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Comparative Studies of Pressure Sensitization of Zirconium Carbide and Zirconium Silicate on Burning Rates in a RDX-AP based Composite Propellant

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Abstract: In a systematic study to compare the effects of the values of burning rate and pressure exponent in RDX-AP based composite propellant, various compositions with varying percentages of zirconium carbide (ZrC) and zirconium silicate ($ZrSiO_4$) were formulated to select a suitable candidate. Various rocket parameters of each formulation were theoretically predicted by the NASA CEC-71 program and the burning rate was evaluated in pressure range of 3–11 MPa. In addition, density, sensitivity, and thermal properties of compositions having maximum effects on pressure exponent's values were also evaluated. It was concluded that $ZrSiO_4$ enhances the pressure exponent "n" value substantially, whereas ZrC doesn't have significant effects on it as compared to base composition and also provides higher density values of composite propellant formulated.

Keywords: Zirconium · Burning rate · Pressure index value · Carbides · Silicates

1 Introduction

The design of rocket motors is significantly affected by the burning rate and pressure exponent values of the rocket propellant, a propellant with a pressure exponent value of zero (plateau burning) or close to zero would be considered advantageous in rocket motor design, where an insensitivity of the burning rate to pressure has enormous significance towards the motor design. In the literature, numerous ingredients of HTPB-AP composite propellants for suppressing the "n" value have been reported viz. triamino trinitrobenzene TATB [1] or neodymium(III) oxide [2], but these were not able to overcome combustion instability. In a series of development of composite propellants for combustion stability, additives like zirconium carbide (ZrC) and zirconium orthosilicate ($ZrSiO_4$) have been incorporated since they are known to suppress combustion instability in reduced smoke composite propellant solid rocket systems [3]. In order to select one out of them in terms of lower pressure exponent values, various compositions were formulated in the pressure range of 3–11 MPa.

2 Experiment

2.1 Propellant Formulations and Raw Material Ingredients

Propellant compositions are listed in Table 1 with approximate percentages. Various formulations with increasing contents of ZrC or $ZrSiO_4$ from 0.5% to 3.0% were investigated. Subsequently, the total AP content was reduced keeping other ingredient's content constant. The binder consists of hydroxyl terminated polybutadiene (HTPB, purchased from M/s Anabond chemicals) cured with toluene diisocyanate (TDI, purchased from M/s Bayer chemicals), dioctyl adipate (DOA, purchased from M/s Indo-nippon chemicals) was used as a processing aid, mixture of trimethylol propane (TMP, purchased from M/s chemsworth industries) and *n*-butane diol (nBD, purchased from M/s spectrochem chemicals) was used as adduct in the formulations. Bimodal ammonium perchlorate (AP, purchased from M/s tamilnadu chlorates) with particle sizes of 300 μm and 80 μm (by grinding 300 μm in fluid energy mill, assay

Table 1. Approximate propellant percentage.

Ingredient	Approximate wt-%
HTPB	11.20
DOA	3.65
TDI	0.76
AP	70.7–73.7
Al	4.0
RDX	6.0
Adduct	0.19
$SrCO_3$	0.5
ZrC	0.5–3.0
$ZrSiO_4$	0.5–3.0

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> 99%), RDX (purchased from OF, Bhandara) with particle sizes of 5–6 μm, zirconium carbide (ZrC, purchased from M/s Surabhi industries, assay 99.2%) and particle sizes of 2–6 μm (density 6.73 g cm^{-3}), zirconium orthosilicate ($ZrSiO_4$, purchased from M/s Umesh enterprises) with particle size 2–3 μm (density 4.56 g cm^{-3}) and strontium carbonate ($SrCO_3$, purchased from M/s S K chemical industries, assay > 99%) were utilized in propellant formulations.

2.2 Processing

Nine compositions containing ZrC and $ZrSiO_4$ with varying percentages from 0.5% to 3.0% were processed, the detailed compositions are tabulated in Table 1. Propellant compositions were mixed in a vertical planetary mixer of 1 L capacity. The propellant slurry (600 g) was cast under vacuum by slurry cast technique [4]. The propellant was cured at 60 °C for 120 h in a water jacketed oven.

