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THERMAL ANALYSIS OF MIXTURES CONTAINING Al POWDER UNDER OXIDIZING ATMOSPHERES: ANALYZING THE POTENTIAL IMPACT OF PROPELLANT FIRES NEAR LAUNCH SITE

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ABSTRACT

The interaction of Al powder with environmental samples harvested at or near launch-pad 17A at Cape Canaveral has been studied at high temperature. The environmental samples were sand/soil, concrete, Martyte™, and asphalt. Thermogravimetric analysis with simultaneous differential scanning calorimetry (TGA/DSC), or with differential thermal analysis (TGA/DTA) was used to characterize the mixtures under oxidizing conditions at temperatures up to 1500 °C.

For binary mixtures containing Al powder, exposure to air, CO_2, and/or H_2O at elevated temperature resulted in a large exotherm and the sample mass increased rapidly. This is assigned to the oxidation of liquid Al to alumina, accompanied by the reaction of alumina and silica to yield mullite ($Al_6Si_2O_{13}$). All of the environmental samples interrogated were found to contain SiO_2. Other reactions may also contribute to the overall energetics of the system, e.g., thermite reactions between Al and SiO_2 or Al and Fe_2O_3. When heating up under either inert or oxidizing conditions, more than one exotherm associated with the reactions were often identified, suggesting that different components of the environmental samples reacted with liquid Al at different temperatures, or at different rates. The exotherms measured by DSC upon exposure to air at 1350 °C of 1:1 (mass) mixtures of Al powder and environmental sample corresponded to energy release ranging from 1100 J g^{-1} (Al + Martyte™) to over 4000 J g^{-1} (Al + concrete). Increasing the temperature of exposure to oxidant generally produced an increase in the energy released.

INTRODUCTION

Powdered aluminum is a key component in most solid rocket propellant formulations. There are two principal reasons for its inclusion: 1) to increase the energy content and specific impulse of the propellant, and 2) as a suppressant of combustion instability [1]. The performance boost offered by including powdered aluminum, however, presents its own problems. The extreme temperatures and chemical reactivity produced by such propellants can present a threat in the event of a rocket launch accident. The consequences of such an accident are particularly severe when considering future deep-space missions employing plutonium as a persistent (nuclear) fuel source; the possibility of dispersion of plutonium into the environment from a rocket launch accident prompts a thorough risk assessment model to be developed. A large body of literature exists which describes the oxidation and ignition properties of aluminum powder and aluminized rocket propellant (see, e.g., [2], [3], and [4]), however little data exists on the reaction between aluminum powder and materials which it may contact if a launch accident were to occur.

The purpose of the present study was to evaluate the interaction at moderately high temperature and under oxidizing conditions of aluminum powder with specimens of material with which it is most likely to come into contact in the case of a rocket launch accident. The results of this study are being used to develop a launch accident risk assessment model. To evaluate the energetics of reaction between the propellant and environmental samples, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were employed, while thermogravimetric analysis (TGA) provided insight into off-gassing and oxidation phenomena. Three oxidizing environments were used: air/Ar, CO_2/Ar, and H_2O/CO_2/Ar, at reaction temperatures up to 1500 °C. Comparisons are drawn between the reaction energetics of aluminum powder with the various environmental samples.

Energetically, the major anticipated contribution to the heat generated upon interaction of Al propellant with environmental materials is the so-called thermite reaction, wherein a metal (here: Al) reacts with a metallic or a non-metallic oxide to form a more stable oxide (here: Al_2O_3) and the corresponding metal or nonmetal of the reactant oxide. This reaction can be generalized as follows:

$$A + BO \rightarrow AO + B + \Delta H$$

where the energy released (ΔH) can be quite significant. Numerous metal-oxides or non-metal oxides can participate in the reaction; for instance, two of the most relevant thermite reactions for the current work are those involving SiO_2 and Fe_2O_3.

$$4Al + 3SiO_2 \rightarrow 3Si + 2Al_2O_3 \qquad \Delta H = -2.15\ kJ\ g^{-1}$$

$$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3 \qquad \Delta H = -3.95\ kJ\ g^{-1}$$

The thermite reaction between Al and SiO_2 has an adiabatic temperature of 1487 °C, [5] however, for the reaction to occur without an initiator, a temperature considerably in excess of 1500 °C may be required. In all cases where a thermite reaction does occur, the resulting reduced metal or non-metal is expected to re-oxidize under the oxidizing environment at high temperature forming, in the case of the two examples given above, SiO_2 and Fe_2O_3, respectively.

