μ, Al 37-45μ; ◇ = Romodanova and Pokhil, AP < 100μ, Al ≤ 1μ; △ = Cohen Nir, AP-55-80μ, Al not indicated.**

observed the combustion of Al until 40% of Al mass fraction, where the average particle size of Al was 18μ. Experiments were not conducted above 40% Al.

To understand the conditions under which Al-rich mixtures may not ignite, experiments were carried out using different particle sizes. Particles in the 90-105μ range did not ignite completely even at 10% Al. This gives an indication that the particle size of Al plays an important role in the complete combustion of AP-Al composite strand. With 90-105μ Al, when the composite strand is ignited due to the heat of ignition wire, AP decomposed very quickly and Al falls down in the bomb of the strand burner. This observation was made after collecting the Al in the bomb on asbestos paper. The same trend was observed even for 63-75μ range Al particles in another set of experiments. Table 2 gives the particle sizes of AP and Al, dimensions of the strands, and whether Al participates or not in the combustion. The observations of the earlier workers are also indicated.

When the AP used was 11μ and Al was 37-45μ, the burning rates of AP-Al composite strands vs the wt.% of Al is presented in Fig. 2, curve b. This clearly reveals that the particle size of Al and stoichiometry play a major role in the combustion of AP-Al. Each point in Fig. 2, curve b, is an average of six readings or six different strands, the error being ±5%. Although the difference in the maximum and minimum burning rate is not anywhere near what one gets using the particle sizes of AP and Al (AP 11μ and Al 18μ, respectively), the data seem to indicate that the burning rate peaks at 10% Al content. This then shows that under certain conditions of particle size for Al, Cohen Nir's[2] results could be reproduced.

Much more work needs to be done to fully understand the role of the particle size of Al in complete combustion, as well as in determining the percentage of Al content where the burning rate of AP-Al will peak.

References

[1]Romodanova, L. D. and Pokhil, P. K., "Action of Silica on the Burning Rates of Ammonium Perchlorate Compositions," *Fizika Goreniya, I. Vzryva.*, Vol. 6, No. 3, 1970, pp. 285-288.

[2]Cohen Nir, E., "Combustion of Powered Metals in Contact with a Solid Oxidiser," *Thirteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, Pa., 1971, pp. 1019-1029.

[3]Boggs, T. L. and Zurn, D. E., "Ammonium Perchlorate Combustion: Effects of Sample Preparation; Ingredient Type; and Pressure, Temperature and Acceleration Environments," *Combustion Science and Technology*, Vol. 7, 1973, pp. 177-183.

[4]Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., and Jaffe, I., "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, 1952.

On the Emissivity of Alumina/Aluminum Composite Particles

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Introduction

THERE is substantial uncertainty concerning the infrared emissivity of alumina particles in the exhausts of aluminized solid-propellant rocket engines. The basic problem is that pure macroscopic samples of alumina have a very small imaginary index of refraction and hence a very small absorbtivity/emissivity. On the other hand, aluminized solid-propellant rocket plumes are observed to radiate quite strongly in the infrared, and much of this radiation comes from the exhaust alumina. In some radiative regimes the particulate radiation dominates the entire plume signature.

In the past, plume radiation modelers have resorted to using phenomenologically determined and relatively large values of particulate emissivity in order to bring predictions into agrement with data.[1,2] While there has been discussion of the physical mechanisms responsible for producing these relatively large values, there is no concensus as to the dominant mechanism.

The purpose of this Note is to examine one possible source of enhanced exhaust alumina emissivity, namely, that the alumina particles contain a small fraction of unburned metallic aluminum. Solid propellants burn fuel rich (e.g., most of the carbon in the propellant comes out as CO rather than CO_2), and it is possible that some aluminum may emerge from the combustion chamber unburned. Furthermore, much of the aluminum combustion is observed to take place in large droplets of aluminum/alumina migrating around on the propellant surface,[3] which may prevent all the aluminum in the droplet from burning before leaving the chamber.

Alumina/Aluminum Composite Particles

The structure of such an alumina/aluminum composite particle is very difficult to predict. It will be a very sensitive function of the time history of the droplet and of the droplet's behavior as it experiences the shear forces during acceleration in the expanding nozzle flow. It will also depend on the details of the liquid droplet's solidification process, which is complicated by the large difference in solidification temperatures between alumina and aluminum. The final particles are likely to be complicated, inhomogeneous composites.

The particulate emissivity is generally calculated using the well-known Mie theory.[4] Once the particle structure is specified, the Mie theory must be cast in the appropriate form. For an inhomogeneous complex composite particle this is a difficult task and, in general, no such theory is available.

For the symmetric case of a composite particle composed of a spherical core surrounded by a spherical mantle, the extension of Mie theory has been considered by Güttler.[5] The complete theory for such particles is complex, but much of the behavior of such composite particles can usefully be studied in the Rayleigh limit:

$$2\pi a/\lambda \ll 1 \tag{1}$$

where a is the particle radius and λ is the wavelength. For this limit the absorption cross section σ_{abs} for a sphere of radius a, made up of two different materials, is given in Refs. 5 and 6. If the complex index of refraction is m_1 out to radius a_1 and m_2 out to radius a (i.e., between a_1 and a), then

$$\sigma_{abs} = -4\pi\kappa Im\beta \tag{2}$$

where $\kappa = 2\pi/\lambda$, and

$$\beta = a^3 \frac{a^3(m_2^2-1)(m_1^2+2m_2^2)+a_1^3(2m_2^2+1)(m_1^2-m^2{}_2)}{a^3(m_2^2+2)(m_1^2+2m_2^2)+a_1^3(2m_2^2-2)(m_1^2-m_2^2)} \tag{3}$$

Note that if $m_1 = m_2$, this reduces to the Rayleigh limit for a single material sphere:

$$\sigma_{abs} = (\pi a^2)\left[-4\frac{2\pi a}{\lambda} Im\left(\frac{m^2-1}{m^2+2}\right)\right] \tag{4}$$

This limit is also obtained if $a_1 = a$ or if $a_1 = 0$, of course.

In the Rayleigh limit the absorption coefficient ($=\sigma_{abs}/\sigma_{geo}$), and hence the emissivity, depends on the particle radius in a simple fashion, as can be seen in Eqs. (2-4). Consequently, a size-independent quantity can be introduced:

$$Y_{Ray} = \sigma_{abs}/(\pi a^2)/(2\pi a/\lambda) \tag{5}$$

Y_{Ray} is, therefore, the emissivity ϵ normalized to the Mie size parameter $q = 2\pi a/\lambda$, or

$$\epsilon = qY_{Ray} \tag{6}$$

The subscript Ray is used to emphasize that what follows is in the Rayleigh limit.

Emissivity Results

In order to evaluate the expressions for the emissivity, the indices of refraction for the subvolumes of the particle are needed; e.g., the indices of refraction of alumina and aluminum. These quantities are quite uncertain, however, so ranges of representative values were chosen for alumina that cover the spread of values that might be considered typical. The spectral region of interest is often the infrared (especially the region from 2-5 μm), so the real and imaginary parts of the index of refraction were chosen to be representative of such wavelengths. The index of refraction of aluminum was chosen to be typical of a conducting material, i.e., with a large imaginary part. Different values of the aluminum index lead to results qualitatively the same as those presented below. These values were chosen to cover an interesting region and are not meant to be definitive values for rocket exhaust alumina and aluminum.

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