Investigation of Pyrotechnic MTV Compositions for Rocket Motor Igniters

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Introduction

PYROTECHNIC compositions based on magnesium-Teflon (MT) formulations are characterized by many advantageous properties as rocket motor igniter materials[1-4]: high-energy content, low hygroscopicity, high degree of safety in preparation, low temperature and pressure dependence of the burning rate, ease of igniter pellet or grain fabrication, favorable aging characteristics, stable burning at low pressures, and low production costs. Viton A copolymer is frequently added to the binary MT mix to increase homogeneity and facilitate product fabrication (by consolidation, extrusion, or injection molding), without a substantial effect on combustion thermochemistry.

In addition to excellent resistance to environmental deterioration, magnesium-Teflon-Viton (MTV) compositions have been noted for good ignition source characteristics. The existence of very hot solid and liquid particles and condensible and reactive species in MTV combustion products enables fast heat transfer to a solid fuel/propellant surface or to combustible gas mixtures by almost all possible modes: conduction from impinging solid particles, forced convection from gaseous species, high thermal radiation, exothermic condensation and solidification, etc. "Soft" ignition of solid-propellant motors (defined by low motor pressurization rate and absence of an ignition peak), which is very desirable in certain propellant grain configurations, is readily obtainable with MT or MTV pellets or granules.[4] For given specific motors and igniter mass flow rates, pyrogen igniters with MTV charges achieved shorter ignition delay times than propellant charges for similar flame temperatures.[5]

Thermochemistry of MTV Combustion

A comprehensive thermochemical study was conducted for different MT and MTV formulations using the NASA Lewis chemical equilibrium computer code.[6] Magnesium and Viton A contents were varied from 10 to 80% and from 0 to 20%, respectively. The lower values of Viton content are suitable for pellet consolidation, whereas the higher values are appropriate for extrusion and injection molding. The burning pressure range covered in the calculations was 0.5-8.0 MPa. The heats of formation of Teflon and Viton A used were −820,870 and −1,392,680 J/mole (−196,100 and −332,700 cal/mole), respectively.[7,8]

The simplified combustion scheme of MTV compositions for stoichiometric (all Mg, H, and F converted into MgF_2 and HF) and magnesium-rich formulations may be expressed by the reaction

$$m\mathrm{Mg} + [-\mathrm{C_2F_4}-] + n[-\mathrm{C_5H_{3.5}F_{6.5}}-] \rightarrow (1.5n+2)\mathrm{MgF_2} + 3.5n\mathrm{HF} + (5n+2)\mathrm{C} + (m-1.5n-2)\mathrm{Mg} \qquad (1)$$

For stoichiometry a value of m corresponds to every n. For $n=0$ (no Viton) the stoichiometric ($m=2$) magnesium mass fraction is 32.7%. For this proportion a theoretical adiabatic flame temperature of 3818 K at 4 MPa was calculated by the computer program. The flame temperature decreases sharply for lower or higher magnesium content, increases with pressure, and is affected very slightly by the addition of Viton.

Major constituents of the combustion products for magnesium-lean (20% Mg and less) MT and MTV formulations are MgF_2 (in gaseous and liquid state), CF_4, C (always solid), and CF_2. For magnesium-rich (40% Mg and more) compositions, the main combustion products are MgF_2 (mostly in the gaseous and liquid states), Mg (mostly gaseous), C (solid only), and some MgF. In the range between 20-40% Mg in the formulation major products are MgF_2 and solid carbon. For compositions containing more than 57.5% Mg, more than one-half by mass fraction of the combustion products are in the condensed phase, consisting of Mg (liquid) and/or MgF_2 (liquid) and C (solid). The addition of Viton by replacement of Teflon slightly increases the carbon fraction in the products and introduces small amounts of HF and MgH, as expected. The combustion pressure mainly affects the equilibrium relation between the gaseous and liquid phases of MgF_2. Considering the results of the thermochemical calculations, one may conclude that certain MTV formulations are suitable for use in ducted rockets and base-drag reduction fumers with or without wake combustion.

The heat of explosion of stoichiometric and magnesium-rich compositions, calculated according to reaction (1) for 0, 4, and 15% Viton is plotted in Fig. 1 vs the magnesium content. The average results of many measurements conducted in a Parr Oxygen Bomb Calorimeter using a 2 MPa argon atmosphere are also presented in Fig. 1. The need for careful purge of the Bomb Calorimeter with argon before each measurement must be emphasized.

