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Effects of calcium carbonate on thermal characteristics, reaction kinetics and combustion behaviors of 5AT/Sr$(NO_3)_2$ propellant

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ABSTRACT

The effects of $CaCO_3$ on thermal and combustion characteristics of solid propellants composed of the novel green energetic material 5AT/Sr$(NO_3)_2$ are examined. Thermogravimetry–derivative thermogravimetry (TG–DTG), thermocouple measurements and closed bomb calorimetry are all employed to study the reaction mechanisms obtained when using $CaCO_3$ as a cooling additive. In this manner, the combustion temperatures, burning rates, pressure exponents, thermal behaviors and non-isothermal reaction kinetics of solid propellant specimens are assessed. The combustion of the 5AT/Sr$(NO_3)_2$ propellant with added $CaCO_3$ can be divided into two regions. The initial region is dominated by condensed phase reactions and exhibits a lower decomposition temperature, lower activation energy and higher burning rate. These results demonstrate that the addition of $CaCO_3$ increases the reactivity of the propellant. The latter region is primarily associated with gas phase reactions, and the decomposition temperature and activation energy all appear to be elevated in this region, although the exhaust gas temperature and burning rate are greatly reduced. The pressure exponent is also reduced significantly in this stage, providing evidence for increased combustion stability. The thermal characteristics of the decomposition reaction as observed microscopically indicate significant synergistic effects of the $CaCO_3$ on the burning behavior. $CaCO_3$ addition has been shown to generate a significant cooling effect and the combination of this compound with 5AT/Sr$(NO_3)_2$ results in a propellant with excellent thermal behavior and steady combustion. This propellant formulation is safe, scalable and inexpensive and therefore $CaCO_3$ appears to be an ideal agent for the modification of the gas generation performance of solid propellants.

1. Introduction

In conventional fire extinguishing technologies, nitrogen gas is commonly used to pressurize a fire extinguishing agent such as Halon 1301 such that it is propelled from the storage bottle. Because of the destructive effects of Halon on the ozone layer, its use is currently restricted and so various substitutes have been explored [1,2]. Neidert et al. have proposed the use of solid propellant gas generators (SPGGs) as a Halon alternative [3], in which the combustion of a solid propellant works to force out various fire suppression agents, such as C_3F_7H, C_2F_5H or K_2CO_3. Such devices have the advantages of compactness, the use of inert gases, the ability to release on demand, the absence of fluid components and easy storage prior to activation. Once the propellant in an SPGG is activated by an initiator, it will combust rapidly (typically within 0.1 s) to produce large quantities of exhaust gases [4]. However, there are two difficult problems associated with the application of SPGGs for fire suppression. One is the high outlet gas temperature (greater than 1500 K), while the other is poor combustion stability associated with high-pressure exponents [5] that can have an extremely deleterious effect on firefighting performance. Therefore, the focus of SPGG research has been the development of effective ways of optimizing the propellant combustion characteristics.

Solid propellant normally consists of oxidants, flammable agents or fuels, adhesives and various additives. In the present work, 5-aminotetrazole (5AT) is chosen as the fuel while Sr$(NO_3)_2$ is employed as the oxidant. The compound 5AT is a so-called green energetic material (GEM) [6] because it is environmentally friendly. It has a high nitrogen content of 82.3%, a density of 1650 kg m^{-3}, an enthalpy of formation of 208.7 kJ mol^{-1}, and moderate mechanical and thermal sensitivity [7]. Its chemical structure is shown in Scheme 1. The combustion reactions between 5AT and Sr$(NO_3)_2$ proceeds rapidly according to the process shown in Eq. (1):

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Nomenclature

Chemicals

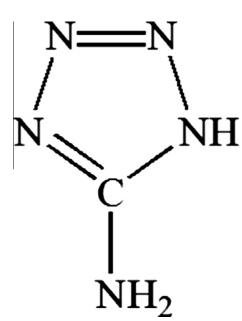
$5AT/CH_3N_5$	5-amino-1H-tetrazole
$Al(OH)_3$	aluminum hydroxide
AP	ammonium perchlorate
$CaCO_3$	calcium carbonate
CaO	calcium oxide
CO_2	carbon dioxide
HN_3	hydragoic acid
H_2O	water
LiF	lithium fluoride
$MgCO_3$	magnesium carbonate
N_2	nitrogen
N_2O	nitrous oxide
PVA	polyvinyl alcohol
SiO_2	silicon dioxide
$SrCO_3$	strontium carbonate
$Sr(NO_3)_2$	strontium nitrate
SrO	strontium oxide