2.3 Characterization Methods

2.3.1 Burning Rate Measurement

The strand burning rates of the propellant were determined in the pressure range of 3–11 MPa by employing an acoustic emission technique [5,6]. The methodology involved combustion of propellant strands of dimension (6 × 6 × 140 mm with a nichrome ignition wire in a nitrogen pressurized steel bomb. Perturbation caused by deflagration of strands is sensed by a piezoelectric transducer (200 KHz) in conjunction with an oscilloscope through water medium. The burning rates were computed from the time that was recorded for the trials conducted for each sample. The standard deviation was in the order of 0.2%.

2.3.2 Sensitivity Measurement

The sensitivity of the propellant compositions to impact stimuli was determined by the fall hammer method (2 kg drop weight) in a Bruceton staircase apparatus [7] and the results are given in terms of the 50% probability of explosion (h_{50}). The friction sensitivity was measured with a Julius Peter apparatus [8] by incrementally increasing the load from 0.2 to 36.0 kg until no ignition or explosion in the five consecutive test samples occurred.

2.3.3 Thermal Analysis

Thermal analysis was carried out by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA was carried out with an equinox 55 (Mettler Toledo, Switzerland; Bruker, Germany) with a heating rate of 20 K min^{-1} and a sample mass of approx. 1 g. DSC was carried out with a Perkin-Elmer instrument with a heating rate of 10 K min^{-1} and a sample size of approx. 2 mg.

2.3.4 Density Measurement

The density of the propellant compositions measured with a Mettler density kit, which works on the Archimedes principle with toluene as fluid.

3 Results and Discussion

3.1 Burning Rate

Nine different samples of propellant compositions based on AP/HTPB/RDX/Al/$SrCO_3$/ZrC/$ZrSiO_4$ were formulated and the theoretical performances of the compositions with respect to the thermochemical properties were computed. The results are shown in Table 2. They clearly imply that zirconium carbide based compositions have an edge over zirconium silicate based compositions in terms of the values of specific impulse (I_{sp}), characteristic velocity (C^*), and flame temperature (T_f), which would ultimately lead to dual benefit of specific impulse and density gain in terms of density impulse. The burning rate data observed in different compositions are tabulated in Table 3. It is obvious that the pressure index values of zirconium silicate in lower (3–7 MPa) (Figure 1) as well as in higher pressure ranges (7–11 MPa) (Figure 2) increases substantially as compared to the base composition however effects were found to be more pronounced in higher pressure ranges (Figure 5). At the same time in zirconium carbide based compositions,

Table 2. Theoritical performance parameters of various compositions.[a)]

Sample No.	Composition	Flame temperature T_f [K]	Characterstic velocity C^* [m s^{-1}]	Specific impulse I_{sp} [kg m^{-1} s^{-2}]	ΔH_f [kJ kg^{-1}]	Density impulse [g s cm^{-1}]
1	base	2440.24	1604.6	242.5	−7607.33	408.37
2	3% ZrC	2436.33	1582.2	239.1	−7506.63	410.06
3	3% $ZrSiO_4$	2409.08	1566.3	236.7	−7729.83	404.52
4	2% ZrC	2442.87	1589.7	240.3	−7540.38	409.71
5	2% $ZrSiO_4$	2436.33	1579.2	238.7	−7689.13	405.79
6	1% ZrC	2451.52	1597.2	241.1	−7573.94	408.42
7	1% $ZrSiO_4$	2442.32	1591.9	240.6	−7648.29	407.10
8	0.5% ZrC	2458.16	1600.9	242.0	−7590.66	408.74
9	0.5% $ZrSiO_4$	2450.21	1598.2	241.6	−7627.82	407.82

Table 3. Burning rate, density, impact, and friction sensitivity results of various compositions.

