Reactivities of aluminium and aluminium–magnesium alloy powders in polymeric composites

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Polymeric compositions containing Al–Mg alloys show higher reactivities, in comparison with similar compositions containing aluminium. This is observed irrespective of the amount of oxidizer, type of oxidizer used, type of polymeric binder, and over a range of the particle sizes of the metal additive. This is evident from the higher calorimetric values obtained for compositions containing the alloy, in comparison to samples containing aluminium. Analysis of the combustion residue shows the increase in calorimetric value to be due to the greater extent of oxidation of the alloy. The interaction between the polymeric binder and the alloy was studied by coating the metal particles with the polymer by a coacervation technique. On ageing in the presence of ammonium perchlorate, cracking of the polymer coating on the alloy was noticed. This was deduced from differential thermal analysis experiments, and confirmed by scanning electron microscopic observations. The increase in stiffness of the coating, leading to cracking, has been traced to the cross-linking of the polymer by magnesium.

1. Introduction

The study of the oxidation of metal powders has been of interest, since metal powders like aluminium have been used in solid rocket propellants, and thermite mixtures like Fe_2O_3–Al, to increase the energy of the compositions. Testing of materials that could be used in high-temperature service, such as in spacecraft, also requires an understanding of the combustion of metals and alloys. The ignition and combustion of metals that are exposed to oxygen-enriched atmospheres is of interest in regard to the identification and analysis of hazards in oxygen systems, and in the design of oxygen systems and components. Recently, the increased interest in utilizing the combustion process between elemental powders resulting in pure ceramic powders and intermetallic compounds, as well as composites, has led to a large number of studies of the so-called self-propagating high-temperature/ combustion synthesis reactions [1–3]. This was an offshoot of the studies of energetic mixtures and propellants, in the search for finding the most satisfactory candidate metals for improving the combustion characteristics of the compositions. The combustion of metal powders results in the liberation of large quantities of heat, because many metals have high heats of combustion/oxidation. Studies abound of the effect of metal powders like aluminium in bringing about increased performance of the compositions.

A few studies have been reported on the use of Al–Mg alloys in bringing about more complete oxidation of the metal additive in such compositions. The introduction of small amounts of the reactive magnesium enhances the reactivity of the metal additive, and hence, more complete reaction can occur. In the present study, similar compositions containing an elastomer and a solid oxidizer, with aluminium powder and Al–Mg alloy powder as additives, have been compared for their reactivities.

The effect of the presence of magnesium on the long-term behaviour of the composition has also been studied. The polymer was studied in the form of a coating on the aluminium powder and alloy powder, to determine what effect the interaction, if any, between the polymer and the aluminium/alloy would have on the properties of the polymer. This study would also be relevant to the behaviour of bulk material, because Al–Mg alloys are used in aircraft structures, and point to any compatibility considerations in the use of certain types of polymers in conjunction with the alloys.

In an earlier study [4], we have shown that aluminium–magnesium alloys are more effective than pure aluminium in increasing the combustion velocity and thermal reactivity of oxidizer ammonium perchlorate (AP). Through our study of pressed pellets of AP–(Al–10% Mg alloy) powder, the alloy was

also shown to undergo a greater extent of reaction compared to the pure metal. Such an increase over aluminium was observed even at a magnesium content of only 10%, i.e. when an (Al–10% Mg) alloy powder was used. The burning rates of AP–Al pellets decreased with increase of aluminium content and a pellet containing 40% Al did not undergo combustion. The AP–(Al–10% Mg) alloy pellets, on the other hand, sustained combustion up to 55% metal additive by weight [4]. Also, the maximum in the heat of combustion was observed at 40% alloy content, and gas chromatographic analyses of combustion gases indicated large quantities of hydrogen for the 40% alloy composition. The presence of hydrogen in the products is due to the oxidation of the alloy by water, which is one of the products of combustion of AP. The higher calorimetric values obtained, and the smaller metal agglomerates observed at the end of the combustion reaction indeed confirmed the higher combustion velocities and larger extent of metal participation in the combustion process.

In addition to a solid oxidizer, a polymeric binder, and metal additives, composite solid propellants, also contain other additives like plasticizers, and bonding agents. It would be of practical interest to study the effect of utilizing the more reactive alloy in place of aluminium. In the 1960s, in the search for energetic compositions, the use of Al–Mg alloys was briefly explored. To date, only a few studies have been reported in the open literature on the use of Al–Mg alloys [5–10] in composite solid propellants. One study reported that the use of a Mg–Al alloy resulted in the complete consumption of the metal in the reaction [5]. In mixtures of AP, urotropine, and Al–Mg alloy, increasing the magnesium content in the alloy was reported to bring about ignition of the alloy particles close to the burning surface [6]. Simms et al. [7] reported that addition of magnesium as an ignition aid was "beneficial", and Cohen [8] showed that this was predictable from thermochemical calculations of the combustion temperatures, T^*, as different amounts of the metal are allowed to oxidize by a slow surface oxidation, and that in the presence of magnesium, aluminium can undergo efficient combustion in a propellant. Cohen and Derr [9] suggested coating aluminium with a Mg–Al eutectic alloy, while Northam and Sullivan [10] achieved the same effect by mixing the eutectic with aluminium.

In the present study, we have made an attempt to compare the reactivities of propellant compositions incorporating aluminium powder and Al–Mg alloy powders, and the heat of combustion, determined by bomb calorimetry, was chosen as a parameter for comparison. Because the particle size of aluminium determines the extent of participation in the reaction with AP [11], the completeness of reaction would be reflected in the calorimetric value of the propellant sample. (The limitation of the bomb calorimetric technique with energetic materials and metals is discussed in another section of this paper).