Experimental Compositions and Pellets

Preliminary experiments with a stoichiometric MTV composition (31.9% Mg, 4% Viton), pressed into standard 3*L*-size tablets, revealed ignition and sustained combustion difficulties. The ease of ignition and burning stability increased substantially with the magnesium-to-Teflon mass ratio. Therefore, most of the experimental investigation concentrated on three fuel-rich MTV formulations, containing 58, 48, and 38% Mg (designated compositions MTV-10, MTV-11, and MTV-12, respectively) with constant 4% Viton A as a binder. This amount of Viton is sufficient to enable convenient pellet fabrication by consolidation and provide adequate pellet crush strength without excessive decrease in the combustion energy release. The magnesium powder used was atomized Type I magnesium with nominal mesh size 200/325 (median particle size of 22 μm). The Teflon

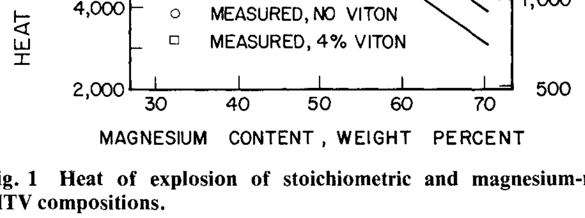

Fig. 1 Heat of explosion of stoichiometric and magnesium-rich MTV compositions.

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Table 1 Calculated thermodynamic properties and composition of MTV-10 combustion products

Composition, %:			
Magnesium powder (22 μm)	58		
Teflon powder (50/50 = 4 μm/375 μm)	38		
Viton A	4		
Property:		2 MPa	8 MPa
Adiabatic flame temperature, K		2494	2621
Mean molecular weight		58.3	60.5
Ratio of specific heats		1.11	1.10
Mass fraction of major combustion products, %:			
C(s)		10.4	10.4
Mg		36.4	36.2
MgF		3.9	3.0
MgF_2(liq)		43.6	47.1
MgF_2		5.2	2.4
MgH		0.4	0.8

granular powder was a 50/50 blend of two different ICI grades: L 170 and G 301 (with median particle size of 4 μm and 375 μm, respectively).

The calculated thermodynamic properties of MTV-10 combustion products at 2 and 8 MPa are listed in Table 1.

The pyrotechnic compositions investigated experimentally were consolidated for ballistic and environmental testing to tubular pellets 3.4 cm long with an inside and outside diameter of 1.05 and 2.35 cm, respectively. There are four main steps in the pellet fabrication: 1) mixing the magnesium and Teflon powders; 2) dissolving Viton A in acetone; 3) preparing the ternary MTV mixture; and 4) pressing. Consolidation pressures of 220, 140, and 130 MPa for compositions MTV-10, MTV-11, and MTV-12, respectively, were determined in a preliminary study so that 98% of the theoretical maximum density and high pellet crush strength are obtained.

Thermoanalytical (TGA and DTA) studies were conducted both on the compositions investigated and their constituents. TGA traces for linear heatup to 500°C at a rate of 78°C/min and nonlinear calibrated heating from 500 to 950°C for 19 min show weight loss starting at 330°C and becoming fast at about 550°C for all three compositions studied. From 650 to 850°C (when a weight gain commences) the trace levels off at 35, 44, and 56% loss for compositions MTV-10, MTV-11, and MTV-12, respectively.

Internal Ballistics and Environmental Testing

A small Pyrotechnic Pellet Test (PPT) motor was designed and used to study the ballistic properties of the compositions investigated, consolidated to the above mentioned tubular pellet configuration. The end surfaces of the pellet were inhibited by perforated asbestos-phenolic disks to provide a constant burning surface during combustion. The PPT motor, shown in Fig. 2, comprises the pyrotechnic pellet, a stainless steel casing, a head-end closure (housing a partly toroidal initiator/igniter), a front elastic pellet holder, an aft support diaphragm, and a nozzle with molybdenum or graphite throat insert. A threaded port in the casing provides for combustion pressure measurement. A replaceable sleeve of A1S1 316 stainless steel or Inconel 601 is inserted into the casing for higher resistance to corrosion and erosion caused by the condensed-phase particles of the combustion products. The o.d. of the casing is 6 cm.

