JOURNAL OF PROPULSION AND POWER
Vol. 19, No. 4, July–August 2003

Combustion and Thermal Studies on Al/Ti/Ni/Zr Composite Modified Double-Base Systems

C. N. Divekar,* S. N. Asthana,† and Haridwar Singh‡
High Energy Materials Research Laboratory, Pune 411 021, India

Slurry-cast metallized ammonium perchlorate (AP)–composite modified double-base (CMDB) propellants incorporating Ni, Ti, and Zr were studied. Aluminized formulations were investigated as reference. Selected ballistic modifiers, namely, copper chromite (Cu–chromite)/ferric oxide (Fe_2O_3)/ferric acetyl acetonate (FeAA)/basic lead salicylate (BLS) + Cu_2O + carbon black (C-black) combinations were also evaluated for their effectiveness. An acoustic emission technique was applied to determine the burning rates in the pressure range of 1–10.8 MPa, and thermal data were generated by applying differential thermal analysis, thermogravimetry, and differential scanning calorimetry techniques. The control formulation based on 30% AP dispersed in a 70% double base matrix, gave stable combustion in the entire pressure range studied. Inclusion of metals (2.5–17.5% at the expense of AP) resulted in a decrease in the burning rates with the increase in metal content. Ni-based formulations exhibited burning rates superior to aluminized formulations particularly with high metal content. The overall best burning-rate results were obtained with Zr, followed by Ti. Among ballistic modifiers, Cu–chromite was found to be the most effective, followed by the BLS + Cu_2O + C-black combination. An interesting composition with super-burning-rate characteristics (10–60 mm/s in the 1–10.8 MPa pressure range) emerged during the research. Thermal studies show the heat sink effect of metals. However, Ni, Ti, and Zr appear to produce compensating heat feedback to a greater extent than Al. Cu–chromite appears to be highly effective in facilitating both condensed- and gas-phase combustion reactions.

Introduction

TREMENDOUS developments have taken place in the field of solid rocket propellants with an increase in the demand for superior performance to propel long-range missiles. Ammonium perchlorate (AP)–Al composite propellants (CP) and composite modified double-base (CMDB) systems are the today's choice. In CMDB systems, nitrocellulose (NC) plays the role of energetic binder and nitroglycerine (NG) that of energetic plasticizer. AP exploits the combustion potential of fuel-rich combustion products of double-base (DB) systems due to its positive oxygen balance (+35%) leading to superior performance. Musso et al.[1] reported that AP–CMDB formulations decompose with one major exotherm at $\sim 250^\circ C$ without exhibiting endothermic/exothermic decompositions at temperatures associated with DB matrix and AP alone, suggesting an interaction between AP and DB binder. Kubota and Masamoto[2] found that AP–CMDB propellants exhibit greater temperature gradient in the fizz zone compared to DB propellants, leading to greater heat feedback from the gas phase to the burning surface, resulting in higher burning rates. AP–Al-based CMDB propellants having theoretical I_{sp} of 260–265 s and burning rates of 11–16.5 mm/s at 6.8 MPa with pressure index of 0.34 are reported by Hau et al.[3] Inclusion of lead and copper salts of inorganic and organic acids as ballistic modifiers, preferably in combination, is recommended as the most effective method for reducing the pressure exponent of this class of propellants.[4–7] Incorporation of Zr, Ta, Mg, Ag, Cu, and Ti staples to realize improvement in the burning-rate characteristics is reported in the literature.[8] Because such a limited amount of studies have been undertaken on AP–Al–CMDB propellants, information on AP–CMDB systems based on metals other than Al is almost nonexistent. Moreover, the effect of inclusion of ballistic modifiers has not been investigated in detail, and related mechanistic aspects also need to be understood.

Therefore, slurry-cast metallized AP-based CMDB propellants incorporating pyrophoric Zr and Ti,[9–11] as well as Ni (catalyst for dark zone reactions of DB matrix),[12] were investigated during the present work. Aluminized formulations were evaluated as reference. The effect of incorporation of selected ballistic modifiers (2 parts over 100 of compositions by weight), namely, copper chromite (Cu–chromite)/ferric oxide (Fe_2O_3)/ferric acetyl acetonate (FeAA)/basic lead salicylate (BLS) + Cu_2O + carbon black (C-black) (mass ratio 2:1:1), was also studied. Differential thermal analysis (DTA), thermogravimetry (TG), and differential scanning calorimetry (DSC) data were generated to obtain information on decomposition patterns. An attempt is made to determine the prevailing mechanism.

Experimental

Propellant Formulations and Processing Method

The control propellant comprised spheroidal NC (SNC) (NC:90, NG:7, sym diethyl diphenyl urea:3) 31.5%, desensitized NG (NG:80, diethyl phthalate:18, 2-nitro diphenyl amine:2) 38.5%, and AP (10 ± 1 μm) 30%. In metallized formulations, 2.5–17.5% metal powder Al/Zr/Ti/Ni (particle sizes $16 \pm 2/7 \pm 2/10 \pm 2/17 \pm 2$ μm, respectively) of 98% purity was incorporated (as replacement of AP) in increments of 2.5%. The particle size of the metals studied was maintained in a narrow range (6–16 μm) to avoid its appreciable effect on burning rates of propellants. The compositions were prepared by slurry-cast technique.[13] The desensitized NG was transferred to a planetary mixer followed by SNC. AP and metal powder were added in separate installments, to the resulting DB matrix. Two parts of Cu–chromite, Fe_2O_3, FeAA, and BLS + Cu_2O + C-black were added in the last step. Mixing was carried out for 1 h (including 45 min under vacuum) at 25°C. The resulting slurry was cast in an evacuated (2–5 mm of Hg) mold, and curing was carried out at 50°C for 10 days.

Presented as Paper 2000-3322 at the AIAA/ASME/SAE/ASEE 36th Joint Propulsion Conference, Huntsville, AL, 17–19 July 2000; received 11 July 2002; revision received 7 February 2003; accepted for publication 28 February 2003. Copyright © 2003 by the American Institute of Aeronautics and Astronautics, Inc. All rights reserved. Copies of this paper may be made for personal or internal use, on condition that the copier pay the $10.00 per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923; include the code 0748-4658/03 $10.00 in correspondence with the CCC.

*Technical Officer, Department of Energetic Materials.

†Group Director, Department of Energetic Materials.

‡Director, High Energy Materials Research Laboratory (HEMRL). Member AIAA.

Studies Conducted

Acoustic emission technique[14] was applied to determine the burning rates in the pressure range of 1–10.8 MPa. The propellant samples in the form of strands (6 × 6 × 100 mm) were placed in the nitrogen pressurized steel bomb and ignited by means of a nicrome wire. The deflagrating samples generated acoustic signals that were sensed by a 200-kHz resonance frequency piezoelectric transducer. The accuracy of the measurement of burning rate as determined by conducting 25 experiments on the same propellant sample was 2–3%. Five experiments were conducted at each pressure for each sample. Standard deviation was of the order of 0.2%. DTA studies were conducted on indigenously fabricated equipment. During this work, a ∼3 mg sample was placed in the furnace and subjected to heating at rates of 5, 10, 15, and 20°C/min in air atmosphere. The activation energy E of propellant sample decomposition was estimated by using the Ozawa relation.[15] The log of the heating rate (degrees Celsius per minute) was plotted against $1/T_{\max}$ (degrees Kelvin), and E was obtained from the slope ($= 0.457\ E/R$). $T_{\max}$ is the peak decomposition temperature, and R is the gas constant. Perkin–Elmer equipment was used for TG and DSC under a nitrogen atmosphere at the heating rate of 10°C/min. For TG, 2.5–2.8 mg samples are used, and in DSC 0.4–0.8 mg samples were tested. Two experiments were carried out for each sample to confirm reliability of data. The accuracy of the instrument was 0.2%.