Because the binder provides the structural integrity to the propellant, any interaction between the alloy and the binder would affect the mechanical properties to

a very great extent. The reactivities of aluminium and Al–Mg alloy powders towards the polymeric binder have been studied by coating the polymer on the aluminium/alloy particles. Because it is well known that the presence of AP affects the nature and kinetics of the reactions taking place, the coated powders were compacted with AP and pellets of AP-coated aluminium/alloy were studied for their thermal behaviour before and after ageing under humid conditions.

2. Experimental procedure
2.1. Aluminium–magnesium alloys
The aluminium and magnesium used for preparation of the alloy were 99.99% pure supplied by the British Aluminium Company, UK, and Dow Chemicals Company, USA, respectively. Alloys were prepared by first melting aluminium in a graphite crucible in air. The melt was held at 700 °C and the required quantity of magnesium was added to obtain alloys having nominal compositions of 5%, 10%, 15% and 28% Mg. The molten alloy was poured into metallic moulds and the ingots were later homogenized for 2 h at 450 °C. The alloy powders were obtained by filing the ingots, and the filings were sieved to obtain the required size fractions. The alloy powders were analysed by X-ray diffractometry (XRD) using CuK_α radiation with nickel filters. A step-scanning technique was employed for collecting the diffractograms from which lattice parameters of aluminium and alloy powders were calculated to ensure that magnesium alloyed with aluminium. The lattice parameter changed from 0.4056 nm for pure aluminium to 0.407 nm for 5% Mg addition and to 0.4094 nm for 10% Mg addition, due to the formation of solid solution of magnesium in aluminium. For the Al–15% and Al–28% Mg alloy, the lattice parameter was 0.4103 nm; additional peaks were obtained due to β-phase (Al_3Mg_2) corresponding to d values of 0.250 and 0.239 nm.

2.2. Preparation of propellant compositions
Ammonium perchlorate (AP)- and potassium perchlorate (KP)-based propellants were prepared as follows: the prepolymer was prepared by weighing out appropriate quantities of lecithin, prepolymer, curing agents (which were a mixture of an epoxide and an aziridine), and dioctyl adipate which was a plasticizer. These were mixed thoroughly, and AP (and Al/Al–Mg alloy powder in formulations containing metal) added in small batches to obtain a homogeneous mixture. This slurry was mixed well and cast in teflon moulds, under vacuum, with simultaneous vibration to ensure good packing of the grain. The cast propellant was cured at room temperature for 1 day and at 80 °C for 3 days. Two binder types, carboxy-terminated polybutadiene (CTPB) and polybutadiene-acrylic-acid-acrylonitrile (PBAN) were used.

Calorimetric values were determined in Parr 1241 Automatic Adiabatic Bomb Calorimeter at 25 atm nitrogen. (The calorimetric value, as opposed to calorific value, which is determined in oxygen, is the heat

liberated when the sample is burnt in nitrogen. Hence, the oxidation of the material is incomplete, and the combustion residue consists of some unreacted metal, and other combustion products.)

2.3. Estimation of residual metal

The residual metal after combustion was estimated by the hydrogen evolution method. A known weight of the combustion residue was treated with dilute HCl and the volume of the hydrogen liberated was measured. This volume was converted to standard temperature and pressure, and the corresponding weight of the metal that would liberate this amount of hydrogen was calculated.

2.4. Differential thermal analysis (DTA)

Differential thermal analysis technique was adopted to determine thermal behaviour of the samples by carrying out experiments in air at a heating rate of $8\,°C\,min^{-1}$. Platinum cups were utilized as containers for sample and reference and a constant weight of sample (50 mg) was chosen for all the experiments. Ignited powdered alumina was used as a reference standard. The instrument was calibrated by determining the melting points of standard metals. The furnace was heated using a proportional controller and the accuracy of the peak temperature was $\pm 2\,°C$.

2.5. Microencapsulation

The aluminium and Al–Mg alloy particles were coated with PBAN by a coacervation technique [12]. To a known weight of the polymer (PBAN) dissolved in benzene, the metal powder was added and the solution concentrated slowly by evaporation on a water bath. When the solution became viscous, a non-solvent (methanol) was added. The metal particles were coated with the polymer after the precipitation of PBAN due to methanol. The coated powder was washed several times in methanol and dried in an oven at 60 °C. The weight of the polymer was chosen such that the ratio of the polymer to the metal was the same as in the propellant, i.e. about 15.3%. The particle size of the metal was 105–151 μm.

2.6. Pelletization procedure

Polymer-coated aluminium and Al–Mg alloy powders were thoroughly mixed with the oxidizer AP. The mixture was poured into a 5 cm diameter die-steel die and was levelled uniformly within the die cavity to eliminate thickness variations within the sample. Pressure was applied slowly at a uniform stroke using a hydraulic press with the aid of an automatic controller. To avoid inhomogeneity in the density of the samples due to axial pressing, the diameter to thickness ratio was kept very high and was within the range 8:1 to 10:1. No weight change was detected after pressing. For understanding the thermal behaviour of pressed pellets, samples were taken from roughly around the same areas of the pellet and this precaution enabled us to obtain consistent and accurate results between identical runs. Our experience with compaction of thermally sensitive energetic compounds [13] showed this to be an important precaution to be considered when evaluating the thermal behaviour of samples even from the same pressed pellet, because the DTA technique can easily detect small changes.