Acronyms

A	pre-exponential factor
b	initial temperature sensitive coefficient
C	isobaric heat capacity
C_{tot}	isobaric heat capacity of total products
d	wall thickness of closed bomb
DTG	derivative thermogravimetry
E_a	the activation energy
ΔH	exothermic enthalpy
k	thermal conductivity
l	length of fine wire for thermocouple
l_c	characteristic length for thermocouple
L	width of closed bomb
n	pressure exponent of burning rate
N	mole number of gas
P	pressure
P_m	peak pressure
q''	heat flux
$q(t)$	heat transfer rate
Q_p	endothermic enthalpy
r	inside radius of closed bomb
r^2	coefficient of determination
R	gas constant
t	time
T	temperature
T_{in}	gas temperature inside closed the bomb
T_{out}	temperature external to the bomb
TC	thermocouple
TG	thermogravimetry
T_o	onset temperature in DTG curve
T_p	peak temperature in DTG curve
V	volume of closed bomb
z	the relative burnt thickness

Symbols

α	the covolume
β	heating rate in TG–DTG tests
χ, λ, ε	shape characteristic parameters for propellants
δ	density of propellants
f	impetus
μ	burning rate
v	gas specific volume
φ	percentage of propellant burnt out
$\varDelta$	loading density of propellants in closed bomb



Scheme 1. The chemical structure of 5AT.

$$CH_3N_5 + 0.7Sr(NO_3)_2 \rightarrow 0.7SrO + 3.2N_2 + CO_2 + 1.5H_2O \quad (1)$$

To date, numerous studies have been conducted with the aim of modifying the propulsive performance of propellants, generally based on two aspects: decreasing the outlet gas temperature and increasing the combustion stability. Cooling the outlet gases has been attempted by modifying the propellant combustion characteristics, such as through the addition of carbonates ($CaCO_3$, $MgCO_3$), hydroxides ($Al(OH)_3$) and organics (biurets and melamine) [8–10]. Most of these studies have focused on traditional propellants, including those based on ammonium perchlorate (AP), ammonium chlorate and sodium azide. Puccio added $CaCO_3$, SiO_2 and LiF to sodium azide propellants, even though such propellants have been gradually phased out because of the toxicity and environmental harm associated with azides [11,12]. This work have found a 2 K decrease in exhaust gas temperature for each 1% of $CaCO_3$ addition, indicating that $CaCO_3$ did not seem to be the best choice for the target temperature. In other work, $CaCO_3$ was used in an attempt to reduce the pressure exponent of AP propellants, but only using a limited number of methods including temperature measurements and thermal analysis [13]. Although studies using $CaCO_3$ as a coolant have been performed, the application of this chemical in GEM formulations has rarely been examined. In fact, the novel $5AT/Sr(NO_3)_2$ propellant composition is referenced in only a few patents. Holland and Wilson [14] proposed adding magnesium carbonate or magnesium hydroxide to gas generating formulas, but only made brief measurements of burning rates without extended experiments or thorough analysis.

Furthermore, various efforts have been invested to expand the burning rate range for propellant, involving the use of positive burning rate catalysts or negative ones. The mechanisms of positive catalysts have been studied extensively [15,16], while only a very few studies have been conducted on catalysts, particularly negative catalysts that can reduce the pressure exponent [17,18].

The use of $CaCO_3$ as a cooling agent specifically for the $5AT/Sr(NO_3)_2$ propellant has not yet been researched, and there has been no systematic investigation on thermal decomposition and combustion for such a formulation. The present work therefore conducts a study of $5AT/Sr(NO_3)_2$ propellants with and without $CaCO_3$ to shed light on the mechanisms that govern the functioning of cooling agents.