Results and Discussions

AP-Based CMDB Compositions with Al/Ni/Ti/Zr Metals

The control composition gave stable combustion in the entire pressure range studied (1–10.8 MPa), and the burning rates obtained were 7–20 mm/s. Incorporation of 2.5–5% Al did not influence the burning rates. The composition containing 7.5% Al exhibited marginally lower burning rates. When Al content was increased to 10–12.5% level, burning rates reduced to the extent of 18–30% (5–17 mm/s), whereas the formulation containing 15% Al content gave 21–37% lower burning rates (4.4–15.7 mm/s) than those for the control. In the pressure range of 2–10.8 MPa, 17.5% Al-based composition also gave similar burning rates. However, it did not exhibit stable combustion at the pressure of 1 MPa (Fig. 1).

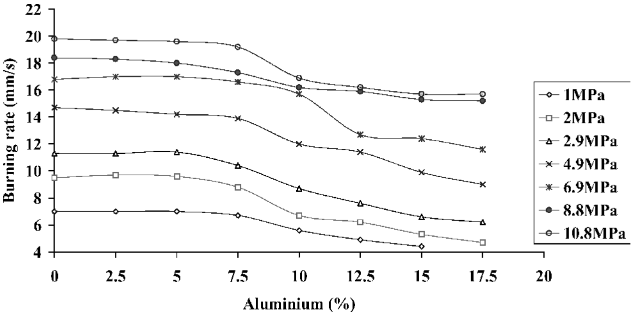

Fig. 1 Burning rate–metal content relationship for AP–Al–CMDB propellants; metallized formulations (%): SNC 31.5, desensitized NG 38.5, AP 27.5–12.5, and Al 2.5–17.5.

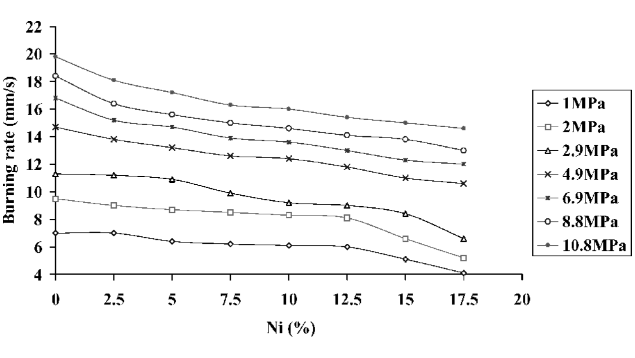

Fig. 2 Burning rate–metal content relationship for AP–Ni–CMDB propellants; metallized formulations (%): SNC 31.5, desensitized NG 38.5, AP 27.5–12.5, and Ni 2.5–17.5.

The AP–CMDB formulation containing 2.5% Ni gave burning rates slightly similar to those for the control (7–11.2 mm/s) in the pressure range of 1–2.9 MPa, whereas 6–9% lower burning rates were observed in the pressure region of 4.9–10.8 MPa (13.8–18.1 mm/s). The composition containing 5% Ni exhibited marginally lower (8–13%) burning rates in the entire pressure range. The formulations based on 7.5–12.5% Ni were found to give 14–22% lower burning rates, whereas compositions containing 15–17.5% Ni exhibited a drop of 25–41% in the burning rates (4.1–15 mm/s in 1–10.8 MPa pressure range) with reference to the control composition. In general, compositions containing 2.5–7.5% Ni gave lower burning rates as compared to corresponding aluminized formulations. Compositions with 10% metal content exhibited comparable burning rates. However, formulations containing 12.5–17.5% Ni gave higher burning rates with respect to corresponding compositions containing Al in the pressure range of 1–6.9 MPa. Moreover, unlike the composition containing 17.5% Al, propellant with the same Ni content exhibited stable combustion even at 1 MPa (Fig. 2).

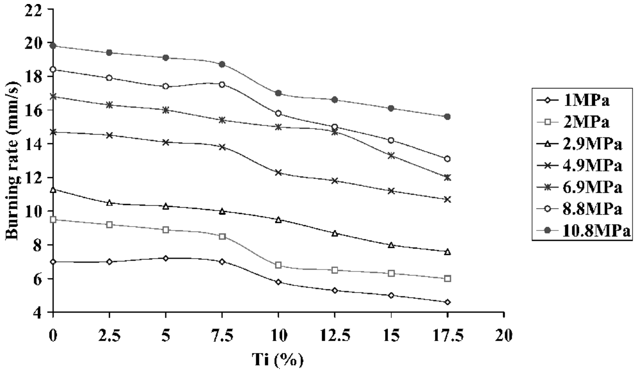

Fig. 3 Burning rate–metal content relationship for AP–Ti–CMDB propellants; metallized formulations (%): SNC 31.5, desensitized NG 38.5, AP 27.5–12.5, and Ti 2.5–17.5.

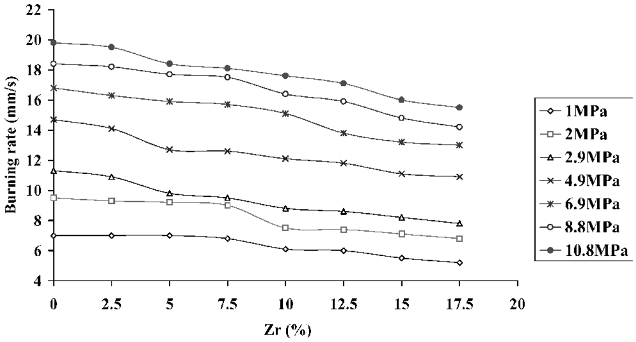

Fig. 4 Burning rate–metal content relationship for AP–Zr–CMDB propellants; metallized formulations (%): SNC 31.5, desensitized NG 38.5, AP 27.5–12.5, and Zr 2.5–17.5.

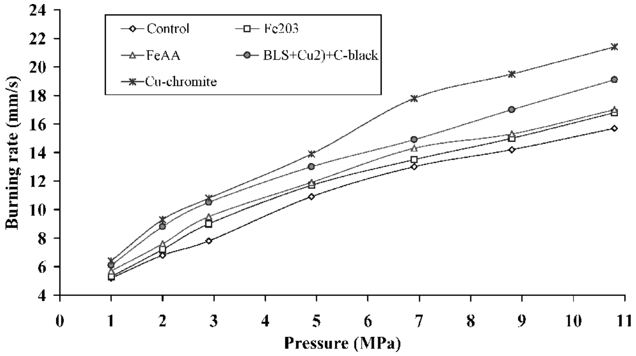

Fig. 5 Pressure–burning rate relationship for ballistically modified AP–Zr–CMDB propellants; control composition (%): SNC 31.5, desensitized NG 38.5, AP 12.5, and Zr 17.5.