3. Results

The calorimetric values for the propellant samples containing KP as the oxidizer, are compared in Table I. It can be seen that the calorimetric value is higher for the composition containing the alloy. Considering that magnesium has a lower heat of combustion ($5.8\,kcal\,g^{-1}$) than aluminium ($7.43\,kcal\,g^{-1}$), this implies that the alloy undergoes a greater extent of oxidation in the combustion reaction compared to pure aluminium. To confirm this, the combustion residue was analysed for free metal content by the hydrogen evolution method. It can be seen (Table I) that the amount of unreacted metal is less in the combustion residue of the propellant containing the alloy. The decrease in the amount of the unreacted metal, multiplied by the heat of oxidation of the alloy, $7.42\,kcal\,g^{-1}$, corresponds to the increase in the calorimetric value by approximately $100\,cal\,g^{-1}$. The system containing KP was used for this determination since KP decomposes into KCl and oxygen and the latter oxidizes the metal powder. Propellants containing AP, on the other hand, give rise to a large number of products including H_2O, HCl, and oxides of nitrogen, which react with the metallic residue. Even the decomposition of pure AP results in several products, and the nature of the products varies depending upon the conditions [14], such as the presence of additives/catalysts, and pressure at which the combustion is carried out. Attempts were made to collect the combustion residue of AP-based propellants, by washing the products in the bomb with water, for

TABLE I Comparison of residual metal after combustion of samples, containing aluminium and (Al–10% Mg) alloy at 25 atm nitrogen

Composition (%)			Calorimetric value[c] (cal g^{-1})	Metal in residue (%)	ΔH increase (cal g^{-1})	
KP[a]	Binder	Metal[b]			Calc.	Exp.
78	12	10, Al	1271	21.3		
78	12	10, Al–10% Mg alloy	1378	6.4	111.5	107 (21.3–6.4) × 7.42

[a] KP particle size 53–105 μm.

[b] Metal particle size 37–53 μm.

[c] Uncertainty in calorimetric value: $\pm 25\,cal\,g^{-1}$.

TABLE II Calorimetric values of compositions containing aluminium and (Al–10% Mg) alloy powders at 30 atm nitrogen

Composition (%)			Calorimetric value $(\text{cal g}^{-1})^a$	
Oxidizer	Binder	Metal	Al	Al–(10% Mg) alloy
Metal particle size: 37–53 μm Oxidizer particle size: 53–105 μm				
AP, 78	CTPB, 12	10	1850	1853
AP, 71	CTPB, 12	17	1750	1895
AP, 68	CTPB, 12	21	1774	1858
Metal particle size: 53–75 μm Oxidizer particle size: 53–105 μm				
71(AP 70%, KP 30%)	CTPB, 12	17	1544	1624
AP, 68	PBAN, 20	12	1241	1338
Metal particle size: 75–105 μm Oxidizer particle size: 53–105 μm				
AP, 68	PBAN, 20	12	1180	1322

^{a} Uncertainty in calorimetric value: $\pm 25 \text{ cal g}^{-1}$

estimating the amount of unreacted metal. Reaction with the metal and the evolution of gases was clearly noticed. Collecting the combustion products of KP propellants in a quantitative manner was relatively simple, because the product was dry, consisting of KCl and the metal agglomerates.

Formulations containing AP as oxidizer have a much higher calorimetric value in comparison with KP-based systems (Table II). At 10% metal addition, there is no difference in the composition containing aluminium and the alloy. As the metal content is increased, however, the calorimetric value of the propellant containing aluminium decreases but that of the propellants containing the alloy does not change, indicative of the relative ease of reaction of the alloy. Table I also shows that when a mixed oxidizer, 70% AP and 30% KP is used, or when the binder content is changed to 20%, the composition containing the alloy shows a higher value. For a given composition, with particle sizes in the same range as that of aluminium

powder, the calorimetric value is always higher for compositions containing the alloy. However, the difference in the calorimetric values of the two propellants becomes less at larger particle sizes of the metallic additive.

The calorimetric values obtained for the different compositions reflect the kinetics of oxidation of the metal particles, because the introduction of magneisum, which has lower heat of oxidation, cannot result in an increase in the energy liberated during reaction. As the magnesium content of the Al–Mg alloys is increased, the calorimetric values increase up to 14% magnesium addition, from 1750 cal g^{-1} for the composition containing pure aluminium to 1949 cal g^{-1} for the composition containing Al–14% Mg alloy. Further increase in the magnesium content of the alloy does not bring about any further change.

