Thermochemical Data And Handling Techniques For Densite Rocket Propellant

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THERMOCHEMICAL DATA AND HANDLING TECHNIQUES

FOR DENSITE ROCKET PROPELLANT

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Since the advent of amateur rocketry, micrograin[1] has been one of the standard rocket propellants for many amateur groups. The fact that it has found such widespread acceptance is understandable in view of its many desirable properties. These properties include low cost, ease of manufacture, and high shock insensitivity. However, mlcrograin is severely outclassed in performance when compared to propellants being used by the professional. In an attempt to find a more powerful propellant suitable for amateur use, Reaction Research Associates[2] has done extensive work with the cast micrograin propellant, a specially heat processed zinc-sulfur mixture. In this report, the theoretical thermochemical constants of the propellant are first discussed. An experiment which indirectly verifies the value of these constants is then described. Various other data, including a section on propellant manufacturing technique, is also contained in this report.

PHYSICAL PROPERTIES

Cast microgram or Densite[3] is a gray solid consisting of 75% zinc and 24.8% sulfur by weight. The remaining .2% consists of chopped fiberglass, an additive used to improve the strength.

Densite is unbelievably insensitive to shock and open flames. Indeed, it requires considerable patience to ignite it with a match.

THERMODYNAMIC PROPERTIES

The Exhaust Products

A simplified chemical equation for the zinc-sulfur reaction is given by

Zn (solid) + S (solid) = ZnS (gas) + heat.

Using the chemical equation above and knowledge of the atomic weights of zinc and sulfur, which are 65.4 and 32.1 respectively, it is easily calculated that zinc and sulfur combine in ratio of 2.04 to 1 by weight. However, all of the zinc is not used in the the molecular weight of the exhaust products. Consider, for example, a 100 lb. grain of Densite. When ignited, 25 lbs. of sulfur will react with 51 lbs. of zinc forming 76 lbs of zinc sulfide. This will leave 24 lbs. of zinc unreacted. Assuming that all of the sulfur is consumed in the reaction, the exhaust products will consist of, by weight, 76% zinc sulfide and 24% zinc.

Molecular Weight of Exhaust Products

If the exhaust products consist of 76% zinc sulfide with a molecular weight of 97.5 and 24% zinc with an atomic weight of 65.4, then the average molecular weight of the exhaust products is simply (.76) (97.5) + (.24) (65.4) = 89.7.

The Gas Constant

The gas constant is defined by the equation

$$R = \frac{R'}{m}$$

where R' is the universal gas constant, 1544 ft-lb/mole R and m is the molecular weight of the exhaust products. For Densite

$$R = \frac{1544}{89.7} = 17.3 \text{ ft} - \text{lb} / \text{lb R}$$

Chamber Temperature

There is no available data on the chamber temperature produced with the Densite propellant. However, because of the similarity between the microgram and Densite reaction, we have assumed that both burn at approximately the same temperature. As microgram is known to burn around 3060 R at 1000 psI, we have adopted this value as the chamber temperature produced in the Densite reaction.

Specific Heat Ratio of Exhaust Products

A good estimate of the specific heat ratio of gaseous zinc sulfide can be easily calculated from theoretical considerations. Briefly, for a diatomic gas with translational, rotational, and vibrational degrees fully excited, the specific heat ratio is 1.28. Because the zinc sulfide vapor is at an extremely high temperature, it can be assumed that all degrees of freedom are extremely close to being fully excited.

Collaborating evidence is also obtained from thermochemical data on magnesium sulfide, a compound one would expect to behave similarly to zinc sulfide. The specific heat ratio for magnesium sulfide at 3060 degree R is 1.29. Lacking better data, we have adopted this as the value of the specific heat ratio for zinc sulfide at 3060 degree R.

Assuming that the exhaust products are 76% zinc sulfide vapor with a specific heat ratio of 1.29 and 24% zinc vapor which is known to have a specific heat ratio of 1.66 in the above temperature range, the average specific heat ratio becomes (.76) (1.29) plus (.24) (1.66) equals 1.37.

PERFORMANCE CALCULATIONS

The Exhaust Velocity

The expression for the exhaust velocity is given by

$$v = \sqrt{\frac{2gk}{k-1} RT \left[1 - \frac{p_2}{p_1} \right]^{\frac{k-1}{k}}}$$

$$v = \sqrt{\frac{2gk}{k-1} RTn}$$

where g is the gravitational constant 32.2 ft/sec^2, k is the specific heat ratio of the exhaust products, T is the chamber temperature, and n is defined as

$$n = 1 - \left[\frac{p_2}{p_1} \right]^{\frac{k-1}{k}}$$

with p_1 and p_2 representIng the chamber and exit pressures respectively.