Ti-based formulations with 2.5–7.5% metal content gave burning rates close to those for the control, whereas reduction in burning rates of 14–17% was observed on increase in Ti content to a 10% level in the pressure range of 1–10.8 MPa (5.8–17 mm/s). Further increase in Ti content to the 12.5–15% level resulted in the burning rate decrease to the order of 18–29% (5–16.6 mm/s), whereas increase to the 17.5% level led to 21–34% decrease (4.6–15.6 mm/s) compared to the control. As in case of Ni-based formulations, burning rates obtained for 2.5–7.5% Ti-based formulations were lower and for the composition containing 10% Ti were comparable to those for the aluminized AP–CMDB propellants. However, 12.5–17.5% Ti-based formulations gave burning rates superior to aluminized formulations, as well as Ni-containing compositions (Fig. 3).

AP–CMDB composition containing 2.5% Zr also gave burning rates close to those for the control. The formulation with 5–7.5% Zr content exhibited marginally lower burning rates. Increase in Zr content to a 10–12.5% level resulted in a 14% decrease in burning rate with respect to the control. On further increase in Zr content to 15–17.5%, burning rates realized were 20–25% lower (5.2–15.7 mm/s) than those for the control. In general, Zr-based

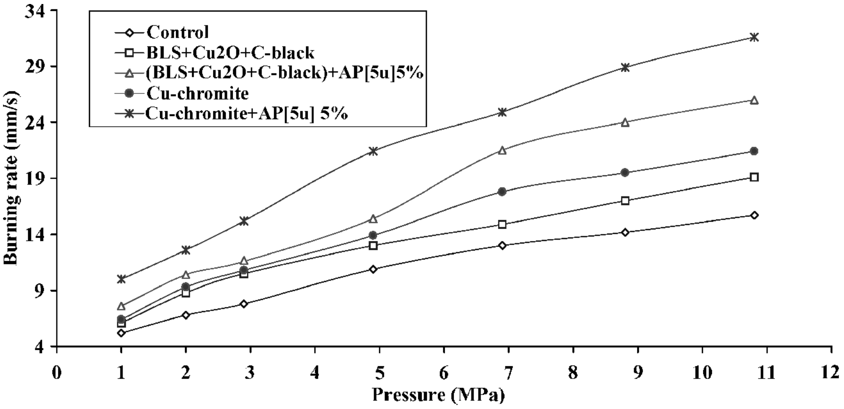

Fig. 6 Pressure–burning rate relationship for ballistically modified metallized AP–CMDB propellant with 5% AP (5 μm); control composition (%): SNC 29, desensitized NG 36, AP (9–10 μm) 12.5, AP (5 μm) 5, and Zr 17.5.

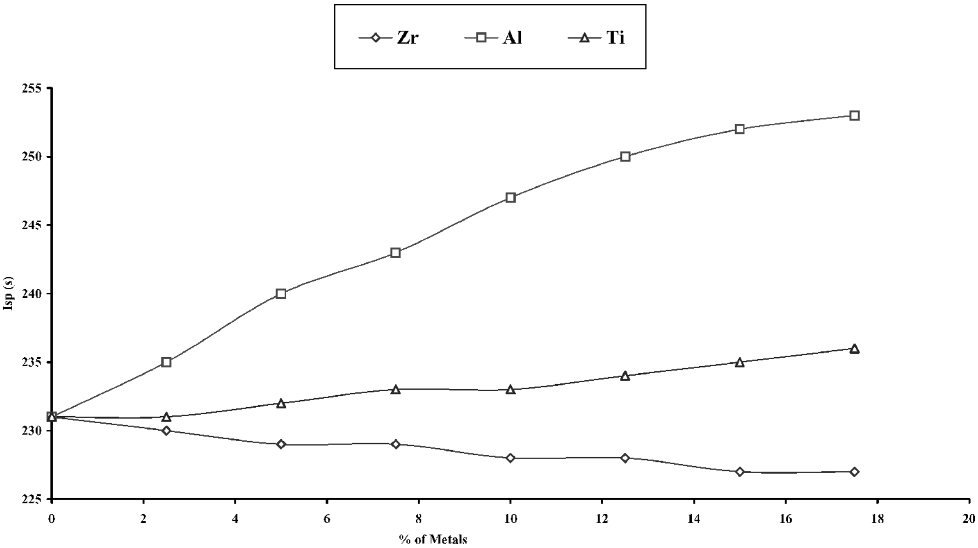

Fig. 7a Relationship of I_{sp} and percentage of metals for AP–CMDB propellants; composition (%): SNC 31.5, desensitized NG 38.5, AP 30–12.5, and metals 0–17.5.

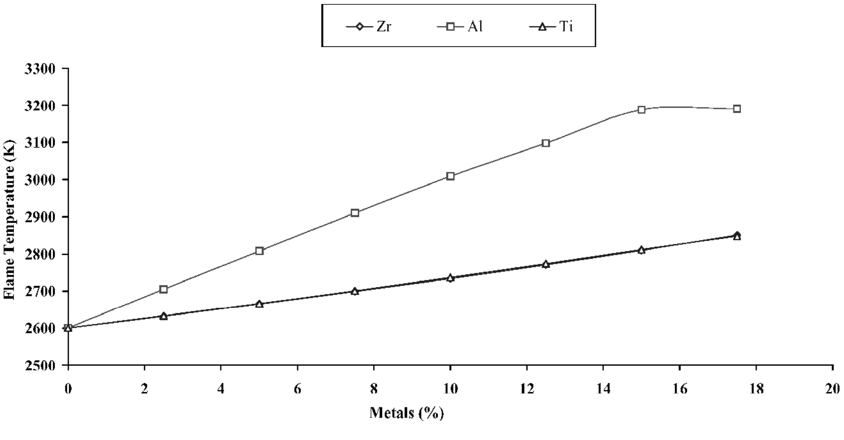

Fig. 7b Relationship of flame temperature and percentage of metals for AP–CMDB propellant systems; basic composition (%): SNC 31.5, desensitized NG 38.5, AP 30–12.5, and metals 0–17.5.

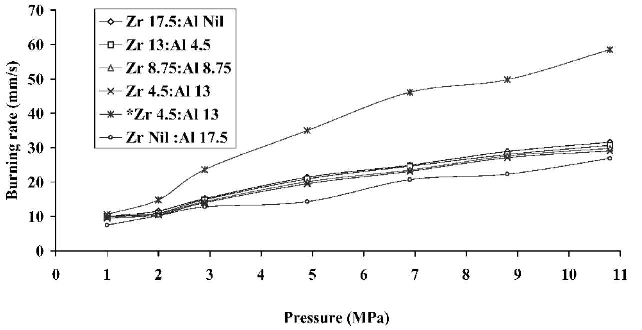

Fig. 8 Pressure–burning rate relationship for the ballistically modified Al/Zr–AP–CMDB propellant systems with 5% AP (5 μm); basic composition (%): SNC 29, desensitized NG 36, AP (9–10 μm) 12.5, AP (5 μm) 5, Zr 17.5, and Cu–chromite 2 parts (*SNC 29, desensitized NG 36, AP 17.5 (5 μm)) Zr 4.5, Al 13, and Cu–chromite 2 parts.