3.1. DTA study of AP-coated Al/Al–10% Mg alloy

The DTA of AP is characterized by an endotherm at 240 °C, corresponding to the phase transformation from orthorhombic to cubic form, followed by exothermic decomposition in two stages (Fig. 1a). The DTA of a compact of AP with 10% Al shows a sensitization (lowering) in the decomposition temperature (Fig. 1b). The sensitization is due to an interfacial reaction between AP and aluminium [11]. The compact of AP–(Al–10%) Mg alloy also shows a sensitization in the first exotherm, which is followed by ignition, at 316 °C (Fig. 2b). In the pellets containing coated metal particles and AP, the polymer coating prevents contact between AP and the metal particles, and hence prevents the interface reaction. In accordance with this, the exothermic reaction is shifted to a temperature higher than even pure AP. This can be seen from Fig. 1c, for the AP-coated aluminium compact, where the first exothermic peak occurs at 303 °C. Similarly, in the AP-coated (Al–10% magnesium) alloy sample, the exothermic peak appearing at 271 °C is shifted to
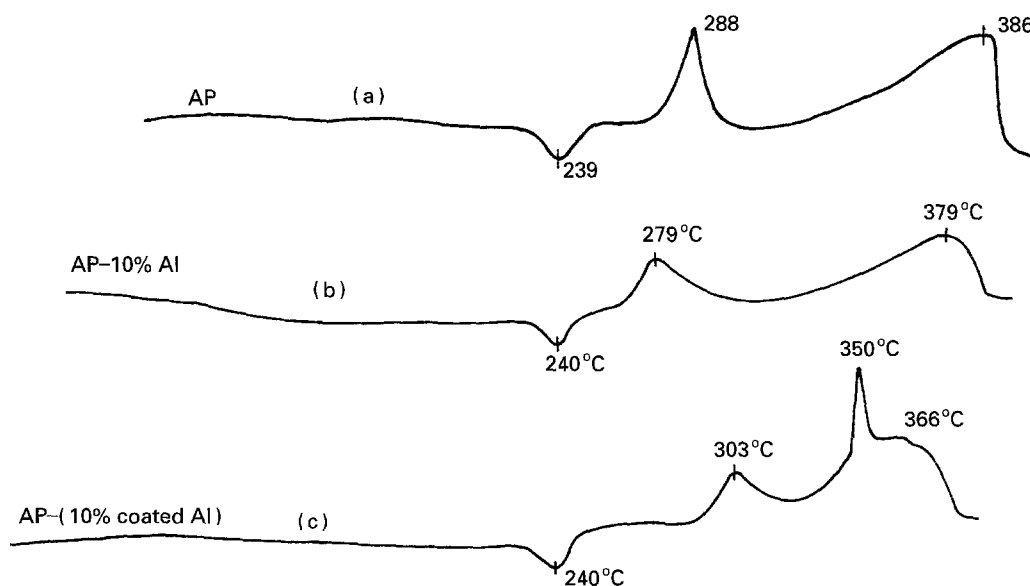

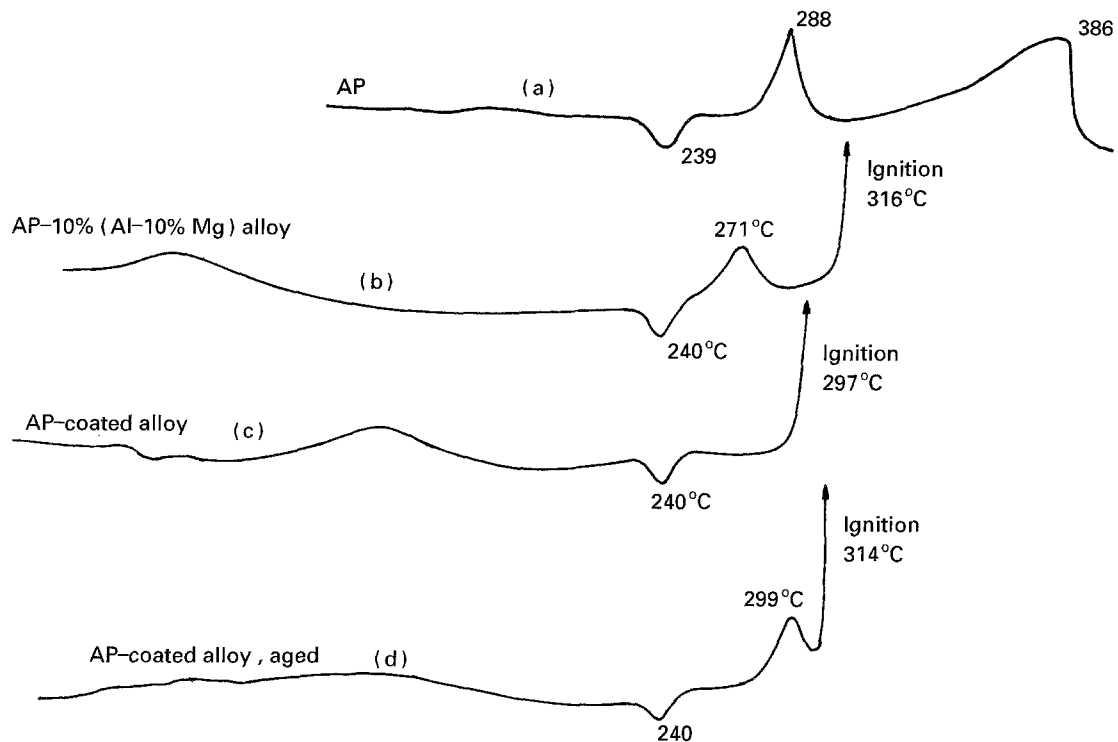Figure 1 DTA traces of compacts of (a) pure AP, (b) AP–10% Al and (c) AP–10% coated Al samples.