To achieve maximum thrust, the exit and ambient pressures must be equal. Hence at sea level, p_2 =14.7 psi. Using the value p_1 = 1000 psi and k equals 1.37, R equals

[1] Microgram is a mixture of 67% zinc dust and 33% powdered sulfur by weight.

[2] Reaction Research Associates is an amateur rocket society organized on the campus of New Mexico State University in April of 1963.

[3] This name was chosen because of the high density of the propellant. The density of the propellant is extremely high, being in the order of .15 lb/inch^3 despite the fact that small air bubbles can be observed throughout the grain. The sulfur in Densite is in the form of long polymerized chains between which particles of zinc and fiberglass are entrapped.

17.3, and T equals 3060 degrees R, all obtalned from the thermochemical section, the exhaust velocity at sea level becomes

$$v = \sqrt{\frac{2(32.2)(1.37)}{.37}(17.3)(3060)\left[1-\left(\frac{14.7}{1000}\right)^{\frac{.37}{1.37}}\right]}$$

$$2900 \text{ ft/sec}$$

For a gas expanding into a vacuum, n assumes the value of 1 and the maximum exhaust velocity is given by

$$v_{MAX} = \sqrt{\frac{2gk}{k-1}RT}$$

The maximum exhaust velocity for Densite is 3540 ft/sec.

Specific Impulse

The ideal specific impulse can be calculated. from the equation

$$I_{MAX} = \frac{v_{MAX}}{g}$$

For the Densite propellant

$$I_{MAX} = \frac{3540}{32.2} = 110 \text{ lb–sec/lb}$$

The actual specific Impulse produced in a rocket motor at sea level is

$$I_{ACTUAL} = L\frac{v}{g}$$

where L is the velocity correction factor. This factor takes into account the energy lost by the exhaust gases due to the departure of a real nozzle from an ideal nozzle. Using .92, the average value of the volocity correction factor, the average specific impulse for Densite at sea level becomes

$$I_{ACTUAL} = \frac{.92(2900)}{32.2} = 83 \text{ lb–sec/lb}$$

This value may vary ± 5 lb-sec/lb depending on the efficiency of the nozzle.

EXPERIMENTAL DATA

Being amateur organization, it was beyond our means to measure any thermochemical constants directly because of the elaborate equipment needed to carry out such measurements. An indirect method was used to measure these constants using experimentally determined specific impulse data. If the experimental and theoretical specific impulse values agreed, this would offer some degree of confirmation of the values computed for the thermochemical constants**.** One of the test runs for determining the specific impulse is described below. Various chamber pressure and burning rate data are also discussed.

The Test Equipment

To determine the specific impulse experimentally, the total impulse produced by the rocket motor must be measured. The test setup to accomplish this task is shown in Fig. 1. The thrust sensor consisted of a small cylinder containing a piston on which the rocket motor rested. A pressure line led from the cylinder to a Bourdon pressure gauge mounted on a recorder. Two lead pencil styluses were attached to the face of the gauge with one providing a center reference mark and the other showing the movement of the pressure indicating needle. The recorder, consisting of two rotating drums upon which pressure sensitive paper was wound, pulled the paper past the styluses of the pressure gauge. When the motor was fired (See Fig. 2), the pressure was recorded on the paper as shown in Fig. 3. A tape recorder was used to measure the burning time of the motor.

The Motor

The motor consisted of a standard 2 1/2 " inside diameter pipe 13" long with a cast iron cap screwed on each end. A hole 13/16" in diameter was drilled on center in one cap to accommodate a steel nozzle. The motor was loaded by simply inserting the grain in the chamber and screwing on the nozzle assembly. To inhibit the grain so that only end burning would occur, the sides were wrapped with black electrical tape. In order to make the grain fit the chamber precisely, it was also wrapped with paper to the proper diameter. The specifications on the motor and propellant grain are:

Weight of motor (9.75 ± .25 lbs); Throat diameter (.314 ± .002"); Exit diameter (.75 ± .03"); Area Expansion Ration(5.7);Nozzle divergence angle (10 degrees ± 1); Dimensions of grain (l2 ± .25" x 2 ± .03") Weight of grain (5.5 ± .1 lb).Total loaded weight (15.25 ± .35 lb)

Data and *Evaluation*

The specific impulse produced by a rocket motor can be calculated from the equation

$$I = \frac{I_t}{W}$$

where the total impulse produced and W is the total weight of the propellant.