AP–CMDB formulations exhibited a combustion pattern similar to Ti-based compositions with relatively higher burning rates (Fig. 4).

All of the compositions exhibited a pressure index value $n = 0.4$–0.6 in the pressure range of 1–10.8 MPa.

Ballistic Modification of AP–Zr Compositions

During this work, the effect of the inclusion of ballistic modifiers was studied with the 17.5% Zr-based AP–CMDB formulation due to its relatively superior burning rates among the metallized formulations studied. Incorporation of Fe_2O_3 led to 10% burning rate enhancement in the pressure range of 1–10.8 MPa. A similar trend was observed for FeAA. Inclusion of the BLS + Cu_2O + C-black combination led to a 17–30% increase in the burning rates (6.1–19.1 mm/s), whereas that of Cu–chromite resulted in 23–36% higher burning rates (6.4–21.4 mm/s) as compared to unmodified propellant in the pressure range of 1–10.8 MPa. Thus, the Cu–chromite and the BLS + Cu_2O + C-black combinations were found to be more effective compared to Fe_2O_3 and FeAA (Fig. 5).

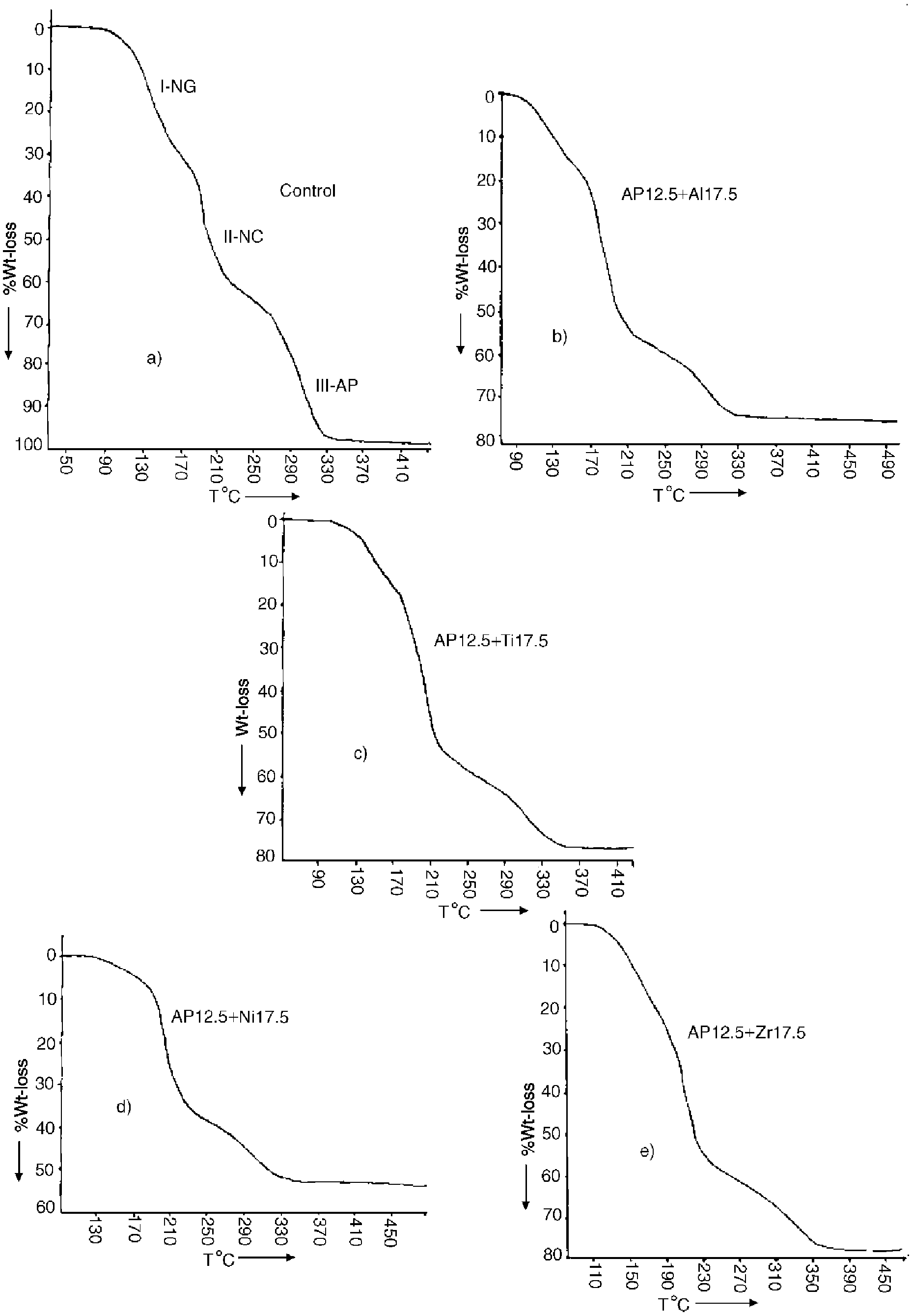

Fig. 9 TG profile of metallized AP–CMDB propellants at heating rate 10°C/min.

Table 1 TGA and DSC results of metallized AP–CMDB propellants

Compositions, %	TGA		DSC			
			ΔH, J/g		Peak temperature, °C	
	Temperature range, °C	Weight loss, %	1	2	1	2
Control[a]	85–185, 185–250, 250–353	31, 28, 34	877	592	195	335
AP 12.5 + Al 17.5	90–160, 160–210, 210–340	21, 34, 20	867	247	202	328
AP 12.5 + Ti 17 .5	110–180, 180–290, 290–360	18, 47, 13	738	187	202	333
AP 12.5 + Ni 17.5	115–245, 245–275, 275–340	10, 32, 12	903	242	202	328
AP 12.5 + Zr 17.5	100–175, 175– 285, 285–380	18, 45, 19	848	234	201	327
AP 12.5 + Zr 17.5 + Fe_2O_3 2 parts	80–170, 170– 270, 270–335	15, 33, 15	778	243	201	325
AP 12.5 + Zr 17.5 + FeAA 2 parts	80–165, 165–280, 280–400	20, 48, 23	1008	339	190	322
AP 12.5 + Zr 17.5 + BLS + Cu_2O + C–black 2 parts	83–165, 165–270, 270–430	25, 45, 19	880	476	201	328
AP 12.5 + Zr 17.5 + Cu–chromite 2 parts	80–190, 190–290, 290–360	19, 43, 20	860	457	197	323
(with 5-μm AP)	(75–150), (150–290), (290–390)	(30), (45), (20)	(895)	(487)	(190)	(312)

[a] Control composition (%) : SNC 31.5, desensitized NG 38.5, and AP 30.

To realize further improvement in the burning rates, AP content was augmented by the addition of 5% AP of 5-μm particle size at the expense of a DB matrix. It resulted in 25–37% burning rate enhancement in the case of the formulation with BLS + Cu_2O + C-black combination (7.6–26 mm/s in the pressure range of 1–10.8 MPa) and 50–56% increase in burning rates (10–31.6 mm/s at 1–10.8 MPa pressure range) for the composition modified with Cu–chromite (Fig. 6).