Figure 2 DTA traces of compacts of (a) pure AP, (b) AP–10% (Al–10% Mg) alloy, (c) AP–10% (coated Al–10% Mg alloy) and (d) aged AP–10% (coated Al–10% Mg alloy) samples.
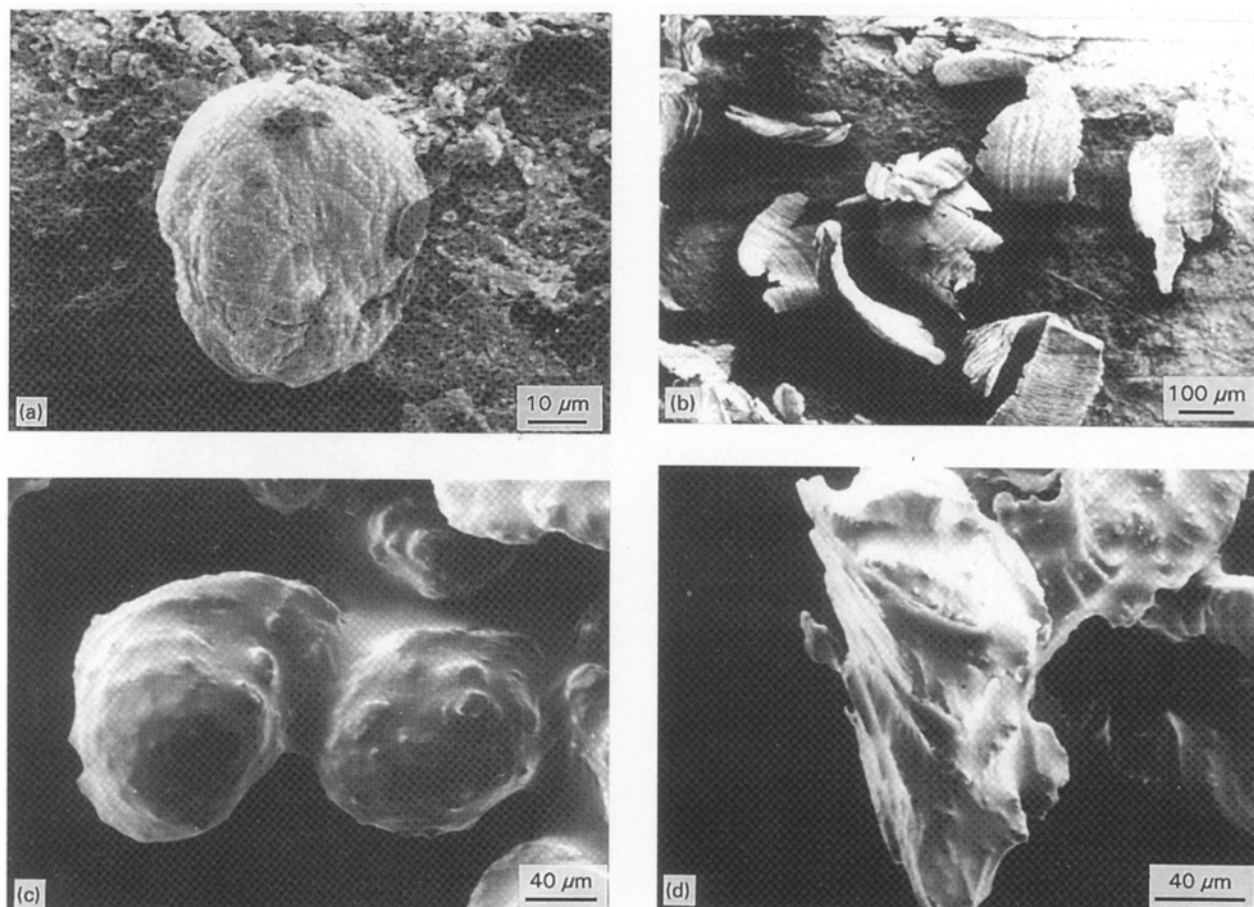

Figure 3 Scanning electron micrographs of (a) aluminium powder, (b) Al–10% Mg alloy powder, (c) aluminium powder coated with PBAN, (d) Al–10% Mg alloy powder coated with PBAN.

a higher temperature, at which stage, because of the reactivity of the Al–Mg alloy, ignition is observed (Fig. 2c). It is evident that the first peak disappears and ignition occurs at 297 °C. Scanning electron micrographs of aluminium powder, PBAN-coated aluminium particles, (Al–10% magnesium) alloy powder, and PBAN-coated (Al–10% magnesium) alloy particles are shown in Fig. 3. The morphology of the

aluminium and alloy particles are different, in that aluminium particles are spherical, whereas the alloy particles are flat.

Pellets of AP with coated aluminium and of AP with coated (Al–10% magnesium) alloy powder, were aged at 75 °C and 50% RH for a period of 25 days, and the DTAs of the aged samples recorded. In the AP-coated aluminium sample, the DTAs of the unaged and aged samples were essentially the same, and the peak temperatures did not show any change due to the ageing. In the AP-coated alloy sample (Fig. 2d), the first peak seen in the DTA of the unaged pellet reappears on ageing, although at a higher temperature, 299 °C. The reappearance of the first peak on ageing indicates that the alloy once again sensitizes the decomposition of AP which is only possible if AP and the alloy particles are in contact. This suggests that the coating on the alloy particle is not coherent. In order to verify this, the coated alloy particles which had been aged with AP in the form of AP-coated alloy pellet, were separated by dissolving the AP in methanol and were then examined in an SEM. It is clearly seen in the SEM that the coating on the alloy particles has cracked (Fig. 4a). The polymer coating appears to have become stiffer on ageing. When the particles contain larger concentrations of magnesium, the polymer coating separates out as flakes, as observed, for example, when Al–28% Mg alloy particles were coated with PBAN and aged with AP (Fig. 4b). This was also observed when magnesium particles were coated with PBAN and aged (Fig. 4c).