Another possible reaction pathway giving rise to the observed exotherm and mass increase is the oxidation of Al to Al_2O_3 and reaction of Al_2O_3 with SiO_2 to form mullite:

$$2Al + 3CO_2 \rightarrow Al_2O_3 + 3CO$$

$$3\ Al_2O_3 + 2SiO_2 \rightarrow Al_6Si_2O_{13} \qquad \Delta H \sim -30 \text{ to } -40\ kJ\ mol^{-1}$$

At the temperatures of the present work, the rate of mullite formation is appreciable [6], and the energy output is modest [7] compared to the thermite reaction.

EXPERIMENTAL DETAILS

MATERIALS

The aluminum powder was obtained from Valimet, Inc., grade H-95, 99.7% pure (nominally 95 μm particles), and was used as received. The environmental samples were consisted of concrete, asphalt, Martyte™,[1] and a mixture of sand and soil. Each environmental sample was individually ground in a mortar and pestle, and then sieved to recover the particles in the size range 90 – 180 μm which was close to the size range of the Al powder. Some additional tests were performed using aluminum powder with a smaller particle size (Valimet, Inc., grade H-10, nominally 10 μm particles); environmental samples were ground to < 45 μm for combination with the H-10 powder. In some tests, ⅓ of the aluminum powder (by mass) was replaced by alumina powder of similar particle size to the aluminum.

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[1] Martyte™ is a ceramic filled, amine-cured epoxy compound used as an ablative thermal barrier coating typically applied to metal structures. It was developed by Martin Marietta.

THERMOGRAVIMETRIC ANALYSIS, DIFFERENTIAL THERMAL ANALYSIS AND DIFFERENTIAL SCANNING CALORIMETRY

The quantities of material used in the TGA/DSC and TGA/DTA studies were intentionally kept small (typically 100 mg or less) in order to avoid excessive heat evolution which may pose a safety risk and damage equipment. In addition, the thermite reaction was moderated in this work due to the presence of other non-reactive or weakly-reactive diluents present in the environmental samples such as calcium oxides, or intentionally added diluents, e.g., alumina.

The mass ratio of aluminum powder to environmental sample was kept constant at 1:1 for these experiments, except for experiments in which ⅓ of the aluminum powder (by mass) was replaced by alumina powder (in such cases, the mass ratio of (Al + Al_2O_3) to environmental sample was kept at 1:1). The specimens were characterized under inert atmosphere (argon) and oxidizing atmosphere (air, CO_2, H_2O, or mixtures thereof) with TGA/DSC (Netzsch STA 449-F3), or TGA/DTA (Netzsch STA 409 CD) during heating to a pre-determined temperature, and oxidizing at that temperature for a set amount of time. In all experiments, a heating rate of 20 °C min^{-1} was used from ambient to 600 °C, and from 700 °C to the final oxidation temperature. In the range 600 to 700 °C a rate of 5 °C min^{-1} was used to enable accurate monitoring of the Al melting temperature (used as an internal temperature standard). Total gas flow rates were maintained at 160 sccm, including a constant protective gas (Ar) flow rate of 40 sccm through the balance. During experiments where the sample was heated under inert atmosphere to the desired oxidation temperature, once that temperature was reached the temperature was allowed to stabilize under flowing inert gas for 15 min prior to initiating the flow of oxidant.

All TGA/DSC and TGA/DTA data have been corrected by baseline subtraction. In order to do this, blank experiments were run under exactly the same conditions as the experimental runs, and the blank data was then subtracted from the experimental data. Prior to starting each TGA/DSC or TGA/DTA experiment where the oxidation temperature was reached under inert conditions, the instrument was evacuated and back-filled with inert three times, then allowed to sit idle under the gas flow conditions to be used in the experiment for at least 15 minutes to ensure a clean, consistent atmosphere and stable balance and thermocouple readings at the start of each run.