Zr–Al Combination

In addition to superior burning rates, Zr-based AP–CMDB formulations have the advantage of higher density than the corresponding aluminized formulations, as well as Ti-based formulations, because of the inherent higher density of Zr. However, with regard to I_{sp} (theoretical), aluminized compositions are superior as a consequence of the relatively higher heat of the Al_2O_3 formation than that for ZrO_2 and the lower mean molecular weight of Al combustion products (Figs. 7a and 7b). Therefore, propellant formulations containing Zr:Al combinations were evaluated to achieve a better combination of burning rates and I_{sp}. The composition containing 17.5% AP (12.5% of 10-μm and 5% of 5-μm particle size), 17.5% Zr, and 65% DB matrix with two parts of Cu–chromite (over 100 of composition by weight) was taken as reference. Zr was replaced by Al in increments of 4.5%. The composition based on 13% Al and 4.5% Zr content was found to be the best. It realized an I_{sp} of 256 s and burning rates of 9.5–29 mm/s in the pressure range of 1–10.8 MPa. Inclusion of 17.5% AP of 5-μm size [instead of the combination of 12.5% of AP (10 μm) and 5% of AP (5 μm)] led to super burning rates of the order of 10.6–58.5 mm/s in the pressure range of 1–10.8 MPa (Fig. 8).

Thermal Decomposition

The ammonium perchlorate-composite modified double base (AP–CMDB) control composition exhibited three-stage decomposition in TGA, corresponding to 31, 28, and 34% weight loss in the temperature ranges of 85–185, 185–250, and 250–353°C, respectively. Incorporation of Ti and Zr, like that of Al, led to the reduction in the extent of weight loss during the third stage, almost corresponding to the metal content in the formulation. DSC revealed two-stage decomposition. The first stage may encompass the overall decomposition of DB matrix (NC and NG) corresponding to initial two-step decomposition observed in TG. In DSC, incorporation of these metals led to decrease in ΔH during the first (738–867 J/g) and second (187–247 J/g) stages of decomposition as compared to nonmetallized propellants, ($\Delta H = 877$ and 592 J/g, respectively). Interestingly, the Ni-based formulation recorded much lower weight loss during first stage of decomposition (10% in the temperature range of 115–245°C) in TG. However, it did not lower the ΔH value (903 J/g) for first stage decomposition in DSC (Figs. 9a–9e and 10a–10e).

Inclusion of Fe_2O_3 in the AP–Zr formulation led to reduction in weight loss during all of the stages in TG. In DSC, the composition exhibited relatively lower ΔH for first stage. The Cu–chromite-based formulation did not show a decrease in the weight loss in TG and gave higher ΔH value (860 and 457 J/g at 197 and 323°C, respectively) in DSC with respect to the control. A more or less similar pattern was obtained with the BLS + Cu_2O + C-black combination. Addition of FeAA led to an increased weight loss (TG) as well as ΔH values (DSC) for all of the stages of decomposition as compared to other ballistically modified formulations (Table 1 and Figs. 11a–11e and 12a–12e).

Because changes in the decomposition pattern were relatively more distinct during the first stage in almost all of the cases, kinetics were determined for this stage by DTA. Control composition exhibited peak decomposition temperatures of 180–199°C at the heating rates of 5–20°C/min in DTA, corresponding to Ea of the order of 30 kcal/mol with frequency factor A of 8.7×10^{13}. Metallized compositions, incorporating Al, Ti, and Zr gave more or less similar peak decomposition temperatures (188–208°C) and Ea (29 ± 4 kcal/mol). However, the Ni-containing composition exhibited peak decomposition temperatures of 177–205°C with relatively lower Ea (20 kcal/mol). Addition of Fe_2O_3, BLS + Cu_2O + C-black combination, and Cu–chromite in AP–Zr formulations led to an increase in Ea (37–45 kcal/mol), whereas FeAA brought down the T_{max} by 14–19°C as well as Ea (by 5 kcal/mol) as compared to the unmodified AP–Zr formulation (Table 2).

Discussion

Studies undertaken during this work show that the incorporation of Al in propellant results in an increase in performance, while it reduces the burning rates, as reported by various researchers.[16–18] Decrease in burning rates with increase in Al content can be explained on the basis of the fact that the metal being coated with protective oxide layer need to be heated up to its melting point to achieve ignition leading to a heat sink effect. An enormous amount of heat is produced on metal combustion; however, it occurs much away from the surface, and therefore, the compensating effect is of less significance.[19,20] Moreover, the heat sink effect, as well as size of the agglomerates, increases with an increase in the metal content, hindering the combustion phenomena.

The relatively lower burning rates of the 2.5–7.5% Ni-based formulations than the aluminized compositions can be attributed to an increase in the heat sink effect due to higher melting and boiling points (1728 and 3039 K, respectively) of Ni. However, the superior combustion behavior of the Ni-based formulations in terms of higher burning rates and lower deflagration limit particularly at higher metal content than aluminized compositions can be explained on the basis of the fact that Ni catalyzes dark zone reactions of the

Table 2 DTA results of metallized AP-CMDB propellants

	DTA					
	Peak temperature (°C) at heating rate (°C/min)					
Compositions, %	5	10	15	20	*Ea*, kcal/mole	*A*, min^{-1}
Control[a]	180	190	194	199	29.7	8.67×10^{13}
AP 12.5 + Al 17.5	191	200	205	209	32.5	9.10×10^{14}
AP 12.5 + Ti 17.5	188	202	206	212	24.5	1.28×10^{11}
AP 12.5 + Ni 17.5	177	190	198	205	20.2	1.73×10^{9}
AP 12.5 + Zr 17.5	188	200	208	210	25	2.25×10^{11}
AP 12.5 + Zr 17.5 + Fe_2O_3 2 parts	194	202	206	210	37.3	1.42×10^{17}
AP 12.5 + Zr 17.5 + BLS + Cu_2O + C-black 2 parts	195	203	208	210	38.1	3.16×10^{17}
AP 12.5 + Zr 17.5 + Cu–chromite 2 parts (with 5 μm AP)	192 (187)	198 (195)	202 (198)	205 (200)	44.7 (42.6)	6.37×10^{20} (1.06×10^{20})
AP 12.5 + Zr 17.5 + FeAA 2 parts	169	182	190	196	20	2.11×10^{9}

[a] Control composition (%) : SNC 31.5, desensitized NG 38.5, and AP 30.