The pressure taken from the graph can be converted into thrust by making use of the equation

$$F = pA$$

where p is the pressure in psi and A is the area of the piston in in^2. The area of the piston was found to be .093 ± .004 in^2. Using this value the thrust equation for this particular test is

$$F = .093p.$$

The average pressure obtained from the graph was 1350 psi for the entire duration of the run. This value must be corrected to take into account the pressure produced on the piston due to the weight of the motor itself. When this is done, the actual pressure produced due to the thrust of the motor is 1200 ± 100 psi. Converting this into thrust

$$F = (l200)(.093) = 112 \text{ lbs.}$$

The motor burned for 4 ± .2 seconds. The specific impulse is then

$$I = \frac{4(112)}{5.5} = 81.5 \text{ lb–sec/lb}$$

The probable error in the above measurement is ± 7 lb-sec/lb. Because of this large probable error, it is impossible to determine the exact value of the specific impulse from the above test. However, the range of values are in close agreement with those calculated from theoretical considerations.

Chamber Pressure and Burning Rate

No direct measurements of the chamber pressure were taken during the test. Yet the chamber pressure can be found using the equation

$$F = A_t p_1 \sqrt{\frac{2k^2}{k-1}\left[\frac{2}{k+1}\right]^{\frac{k+1}{k-1}}\left[1-\left[\frac{p_2}{p_1}\right]^{\frac{k-1}{k}}\right]}$$

Using F equal to 112, k equal to 1.37, p_1 equal to 14.7 psi, and the area of the throat A_t equal to .075 in., this equation gave a value of 1000 psi for the chamber pressure.

The burning rate at this pressure was (3 ± .1") at an ambient temperature of 90 ± 5 F.

PERFORMANCE COMPARISON WITH MICROGRAIN

The velocity achieved in a vacuum by a rocket motor with an ideal nozzle

$$v_{MOTOR} = v_{MAX}(\ln\lambda)$$

where λ is the mass ratio and is defined as

$$\lambda = \frac{\text{Initial Vehicle Mass}}{\text{Final Vehicle Mass}}$$

Consider a motor whose casing weight is 1.86 lbs and has a chamber volume of 37 in^3 .Table 1, which was compiled using the equations above, shows the velocity that will be reached by the motor when loaded with each propellant. The superior performance of Densite is clearly evident.

Propellant	**Density ρ in^3**	**Maximum Specific Impulse**	**Density Impulse lbs/in^3**	**Motor Propellant Weight**	**Mass Ratio**	**Log Mass Ratio**	**Exhaust velocity ft/sec**	**Rocket velocity ft/sec**
Densite	**.15**	**110**	**16.5**	**5.5**	**3.96**	**1.38**	**3540**	**4870**
Micrograin	**.093**	**30**	**2.79**	**3.44**	**2.85**	**1.05**	**965**	**1010**

CASTING TECHNIQUE

When heat is applied to a powdered zinc-sulfur mixture, a liquid which can be easily poured is formed. Upon cooling, this liquid becomes a dense gray solid. This solid is Densite.

To the reader who is acquainted with microgram, the first emotion displayed at the thought of applying heat to a zinc-sulfur mixture was probably that of stark terror. Yet the hot casting technique, when properly conducted, is a safe operation. This statement is based on the following reasons:

(1) The mixture is heated at a temperature of 320 degrees F in the casting procedure. Flash tests have shown that the propellant will ignite at 500 degrees F. Thus there is over 180 degrees F separating the working temperature and the flash temperature.

(2) Before the Densite reaction takes place, the sulfur will ignite first and burn with a blue flame on top of the melted mixture. After the appearance of this flame, it will take approximately 3 seconds before the main reaction takes place. This is ample time to get away in case the mixture is heated above the flash temperature.

(3) Unlike microgram in which the flame front travels through the entire mixture at a very rapid rate producing nearly a low order detonation effect, the liquid mixture has the advantage that burning takes place only on its surface. At this point, it might be wise to add that these statements are not to be construed as an excuse for not taking adequate safety measures. Suffice it to say here that face shield and loose gloves should be worn during the casting operation.