By calibrating the DSC signal using high-purity materials with known enthalpy of melting, it was possible to quantify the energy output measured during oxidation of materials. Several DSC experiments were repeated with the DTA instrument, allowing a crude calibration of the DTA signal to be made based upon the calibrated signal from the DSC. To do this, the peak areas of the exotherms in the DTA plots for each binary mixture were plotted against the calibrated energy output for the same binary mixtures in the DSC plots. The resulting trend fit, with the exception of one outlier, on a 2nd order polynomial curve passing through the origin with R2 = 0.9999; this polynomial function was then used to convert the measured DTA peak areas into values of J g^{-1}.

CHEMICAL ANALYSIS THROUGH X-RAY FLUORESCNCE SPECTROSCOPY

Quantitative chemical analysis of all materials was achieved with X-ray Fluorescence Spectroscopy (XRF) using a Bruker Tornado M4 XRF. Samples were characterized in the crushed and sieved form without further treatment. Element-specific maps were generated for all elements discovered, and elemental compositions were quantified using Bruker's standard XRF factors in M-Quant. Note that XRF is insensitive to elements lighter than sodium, so carbon, nitrogen, oxygen, etc. are not included in the quantification.

STRUCTURAL ANALYSIS THROUGH X-RAY DIFFRACTION

Quantitative structural analysis of materials was achieved using powder X-ray Diffraction (XRD) using a PANalytical X'Pert PRO diffractometer with Cu Kα radiation. Individual components were characterized as fine powders without further treatment, and the binary mixtures were characterized by XRD after thermal treatment in the TGA/DSC or TGA/DTA. Peaks in the XRD patterns were assigned to specific chemical components where possible using Jade software.

RESULTS AND DISCUSSION

QUANTITATIVE CHEMICAL ANALYSIS – X-RAY FLUORESCENCE

The XRF data is summarized in Table 1; only elements present at 0.1 atomic-% or greater are included in the table. In short, the Al powder is 99.9% pure, and all environmental samples contain significant levels of calcium and silicon. The sand/soil also contains moderate levels of aluminum and iron, while Martyte™ has a significant content of magnesium. The other elements detected (not included in Table 1) constitute less than 0.3% for all samples.

Table 1. Elemental analysis of the Al powder and environmental samples determined by XRF.

Element / atomic-% [a]	Aluminum H-95	Asphalt	Concrete	Martyte™	Sand-Soil
Aluminum	99.86	1.04	2.6	0.98	8.38
Calcium		84.08	79.6	18.92	50.83
Chromium		0.36			
Iron	0.13	1.39	4.21	0.36	11.05
Magnesium		0.24	0.21	12.59	0.61
Manganese				0.27	0.18
Phosphorus					0.27
Potassium		0.38	0.33	0.42	0.87
Silicon		10.67	11.86	66.11	23.93
Sulfur		1.33	0.44		0.1
Titanium		0.24	0.55	0.17	2.98
Zinc					0.67
Total:	*99.99*	*99.73*	*99.8*	*99.82*	*99.87*

[a] Only elements heavier than sodium in the periodic table are detectable. Atomic-% represents the percentage of that element as a total of all elements detected (i.e., not including oxygen, carbon, etc.)