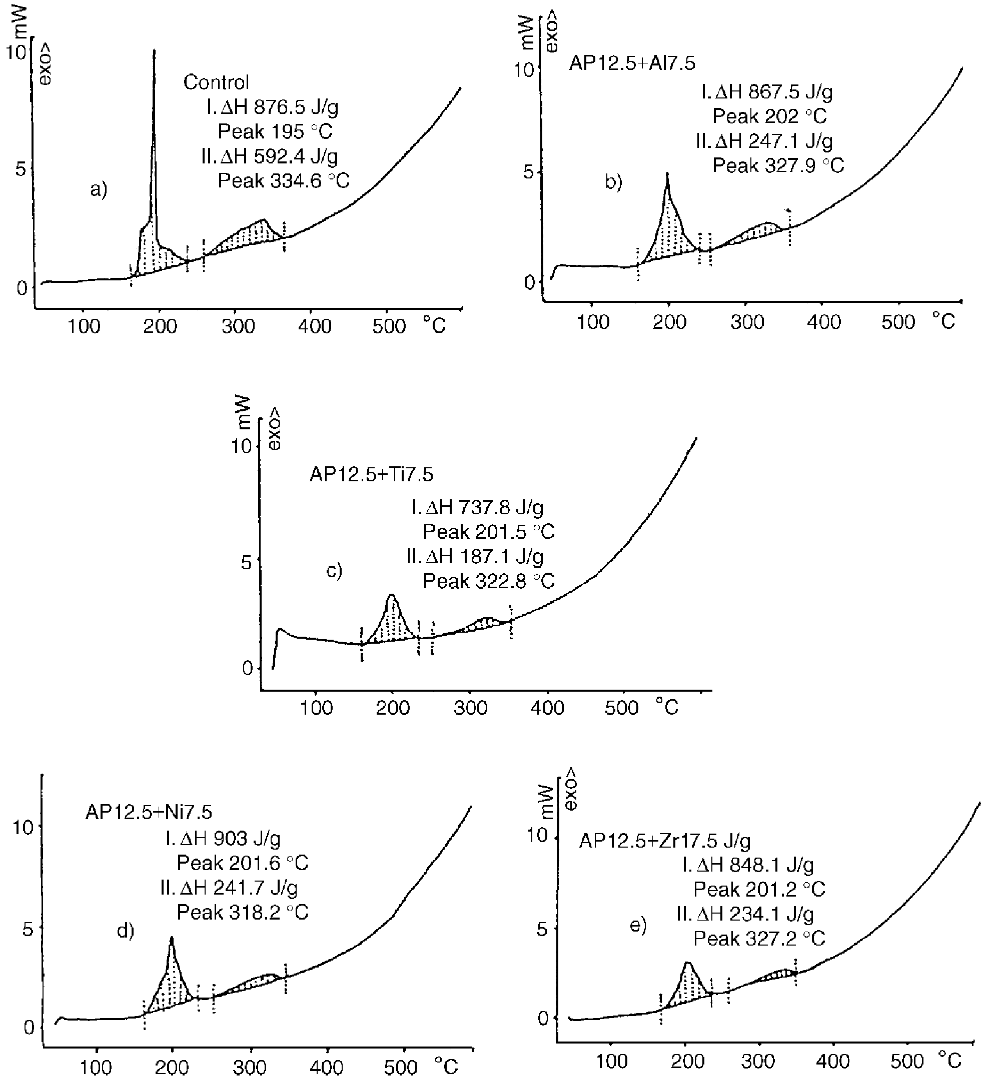

Fig. 10 DSC profile of metallized AP–CMDB propellants at heating rate 10°C/min.

DB matrix, leading to a decrease in the standoff distance of the luminous flame.[12]

AP–CMDB propellants containing Ti/Zr gave burning rates overall superior to the aluminized formulations evaluated during this work. This can be because the oxides of Ti/Zr formed during combustion are soluble in molten metal, leading to the possibility of the diffusion of the metal out of the oxide layer. As a consequence, combustion of Ti/Zr can occur nearer to the deflagrating propellant surface as compared to Al, resulting in considerable heat feedback.[9–11] The superior burning rate pattern of Zr-based compositions can be explained by the heat of formation of ZrO_2 being higher than that of TiO_2. Moreover, Zr has the advantage of lower ignition temperature (about 1100°C) in an oxidizing environment.[9,10]

The first and second step of the decomposition during TG experiments on the AP–CMDB formulation may be attributed to the overall degradation of the DB matrix. AP decomposition follows in the third step. Ti and Zr, like Al-based formulations, exhibited reduction in the extent of weight loss during the third stage, almost

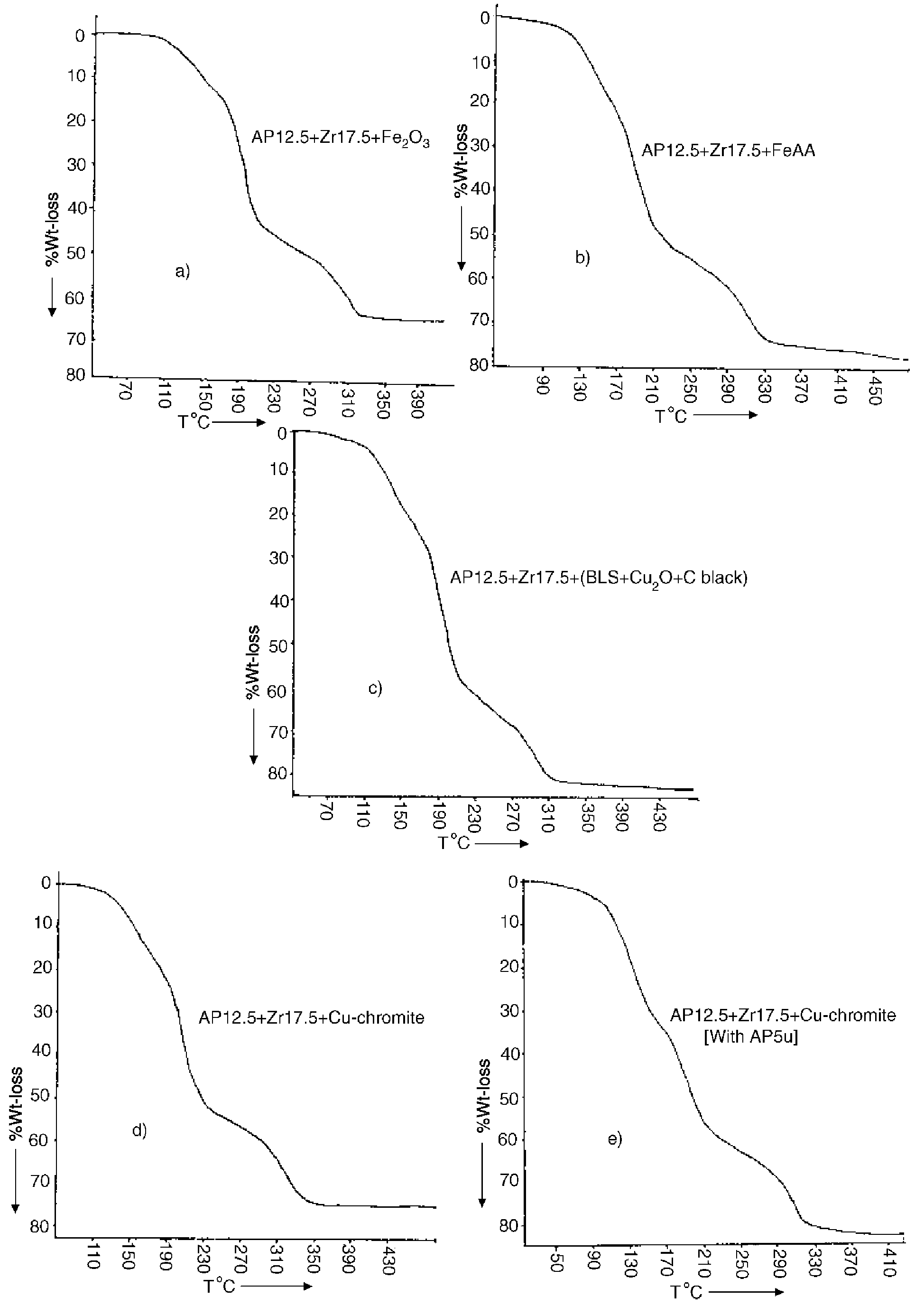

Fig. 11 TG profile of ballistically modified Zr/AP–CMDB propellants at heating rate 10°C/min.