3.2. Infrared studies

In order to elucidate the role of magnesium in the ageing of the polymer, infrared studies were carried out on the binders aged in the presence of AP and Al/(Al–10% magnesium) alloy powders. Samples of AP-PBAN in the ratio 80:20; AP-Al-PBAN, and AP-(Al–10% magnesium) alloy-PBAN mixtures in the ratio 68:12:20, were prepared. Curing agents and other additives like plasticizer and bonding agents were not added. These mixtures were aged at a relative humidity of 50% at various temperatures for different periods of time. The aged polymers were extracted in benzene and the infrared spectra of the polymer solutions in benzene were recorded. Fig. 5a is the spectrum of the unaged polymer, which shows the following prominent bands: CH_2 stretch at 2815 cm^{-1}, a broad band around 2500 cm^{-1} due to absorption by OH of the –COOH group: $C\equiv N$ absorption at 2220 cm^{-1}; $C=O$ absorption at 1695 cm^{-1}; $C=C$ at 1630 cm^{-1} and out of plane hydrogen bend at 910 cm^{-1}. The infrared spectrum of the polymer aged in the presence of AP (Fig. 5d) and that of the polymer aged in the presence of AP and aluminium (Fig. 5c) show the same features as that of the unaged polymer. When the polymer is aged in the presence of AP and (Al–10% magnesium) alloy, there is a shift in carbonyl absorption to lower values, from 1695 cm^{-1} to 1590 cm^{-1}. The latter corresponds to the asymmetric stretch of COO^- [14]. (The symmetric stretch of COO^- occurs at 1410 cm^{-1}.) The $C=O$ absorption at 1695 cm^{-1} is
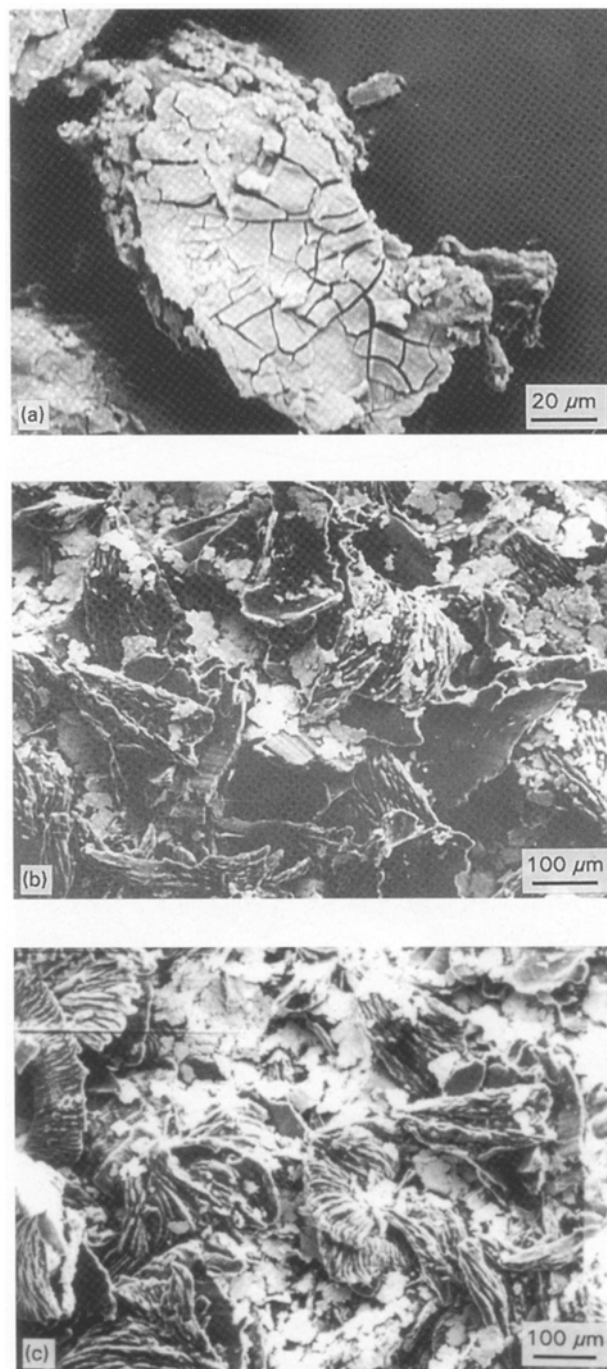

Figure 4 Scanning electron micrographs of (a) (Al–10% Mg) alloy powder coated with PBAN, aged, (b) (Al–28% Mg) alloy powder coated with PBAN, aged, and (c) magnesium powder, coated with PBAN, aged.

reduced in intensity, and the broad adsorption due to OH around 2500 cm^{-1} has decreased, confirming the decrease in –COOH content on ageing. As the ageing temperature or ageing time is increased (Fig. 6), it is apparent that the $C=O$ absorption decreases and the peak corresponding to the asymmetric stretch of COO^- grows. Thus, carboxylate salt formation is enhanced at higher temperatures and longer times of ageing.

3.3. Lattice parameter changes

The lattice parameter of aluminium is 0.4048 nm, and when alloyed with magnesium, the lattice parameter
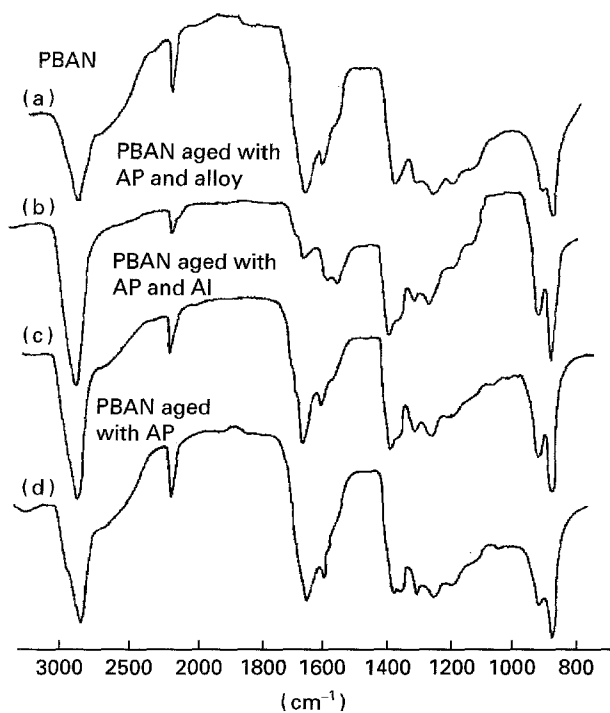
Figure 5 Infrared spectra of PBAN (in benzene) aged under various conditions.