THERMOGRAVIMETRIC ANALYSIS – DIFFERENTIAL SCANNING CALORIMETRY

The TGA/DSC runs performed on the individual components Al, sand/soil, concrete, Martyte™, and asphalt with exposure to air at 1350 °C are summarized in Figure 1. The Al powder showed virtually no change in mass upon heating to 1350 °C under Ar, while an almost imperceptible, slow rate of mass increase occurred upon exposure to air at that temperature, in agreement with experiments carried out using high-purity Al foil. [8] The DSC trace showed a sharp endotherm on melting of Al (on-set at 656.9 °C, theoretical 660.3 °C for pure Al), as well as a small, sharp exotherm on first exposure to air at 1350 °C. Alloying of Al with other metals is known to decrease the melting point; the lower melting point of the Al powder compared to pure Al indicates that there are probably some impurities present; as seen in Table 1, about 0.13 atomic-% iron was detected by XRF in the aluminum. All other environmental samples showed significant mass loss during heating to 1350 °C under Ar, details of which are given in Table 2. Asphalt, concrete, and, to a lesser extent, sand/soil all exhibited an endothermic event at just above 700 °C coinciding with their major mass loss steps. A similar, but broad endotherm can be discerned for Martyte™ at around 400 °C, also consistent with its major mass loss step. All environmental samples, except sand/soil, showed small, sharp exotherms upon first exposure to air. None of the environmental samples increased in mass significantly during exposure to air at 1350 °C.

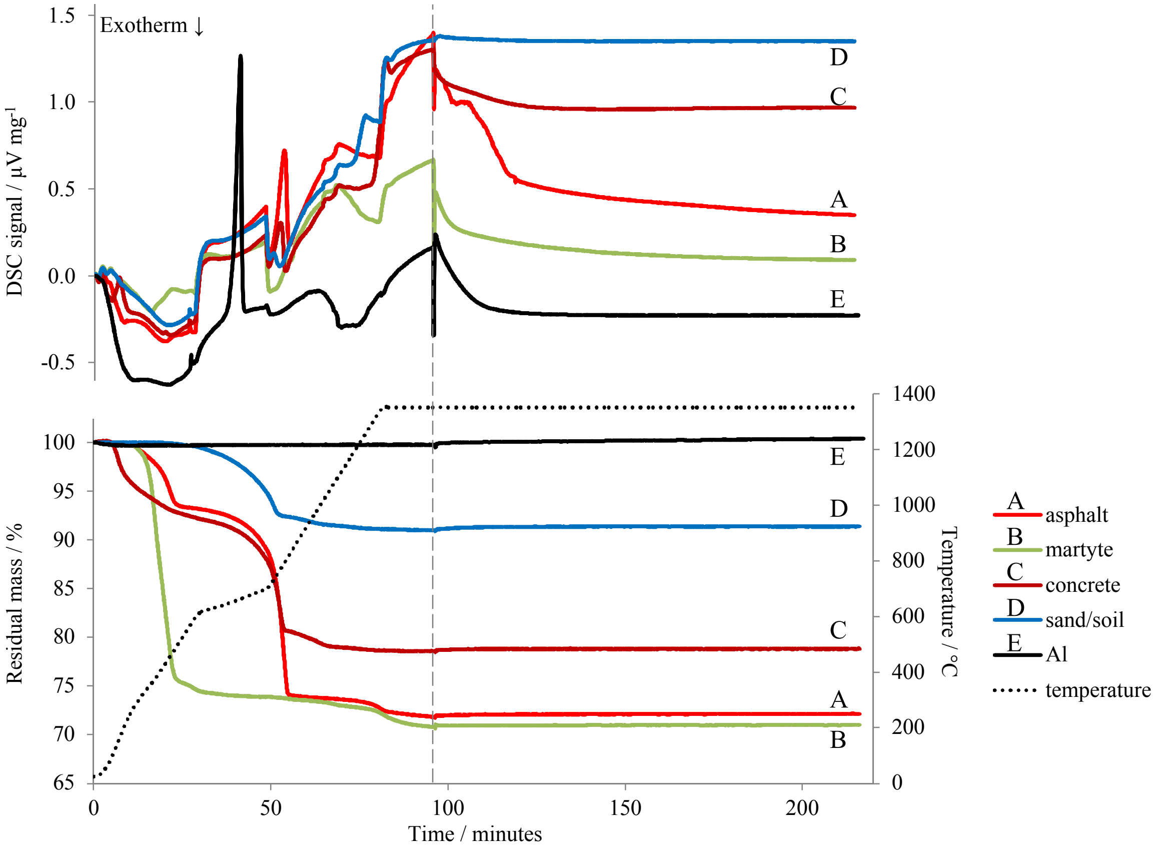

Figure 1. TGA (lower) and DSC (upper) results for individual components heated under Ar to 1350 °C, then exposed to air (at dashed vertical line).