corresponding to the metal content in the formulation. These results show that the metals are not involved in the basic decomposition process of the condensed phase as reported earlier for nitramine–CMDB propellants.[21] In DSC, incorporation of these metals led to a decrease in ΔH during all of the stages of decomposition, which may be an outcome of the heat sink effect due to the high melting and boiling points of metals. Ni-based formulations recorded much lower weight loss during the first stage of decomposition. Higher ΔH of the AP–Ni–CMDB system in the first stage of DSC could be explained due to decomposition of NG retained in the condensed phase as indicated by TG results. However, these aspects need detailed investigations.

Incorporation of Fe_2O_3 in the AP–Zr CMDB formulation led to reduction in weight loss, suggesting its inhibiting effect was probably due to the necessity to heat it to 900–1300°C before realizing a catalytic effect.[22] In view of the low concentration and due to the accumulation on the surface, it is suggested that Fe_2O_3 gets sporadically distributed in the gas phase instantaneously, and thereby, it does not have opportunity to catalyze surface reactions directly.[21] The decrease in ΔH value observed during first stage of decomposition in DSC may also be attributed to these facts. ΔH for the second stage remained almost unaffected, which may be due to the compensating heat feedback from reactions in near surface gas-phase reactions, which are reported to be catalyzed by Fe_2O_3.[23]

Cu–chromite-based formulation did not show a decrease in the weight loss with respect to the control. This may be because the exothermic redox reactions occurring on the surface compensate the heat sink effect. There is also a possibility of heat feedback due to an increased gas-phase combustion because of the enhancement of the reaction between ammonia or C/H compounds (originating from the DB matrix) with $HClO_4$ or oxygen. Catalysts may also be promoting the reaction of perchloric acid vapor with solid fuel.[24–26]

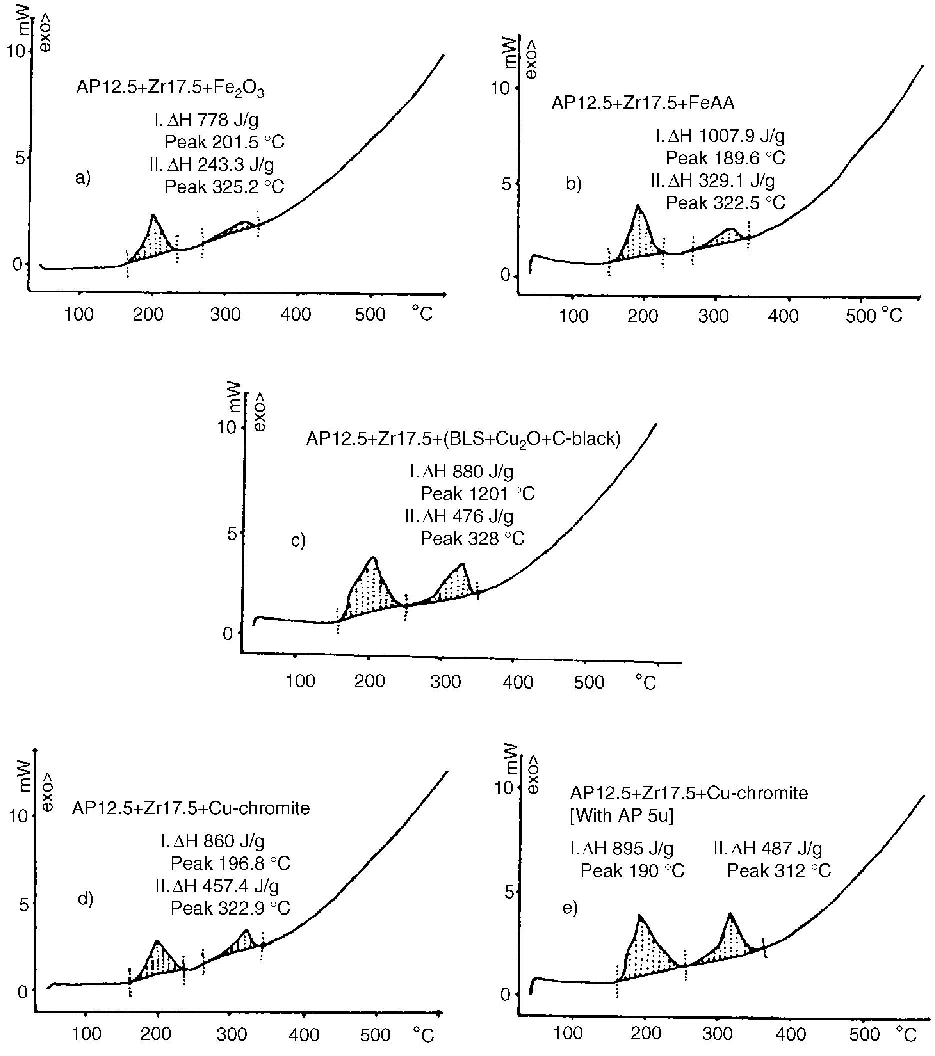

Fig. 12 DSC profile of ballistically modified Zr/AP–CMDB propellants at heating rate 10°C/min.

Increase in ΔH for the first as well as second stage of decomposition on incorporation of Cu–chromite can be explained based on this reasoning. The pronounced effect of Cu–chromite on the second stage of decomposition shows that it catalyzes the reactions between AP/decomposition products of AP and the DB matrix. A similar trend was obtained for BLS + Cu$_2$O + C-black-containing compositions. Lengelle et al.[27] reported that Pb salts need to be heated to ~700°C to obtain the active form of PbO. This phenomenon occurs above the surface, where PbO is trapped in the carbon residue. It is opined that the likely site of action of the lead additives is the gas phase rather than the condensed phase. Youfang[28] has proposed that a reaction between PbO and carbonaceous decomposition products of a DB matrix results in the formation of carbon nuclei that undergo growth, producing char deposits on the burning surface, leading to the shift of the reducing site of NO nearer to the burning surface, and resulting in greater temperature gradient. These processes may explain the trend observed. Inclusion of FeAA led to an increase in the weight loss as well as the ΔH value, remarkably, suggesting catalytic effect of FeAA in the condensed phase. DTA results also support these trends. However, Cu–chromite gave burning rates superior to FeAA and BLS + Cu$_2$O + C-black combination showing that its activity is both in the condensed and the gas phases.

Conclusions

1) The incorporation of Al results in a burning rate decrease due to overall heat sink effect. The superior combustion behavior of Ni-based formulations observed in terms of burning rates and low-pressure deflagartion limit, particularly at higher metal content, than aluminized compositions may be because it catalyzes the dark zone reactions of the DB matrix. The relatively superior burning rates of Zr followed by propellants containing Ti emanate from their oxides being soluble in molten metal and the relatively more pyrophoric nature of Zr.