Sample No	Burning rate r [mm s^{-1}] at pressure [MPa]					Density [g cm^{-3}]	Impact sensitivity h_{50} [cm]	Friction sensitivity [kg]
	3	5	7	9	11			
1	4.68	5.68	6.04	6.35	6.58	1.684	27	24
2	4.80	5.82	6.24	6.51	6.89	1.715	31	28
3	4.75	5.90	6.90	7.85	8.39	1.709	29	26
4	4.62	5.65	6.10	6.24	6.53	1.705	30	27
5	4.71	5.84	6.77	7.44	7.93	1.700	28	25
6	4.69	5.71	6.11	6.40	6.84	1.694	29	27
7	4.75	5.84	6.77	7.45	7.92	1.692	28	24
8	4.79	5.84	6.38	6.64	6.78	1.689	29	26
9	4.78	5.79	6.74	7.35	7.80	1.688	27	24

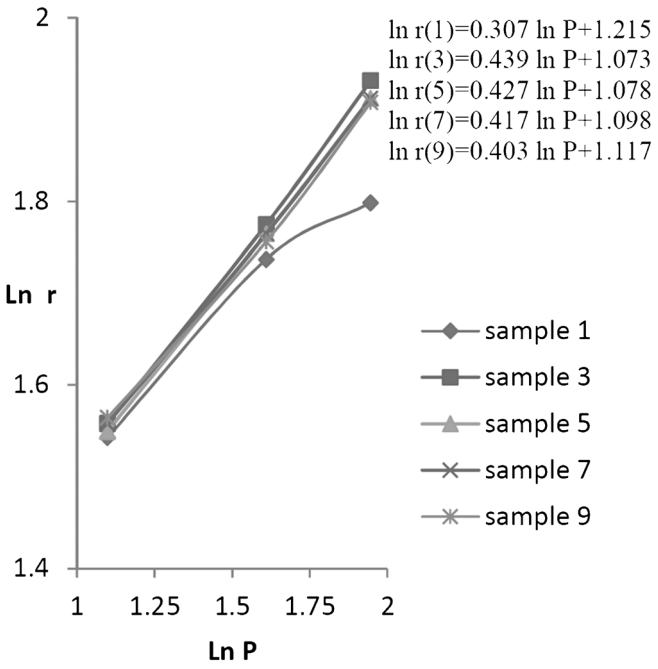

Figure 1. Calculation of the "n" value for base and $ZrSiO_4$ samples in the pressure range 3–7 MPa.

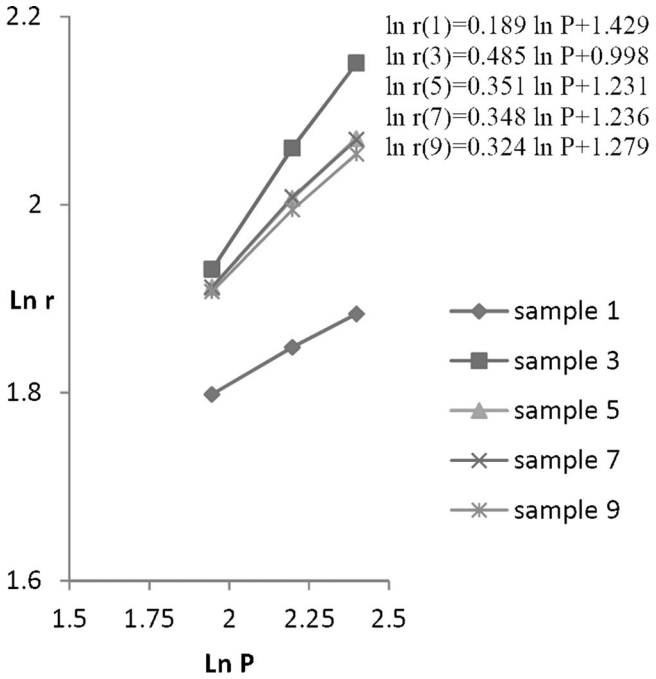

Figure 2. Calculation of the "n" value for base and $ZrSiO_4$ samples in the pressure range 7–11 MPa.

variations in the pressure index values for both pressure ranges (Figure 3 and Figure 4) were observed to be not as significant as those of zirconium silicate but the effects were found to be more pronounced in a higher pressure range (Figure 5, Figure 6).

3.2 Thermal Characterization

Since maximum effects on pressure index values were observed in samples with maximum percentages of zirconium carbide and zirconium silicate, DSC (Table 4) and TGA (Table 5) measurements of the base composition i.e. sample 1, sample 2, and sample 3 were carried out. The results indicate that 97.378% decomposition were observed in sample 1 compared to 91.2421 and 90.7502% in sample 2 and sample 3, respectively, but in DSC thermal decomposition peaks at ca. 242 °C and at approx. 390 °C were observed in all three cases, thus it can be concluded that zirconium carbide and zirconium silicate do not play any role in the decomposition of AP.