More than 100 firings were conducted with the PPT motor at ambient (18-25°C), high (70°C), and low (−40°C) temperatures with various nozzle throat sizes to find the ballistic properties of the compositions tested in the combustion pressure range 0.8-4.2 MPa. Pellet ignition problems were encountered when only small particle size (4 μm) Teflon was used, whereas very high consolidation pressures were necessary to obtain reasonable densities and crush strength with a large particle size (375 μm). A bimodal 50/50 mix of the two particle sizes was found to be a very good compromise.

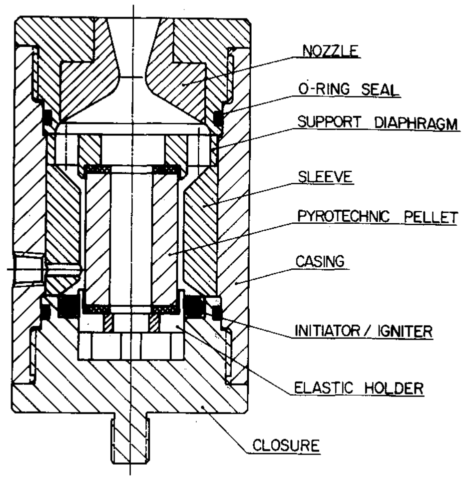

Fig. 2 Pyrotechnic pellet test motor.

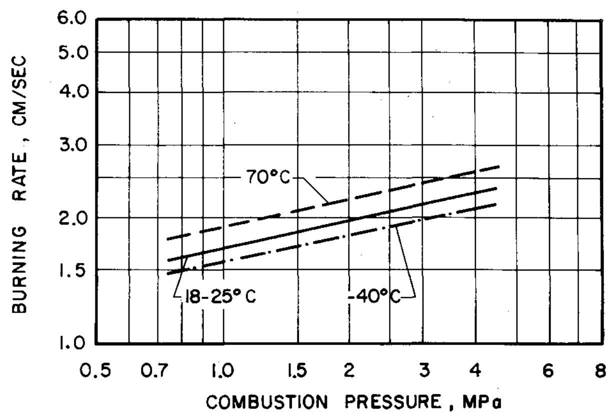

Fig. 3 Experimentally determined burning rate vs combustion pressure of composition MTV-10.

Tests with compositions MTV-11 and MTV-12 revealed undesirable phenomena of slow flame spreading and unstable burning in many cases. Therefore, most experiments were conducted with composition MTV-10, which shows fast flame spreading, reproducible results, and no combustion problems. The following burning rate law was derived for this composition at ambient temperatures over the pressure range 0.8-4.2 MPa when consolidated at 220 MPa:

$$r(\text{cm/s}) = 1.69p(\text{MPa})^{0.22} \quad (2)$$

Figure 3 shows a log-log plot of the burning rate vs combustion pressure at ambient, high, and low temperatures for composition MTV-10. No noticeable variation of the pressure exponent in the burning rate law with temperature has been detected. An increase of about 4 and 15% in the burning rate was found for pellets, consolidated at 150 and 100 MPa, respectively.

The successful use of composition MTV-10 in ignition of small research and propellant test motors[9] led to a series of environmental tests carried out to evaluate its capability to withstand the effects of severe environments. Hygroscopicity tests showed a weight gain of only 0.31% after 35 days at a relative humidity of 94%, and a constant temperature of

30°C, as compared to 5.07% with conventional $BKNO_3$ composition for the same conditions and consolidation pressure of 220 MPa. Successful firings of the PPT motor were carried out in a temperature-altitude cell at conditions of −54°C and 4.4 kPa. No changes in the ballistic properties and crush strength of the pellets due to temperature cycling between +70 and −50°C were found. Firing of pellets after storage at 65°C in a sealed container for three months did not show any noticeable change in the burning rate law as compared with pellets from the same production batch stored at ambient temperature. Decrease in burning rate was found for pellets stored for 38 months at ambient temperatures.

Summary and Conclusions

Extensive theoretical and experimental studies of pyrotechnic MTV compositions have been conducted to investigate their properties as rocket motor igniter materials. Near-stoichiometric formulations have high flame temperature and heat of explosion. However, ignition/combustion considerations impose the use of magnesium-rich compositions, which have a large amount of condensed phase particles in their combustion products. The burning rate law of a very promising composition, containing 58% Mg and 4% Viton, and successfully used to ignite propellant test motors, shows low pressure exponent and dependence on the consolidation pressure.

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