2) TG and DSC data for metallized formulations show that Al/Zr/Ti do not play any role directly in the condensed phase.

3) Cu–chromite was found to be a more effective ballistic modifier for Zr-based AP–CMDB propellants compared to Fe$_2$O$_3$ and FeAA. The BLS + Cu$_2$O + C-black combination gave intermediate results.

4) Thermal data suggest that FeAA is effective in the condensed phase and that Fe$_2$O$_3$ is mainly effective in the gas phase, whereas Cu–chromite is effective in both the condensed and the gas phases.

References

[1] Musso, R. C., and Grigor, A. F., "Decomposition Studies of Propellant Ingredients and Ingredient Combinations," AIAA Paper, 68-495, ICRPG/AZAA 3rd Solid Propulsion Conference, Atlantic City, N.J., June 1968.

[2] Kubota, N., and Masamoto, T., "Flame Structure and Burning Rate—Characteristics of CMDB Propellants," *Sixteenth Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1977, pp. 1201–1209.

[3] Hau, Z., Feng, Z., Wang, E., and Han, P., "The Energy and Pressure Exponent of Composite Modified Double-Base Propellants," *Propellants, Explosives, Pyrotechnics*, Vol. 17, No. 2, 1992, pp. 59–62.

[4] Duterque, J., Hommel, J., and Lengelle, G., "Experimental Study of Double-Base Propellants, Combustion Mechanism," *Propellants, Explosives, Pyrotechnics*, Vol. 10, No. 1, 1985, pp. 18–25.

[5] Swaminathan, V., and Marian, M. S., "On the Burning Rate Characteristics of CMDB Propellants," *Propellants, Explosives, Pyrotechnics*, Vol. 4, No. 3, 1979, pp. 107–111.

[6] Raman, K. V., Singh, H., and Rao, K. R. K., "Ballistic Modification of Composite Modified Double-Base Propellants Containing Ammonium Perchlorate," *Propellants, Explosives, Pyrotechnics*, Vol. 12, No. 1, 1987, pp. 13–16.

[7] Raman, K. V., and Singh, H., "Ballistic Modification of RDX-Based CMDB Propellants," *Propellants, Explosives, Pyrotechnics*, Vol. 13, No. 5, 1988, pp. 149–151.

[8] Ronald, L., "Random Orientation of Staple in Slurry Cast Propellants," U.S. Patent 3,813,458, 28 May 1974.

[9] Rastogi, R. P., and Deepak, D., "Combustion of Metallized Propellants," *Journal of Scientific and Industrial Research*, Vol. 36, Oct. 1977, pp. 470–490.

[10] Athawale, B. K., Asthana, S. N., and Singh, H., "Metallized Fuel-Rich Propellants for Solid Rockets—Review," *Defence Science Journal*, Vol. 44, No. 4, 1994, pp. 269–278.

[11] Mama, H. P., "Solid Rocket Propellants. The European Scene," *International Defence Review*, March 1988, pp. 219–295.

[12] Kubota, N., "Role of Additive in Combustion Waves and Effect on Stable Combustion Limit of Double Base Propellants," *Propellants and Explosives*, Vol. 3, Dec. 1978, pp. 163–168.

[13] Bhat, V. K., Singh, H., and Rao, K. R. K., "Processing of High Energy Crosslinked Composite Modified Double Base Propellants," *18th International Jahrestag Fraunhofer Inst. Treib Explosivst*, Karlsruhe, Federal Republic of Germany, July, 1987, pp. 18/1–18/10.

[14] Rindorf, H. J., *A Technical review to Advanced Techniques in Acoustical, Electrical and Mechanical Measurements*, Bruel Kjaer, Naerum, Denmark, No. 2, 1981, pp. 41–44.

[15] Ozawa, T., "Kinertic Analysis of Derivative Curves in Thermal Analysis," *Journal of Thermal Analysis*, Vol. 2, No. 2, 1970, pp. 301–324.

[16] Scurlock, A. C., Rumbel, K. E., and Rice, M. L., U.S. Patent 3,107, "Solid Poly(vinyl chloride) Propellant Containing Metal" 186, 15th Oct. 1963.

[17] Duerksen, R. L., and Cohen, J., "Solid Propellant with Polyurethane Binder," U.S. Patent 3,793,099, 19th Feb. 1974.

[18] Sutton, G. P., *Rocket Propulsion Elements*, 6th ed., Wiley, New York, 1992, Chap. 12, pp. 416–455.

[19] Brewster, M. Q., and Hardt, B. E., "Influence of Metal Agglomeration and Heat Feedback on Composite Propellants Burning Rate," *Journal of Propulsion*, Vol. 7, No. 6, 1991, pp. 1076–1078.

[20] Ishihara, A., Brewster, M. Q., Sheridan, T. A., and Krier, H., "The Influence of Radioactive Heat Feedback on Burning Rate in Aluminized Propellants," *Combustion and Flame*, Vol. 84, No. 1–2, March, 1991, pp. 141–153.

[21] Divekar, C. N., Asthana, S. N., and Singh, H., "Studies on Combustion of Metallized RDX-Based CMDB Propellants," *Journal of Propulsion and Power*, Vol. 17, No. 1. 2000, pp. 58–64.

[22] Kishore, K., and Gayathri, V., "Chemistry of Ignition and Combustion of Ammonium Perchlorate-Based Propellants," *Fundamentals of Solid Propellants Combustion*, edited by K. K. Kuo and M. Summerfield, Progress in Aeronautics and Astronautics, Vol. 90, AIAA, New York, 1984, pp. 53–119.

[23] Pittman, C. U., "Location of Action of Burning Rate Catalysts in Composite Propellant Combustion," *AIAA Journal*, Vol. 7, No. 2, 1969, pp. 328–334.

[24] Krishnan, S., and Jeenu, R., "Combustion Characteristics of AP/HTPB Propellants with Burning Rate Modifiers," *Journal of Propulsion and Power*, Vol. 8, No. 4, 1992, pp. 748–755.

[25] Pearson, G. S., "Composite Propellant Catalysts: Copper Chromate and Chromite," *Combustion and Flame*, Vol. 14, No. 1, Feb. 1970, pp. 73–84.

[26] Inami, S. H., Rajapokse, Y., Shaw, R., and Wise, H., "Solid Propellant Kinetics I: The Ammonium Perchlorate–Chromite Fuel System," *Combustion Flame*, Vol. 17, No. 2, 1971, pp. 189–196.

[27] Lengelle, G., Bizot, A., Duterque, J., and Trubert, J. F., "Steady State Burning of Homogeneous Propellants," *Fundamentals of Solid Propellants Combustion*, edited by K. K. Kuo and M. Summerfield, Progress in Aeronautics and Astronautics, Vol. 90, AIAA, New York, 1984, pp. 361–407.

[28] Youfang, C., "Combustion Mechanism of Double-Base Propellants with Lead Burning," *Propellants, Explosives, Pyrotechnics*, Vol. 12, Dec. 1987, pp. 209–214.