4 Conclusions

Zirconium carbide based RDX-AP compositions are observed to be superior to the zirconium silicate based RDX-AP compositions in terms of pressure index values in lower (3–7 MPa) as well as in high pressure ranges (7–11 MPa). It has also been proved to exhibit a higher density than zirconium silicate, which ultimately leads to better density impulse. Higher "n" values in case of zirconium silicate based compositions might be due to several simultaneously occurring factors. These include: lowering of the activation energy of combustion by zirconium silicate in higher pres-

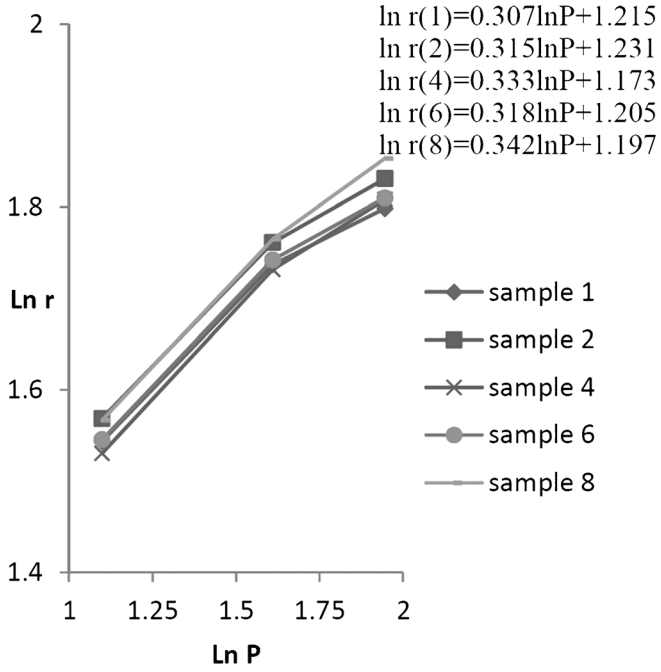

Figure 3. Calculation of the "n" value for base and ZrC samples in the pressure range 3–7 MPa.

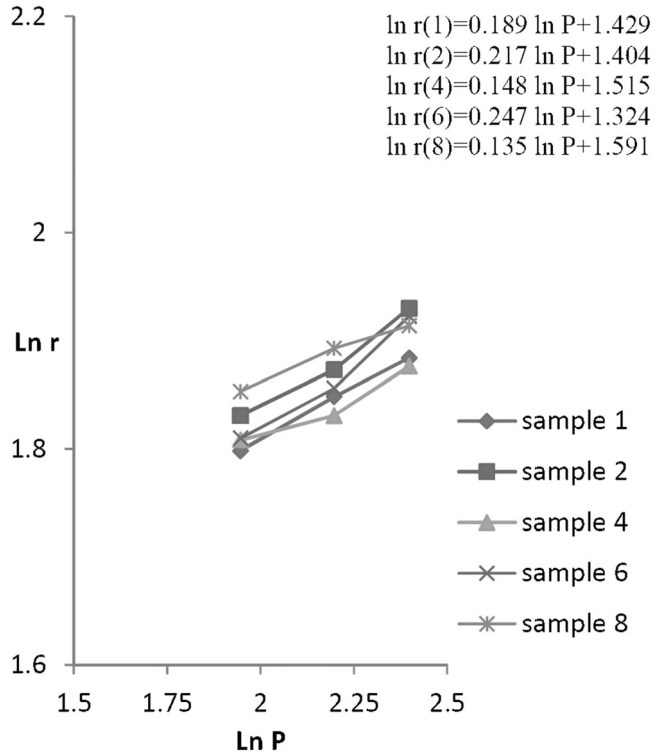

Figure 4. Calculation of the "n" value for base and ZrC samples in the pressure range 7–11 MPa.