We do not recommend casting this propellant directly into the combustion chamber of a rocket motor. When this propellant cools it contracts and in doing so might separate from the sides of the chamber. This will expose, the sides of the propellant to the flame front and could possibly lead to an explosion. We believe that the best results can be achieved by casting the propellant into small ingots. These can be bonded together with epoxy cement and suitably inhibited to form the grain. This method also has the following advantages:

(1) Most amateurs do not have at their disposal a heating element with suitable temperature control capable of melting large quantities of propellant. The ingots lend themselves to the use of small controlled heating elements, such as electric frying pans, which can be readily obtained.

(2) If large quantities are melted, the zinc tends to settle to the bottom of the mixture. While this is not altogether eliminated when casting ingots, the tendency is reduced.

To insure a uniform heating of the mixture, the best results can be obtained using the “oil bath technique”. In this process oil is poured into the heating device and pans containing the propellant are immersed in the oil.

The sulfur used must be at least 99% pure. If this standard is not maintained, the melted mixture becomes extremely viscous and cannot be poured easily. The fiberglass. should be in the form of fibers approximately ¼” in long. These must be well dispersed in the mixture.

A casting mold can be constructed from a pipe of suitable inside diameter which should be slightly less than the diameter of the combustion chamber in order to allow space for the liner. The pipe is first cut to a faced square on both ends. Next, the inside surface is is polished until a smooth finish is length approximately equal to its diameter and then obtained. The final step is making a hacksaw cut through the wall along the length of the pipe.

Two flat plates are also needed to fit over the ends of the section described above. In the center of one plate, a hole must be drilled with a diameter equal to 1/3 the diameter of the ingot. To assemble the mold, two band clamps are placed around the cylindrical section and tightened until the cut closes. The two plates are then clamped on the ends of the circular section. A cardboard tube approximately 3 in. long is then taped over the hole in the plate forming an extension of the mold. During the casting operation this tube must be filled with the liquid propellant mixture or a large indentation will form in the center of the ingot due to its contracting while cooling. After the liquid hardens, the clamps are removed and the cardboard tube, along with the propellant it contains, is sawed off the main ingot. Any rough edges resulting from this process can be sanded smooth. Fig. 4 shows a completed casting mold.

The Densite propellant not only retains the desirable properties of microgram but, in addition, is vastly superior in performance. For the serious amateur who is willing to take the time and effort required in using this propellant, a new dimension in amateur propulsion systems is possible.

REFERENCES

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FIGURE 1. Moving clockwise the photo shows the tape recorder, graph recorder, and rocket motor. A similar but larger motor was used in the test described in this paper.

FIGURE 2. Static test firing of the motor. The flame is approximately 7 ft. long.