Figure 6 Effect of ageing of PBAN with AP–(Al–10% Mg) alloy mixtures under various conditions on the carbonyl absorption band.

increases, depending upon the magnesium content [16]. The lattice parameters of Al–5% Mg alloy and Al–10% Mg alloy are 0.4074 and 0.4098 nm, respectively. On ageing, the lattice parameter of aluminium in AP–(Al–10% Mg) alloy pellets, as well as in propellants, decreased (Tables III and IV), while there was no change in the samples containing aluminium. This suggests that magnesium gradually diffuses out of the alloy and reacts with AP and/or moisture, resulting in the lattice parameter becoming nearly equal to that of aluminium.

4. Discussion

In the present study, the calorimetric values of propellant compositions containing Al–Mg alloys and aluminium have been used to compare the reactivities of the samples. In any calorimetric determination, it is essential to know (i) the enthalpy change in the process, and (ii) the precise amounts of chemical substances converted from the initial state to the final state of the process [17]. When a composition such as AP–PBAN–Al is burnt in a bomb calorimeter in
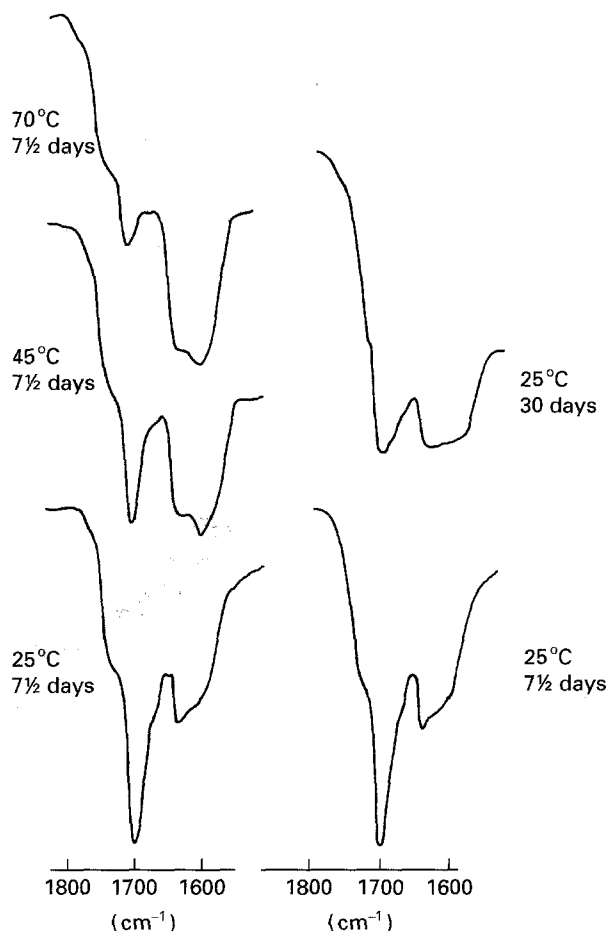
nitrogen, the following difficulties arise: (i) these mixtures are fuel rich, and so the reaction would be essentially incomplete, the product always containing some unburned aluminium; (ii) the reaction between the components is complex, and a large number of products is possible. It has been noted, that for AP alone, the products of decomposition/combustion are different under different conditions such as pressure, temperature of decomposition [14], presence of additive/catalyst, etc. Also, in the combustion of formulations containing a metal such as aluminium, a variety of polymorphs of aluminium oxide can be obtained [17]; (iii) uncertainty exists regarding the contribution to the observed overall heat of the reaction from residence time of the metal particles in the flame and during the stay time after the combustion. The

TABLE III Lattice parameter of aluminium in aged AP–Al/(Al–10% Mg) alloy pellets and AP–Al/(Al–10% Mg) alloy–PBAN composites. Time of ageing, 30 days; lattice parameter aluminium, 0.4059 nm; lattice parameter of (Al–10% Mg) alloy, 0.4094 nm

Ageing conditions		Lattice parameter of Al, nm			
(°C)	RH (%)	AP–Al pellet	AP–Al–PBAN	AP–(Al–10% Mg) alloy pellet	AP–(Al–10% Mg) alloy–PBAN
75	25			4.068 ± 0.003	
75	75	4.058 ± 0.003		4.075 ± 0.005	
90	50			4.060 ± 0.002	
25	50		4.055 ± 0.002		4.082 ± 0.003
75	50		4.052 ± 0.003		4.066 ± 0.003

TABLE IV Lattice parameter of aluminium in AP–(Al–5% Mg) alloy–PBAN composite aged at various temperatures and humidities. Time of ageing, 22.8 days; lattice parameter of Al–5% Mg alloy, 0.4074 nm

Ageing conditions		Lattice parameter (nm)
(°C)	RH (%)	
45	50	0.4067 ± 0.005
75	50	0.4058 ± 0.004
90	50	0.4054 ± 0.003
75	0	0.4078 ± 0.006
75	25	0.4076 ± 0.003
75	50	0.4060 ± 0.005

combustion products contain acids, such as HCl and these can react with the unburned aluminium even after the main combustion reaction is over. Owing to these uncertainties, the calorimetric values have been used in the present study only to throw light on the comparative reactivities of the mixtures within the limits of reproducibility of the calorimetric determination.