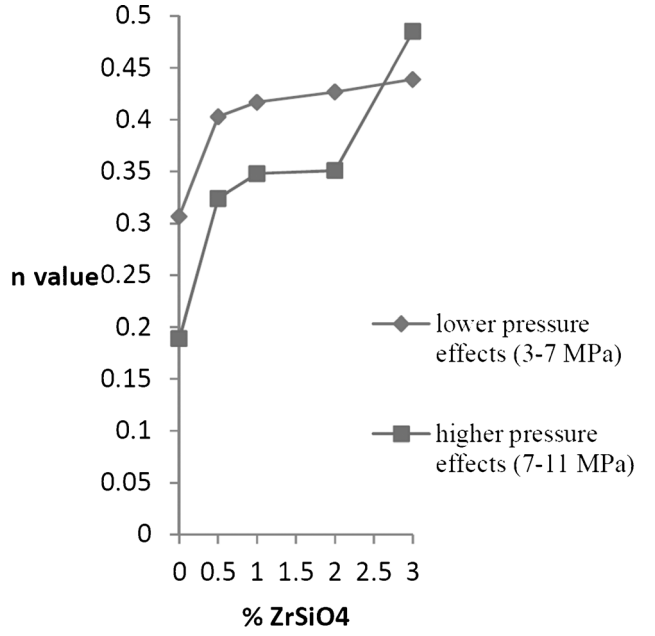

Figure 5. Variation of the "n" value with the change in concentration of $ZrSiO_4$ in the pressure ranges 3–7 MPa and 7–11 MPa.

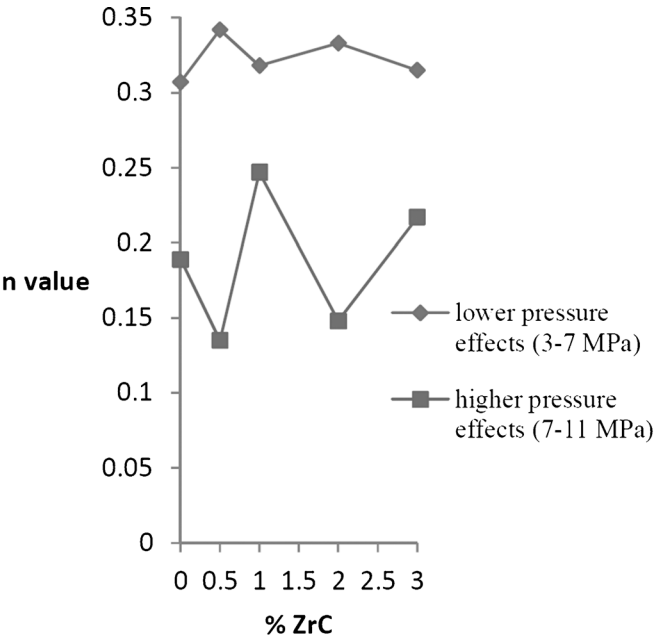

Figure 6. Variation of the "n" value with the change in concentration of $ZrSiO_4$ in the pressure ranges 3–7 MPa and 7–11 MPa.

sure ranges, a higher oxygen balance of zirconium silicate than zirconium carbide, which can ultimately improve the combustion characteristics, and also a higher melting point of zirconium carbide (3540 °C) than of zirconium silicate (2550 °C), which inhibits zirconium carbide to play a role in combustion since substantial gaseous products would not be available to enhance the heat flux rate to burning surface that could have ultimately increased burning rate especially at higher pressures i.e. pressure index values. Certainly, dedicated work is required to finally explore and

Table 4. TGA results.

Sample	TGA % decomposition	T_{min}, T_{max} [°C]
1	Step 1–9.2549	140.91, 242.50
	Step 2–19.9044	242.50, 310.82
	Step 3–62.7687	310.82, 398.44
	Step 4–5.4500	399.01, 526.51
2	Step 1–10.8543	138.32, 238.45
	Step 2–16.5422	238.45, 307.73
	Step 3–56.8728	307.13, 394.42
	Step 4–6.9728	394.42, 520.73
3	Step 1–9.8662	138.55, 242.99
	Step 2–19.7600	242.99, 314.06
	Step 3–52.5963	314.06, 395.34
	Step 4–8.5277	395.65, 527.25

Table 5. DSC results.

Sample	DSC peak temperature [°C]	$\triangle H$ [J g^{-1}]
1	242.03	+65.822
	390.90	−2462.337
2	244.27	+57.939
	385.50	−2122.674
3	244.47	+62.075
	388.40	−2070.379

arrive at the exact trend/mechanism, which is following in this particular system.

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