Table 2. Summary of TGA data for individual environmental samples and Al powder heated under inert atmosphere to 1350 °C then exposed to air at 1350 °C for 2 hr.

Sample	Mass loss during inert ramp / %	Temperature range / °C	Mass gain on oxidation / %
Aluminum H-95	0.25	25 – 1350	0.61
Sand/soil	7.53 1.48	25 – 775 775-1350	0.40
Concrete	19.32 2.1	25-795 795-1350	0.20
Martyte™	24.3 1.14 3.82	25-490 490-600 600-1350	0.19
Asphalt	6.5 19.43 2.24	25-505 505-830 830-1350	0.61

The mass changes observed during heating of (Al + environmental sample) mixtures under inert atmosphere were qualitatively similar to those of the individual components, and scaled to the amounts of each component present, i.e., the mixture behaved as two non-interacting solids (Figure 2). Upon exposure to air at 1350 °C, a rapid increase in mass was observed for all binary mixtures, which was not a combination of TGA responses for the individual components, i.e., in the presence of air at high temperature the components do interact. There was no discernible reaction between components at the same temperature under inert atmosphere prior to introduction of air. The mass change data is summarized for the binary mixtures in Table 3. Considering now the DSC data, one sees the melting of Al as an endothermic peak as before, and the integrated area of the peak scales to the amount of Al in the mixture. Other features of the DSC curves during the inert portion of each experiment are again qualitatively the same as those in Figure 1. Once air was introduced, a large, almost instantaneous exotherm was recorded for each binary mixture, corresponding to the on-set of the mass increase (oxidation of Al to Al_2O_3 with formation of mullite, or thermite reaction accompanied by re-oxidation of Si or other reduced metal that was produced). As can be seen in the inset figure, the exothermic peak is in all cases actually a composite of at least two peaks; one sharp initial peak that is similar for all samples, and one broader feature that is sample-dependent. The breadth of the exotherm correlates loosely with the magnitude of the initial mass increase during the first few minutes of exposure to air, e.g., in order of increasing broadness: Al/Martyte™ < Al/sand-soil < Al/asphalt < Al/concrete. The fact that a mixture of Al powder with an environmental sample was required for the exotherm and mass increase to be observed upon exposure to oxidant shows that interaction must occur between the Al and SiO_2 (or other compounds), which points to a thermite-type reaction rather than oxidation of Al to Al_2O_3 and mullite formation. Referring back to Figure 1, we recall that the oxidation of Al (in the absence of environmental sample) is virtually undetectable at 1350 °C. Even though the thermite reactions do not involve gaseous oxygen as written, it is interesting that an oxidant was required at 1350 °C for the reaction to be initiated. One possible explanation for this behavior is that the introduction of oxygen at 1350 °C initiates a re-crystallization of the alumina layer that covers the Al particles from a less dense to a more dense phase, resulting in the opening of small cracks in the alumina coating which enabled better contact between the molten Al (or its vapor) and the environmental sample. In the absence of an environmental sample (Figure 1) the alumina shell heals quickly in the presence of the oxidant, whereas in the presence of the environmental sample interaction of Al liquid or vapor with SiO_2 (or other compound) is rapid and acts as a sink for oxygen, slowing the healing of the alumina shell.

Post mortem characterization of the oxidized samples using XRD revealed that the major identifiable compounds present were alumina, silica, aluminum and silicon, as well as calcium aluminate in samples containing a large fraction of calcium. The observance of elemental silicon confirms that a thermite-type reaction must have occurred to some extent. Elemental silicon was not observed in any of the individual components prior to oxidation. The presence of metallic Al and Si attests to the fact that oxidation/reaction had not gone to completion; indeed the TGA curves in Figure 2 show continued increase in mass at the termination of the oxidation step.

Table 3. Summary of TGA/DSC data for binary mixtures (1:1 by mass) of Al powder and environmental samples heated under inert atmosphere to 1350 °C then exposed to air at 1350 °C for 2 hr.