As in the case of AP–metal mixtures [4], the lower ignition temperature and faster burning rate of the alloys compared to pure aluminium, enables the oxidation of the metal to proceed to a larger extent. This is derived from the destruction of the protective nature of the oxide coating on aluminium. The Pilling Bedworth ratio [18], defined as the ratio of the molar volume of the oxide to the molar volume of the metal, is close to unity for aluminium, showing that the oxide, once formed, is protective, and prevents further oxidation. Hence for aluminium to burn, the particle has to be heated to the melting point of alumina, which is about 2323 K. The surface of Al–Mg alloys, on the other hand (reported to consist entirely of MgO [19] when the magnesium content is greater than 1%), provides easy access for oxidation by the gases liberated during combustion/decomposition of AP. As the alloy undergoes easier ignition and faster oxidation, the contribution to the combustion reaction is higher, and the calorimetric values are higher, though thermodynamically, composites containing aluminium should show higher heats of reaction. As the magnesium content is increased, the ignition temperature is lowered further, the burning rates enhanced, and the composition containing these alloys show higher calorimetric values. For the same reasons, the alloy oxidation is less sensitive to particle size. Owing to the higher reactivity, agglomeration of the alloy on the burning surface would be quite small, as seen from the combustion residue obtained when AP–Al/Al–10% Mg alloy mixtures were burned at 25 atm nitrogen: in the former, the unreacted metal was ~2 mm diameter while in the latter, the metal particles were fine.

It was shown in our earlier study [20] that the lattice parameter of the alloy decreases on ageing in humid atmospheres due to the depletion of magnesium from the alloy. The two significant observations in this study are (1) the decrease in the lattice parameter of the alloy during ageing, and the appearance

of COO⁻ vibrations as seen from the infrared spectra, on ageing, and (2) the cracking of the polymer coating on the alloy particle, after ageing. The former points to the diffusion of magnesium out of the Al–Mg alloy particles, and reaction of magnesium with the carboxyl groups, with the formation of a magnesium salt. The reaction between the polymer and the alloy can be understood when it is recalled that –COOH containing elastomers can be vulcanized using divalent metallic oxides like ZnO, and MgO as cross-linking agents [21]. These form a bridge between two –COOH groups and the metal salt formed is the cross-link.

$$2[-CH_2-CH_2-COOH] + MgO \rightarrow$$

$$-(CH_2-CH_2-COOH)_2Mg + H_2O \qquad (1)$$
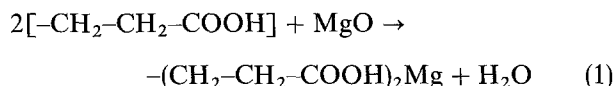
Thus, during ageing of the (Al–Mg) alloy under humid conditions, magnesium reacts with AP and water. Either the product of this reaction, which is predominantly magnesium perchlorate, or free magnesium metal, or MgO, can react with –COOH groups on adjacent polymer chains and effect cross-linking between them through the formation of a magnesium carboxylate salt bridge. This cross-linking brings about stiffness in the polymer, and the observed cracking of the polymer coating on the alloy particle is probably due to the escape of gaseous products. Additional proof for the cross-linking was obtained by determining the gel content of the AP–Al–PBAN and AP–(Al–10% magnesium) alloy–PBAN mixtures to which no curing agents had been added. The gel content in the AP–Al–PBAN mixture aged at 90 °C 50% RH for 30 days, was zero. In the AP–(Al–10% magnesium) alloy–PBAN mixture aged under similar conditions, a gel content of 29% was obtained.

5. Conclusion

Our study indicates that the use of Al–Mg alloy brings about greater oxidation of the metal during combustion. As a result, the calorimetric value of the formulation increases, and there is a decrease in the amount of unburnt metal in the combustion residue. This is in keeping with the increased burn rate, and lower ignition temperature of the alloy particles, which is in turn derived from the increased reactivity of the particles as the protective alumina layer on aluminium is replaced by a more porous oxide layer.

The effect of ageing the PBAN polymer as a coating on the alloy reveals that the polymer and the alloy undergo a reaction with each other. It should be emphasized that fundamental differences exist in the adhesion of the polymer on the aluminium and the alloy, because the oxide contents and surface chemistries of the two powders are different. However, it appears that the polymer becomes stiff after ageing under humid conditions in proximity with the alloy. In our earlier study, we showed that the compression strength of the propellants aged in humid atmospheres increased [19]. This suggests that small amounts of magnesium might be beneficial in a propellant, and, through proper control, can offset the decrease in

strength experienced by propellants when exposed to humidity. Most of the propellant programs now in use employ hydroxy-terminated polybutadiene (HTPB) as the binder in view of the clean stoichiometric reaction between–OH and an amine, forming urethanes. In these compositions, the absence of free carboxyl groups (or OH groups) in the cured propellants indicates that there should not be any reaction with magnesium.

The present study throws light on the interaction between the polymer and magnesium, through a novel study of the polymer in the form of a coating on the metal particle. This study for the first time shows the origin of a macroscopic property such as the modulus at the microstructural level. It also shows for the first time that a simple technique such as DTA could reveal the state of the polymeric film on the metal particle.

Acknowledgements

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