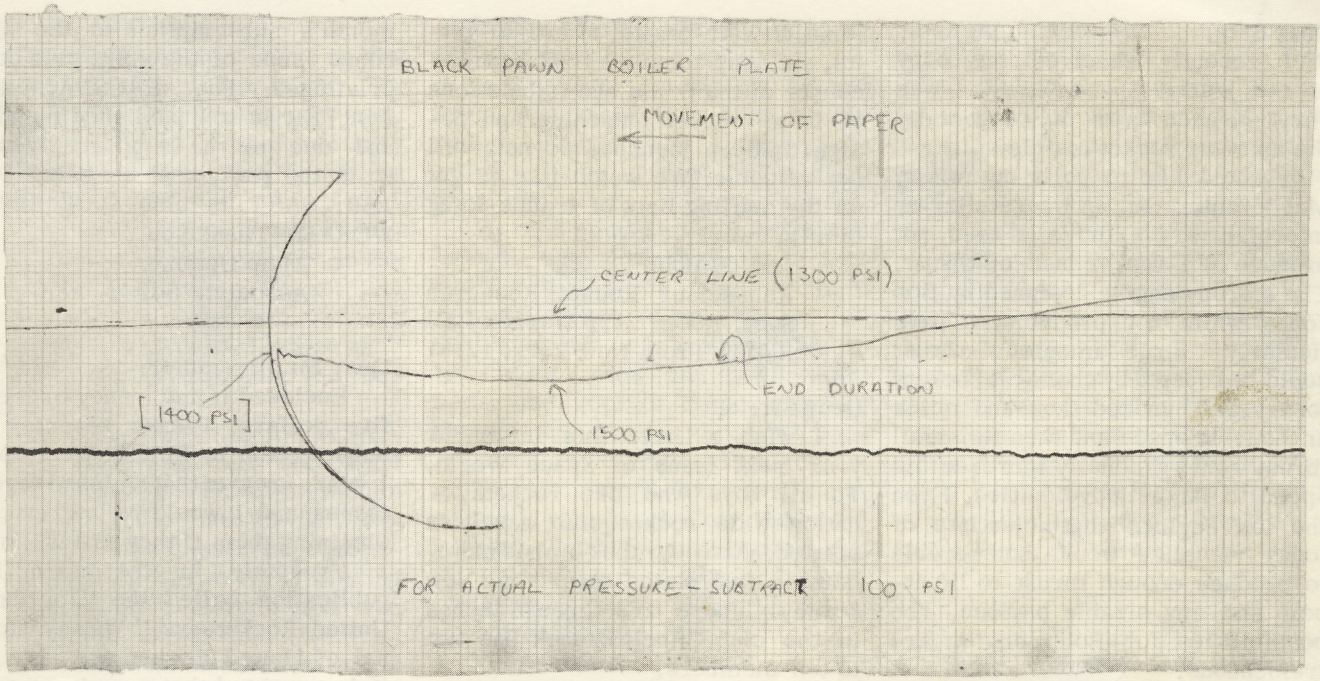

FIGURE 3. Pressure data taken from graph recorder.

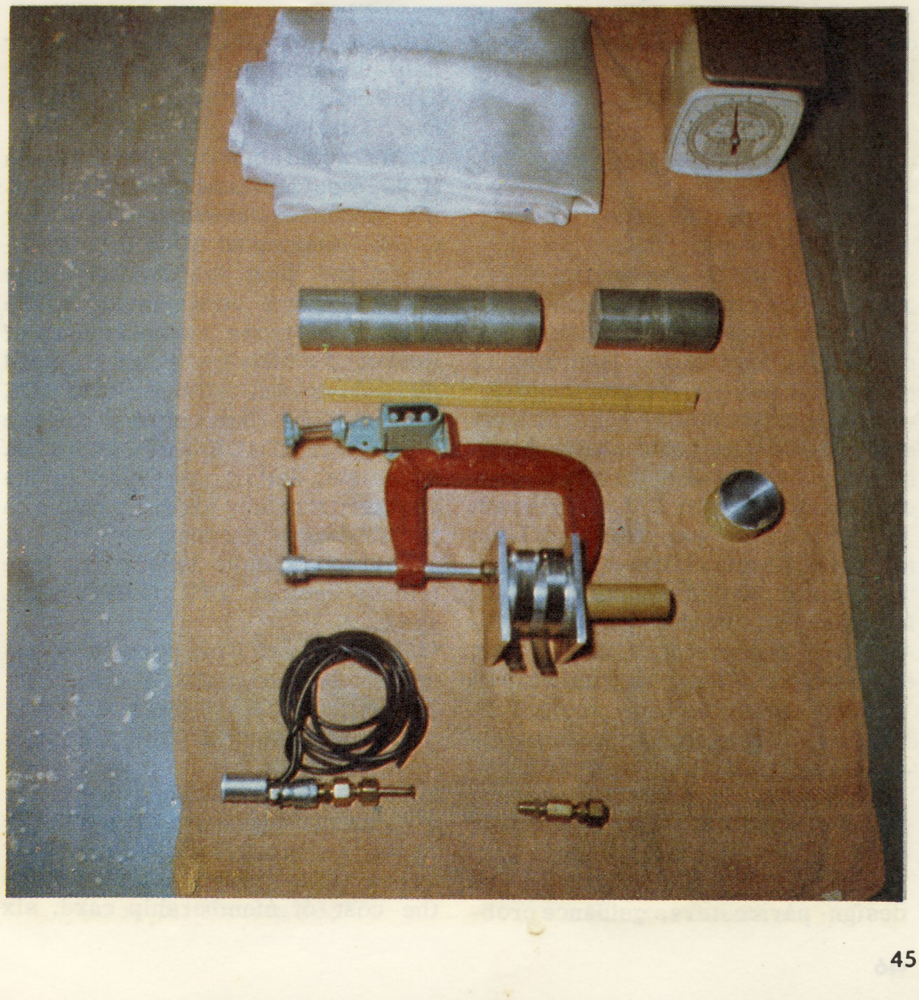

FIGURE 4. Casting mold and partially completed propellant grain.