Sample added to Al H-95 powder	Mass loss during inert ramp / %	Temperature range / °C	Mass gain upon exposure to air / %	Energy output upon exposure to air / J g^{-1}
Sand/soil	4.83	25-775	21.93	2380
Concrete	8.00	25-805	25.49	4117
Martyte™	12.38	25-485	9.77	1140
	0.64	485-615		
	1.49	615-1350		
Asphalt	3.37	25-500	26.67	3363
	9.91	500-830		

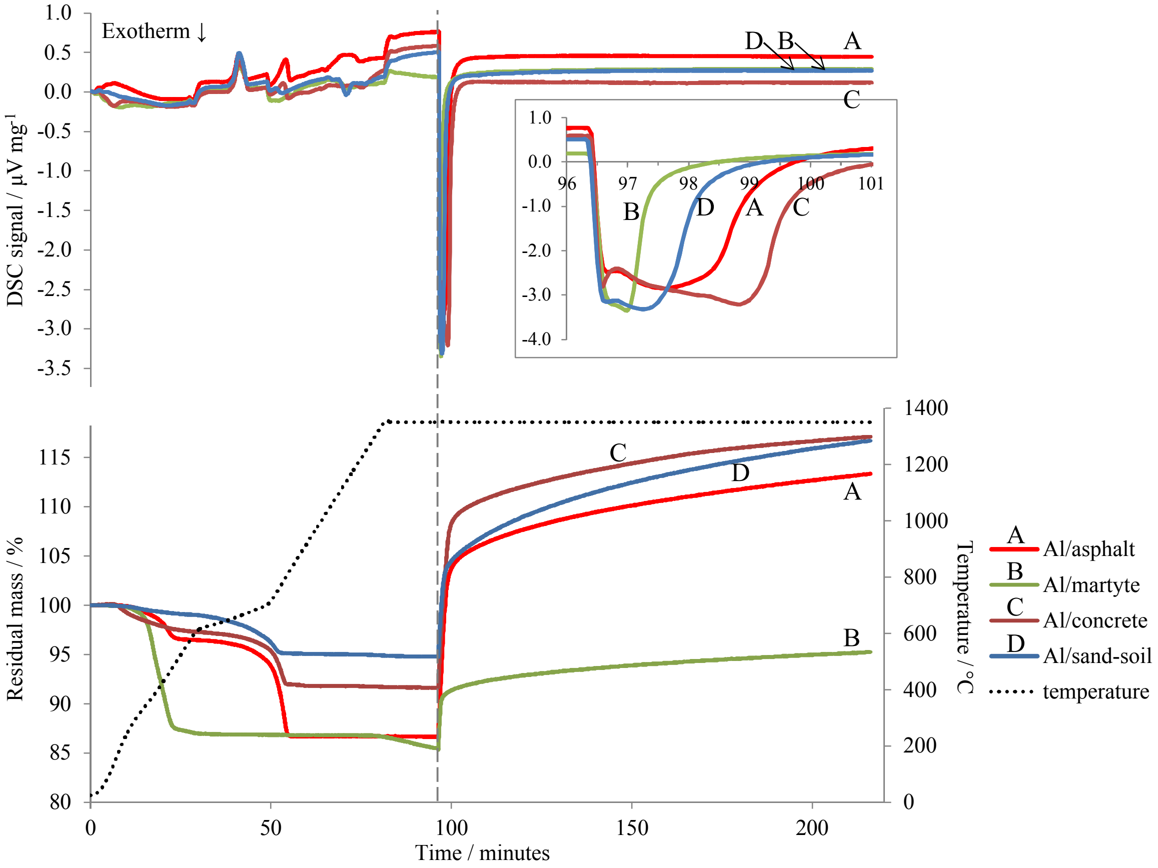

Figure 2. TGA (lower) and DSC (upper) results for binary mixtures of (Al + environmental sample component) heated under Ar to 1350 °C, then exposed to air (at dashed vertical line). The inset in the DSC plot is an expansion of the exotherm region upon initial introduction of air.

ALUMINUM POWDER - CONCRETE; EFFECT OF OXIDATION BY AIR AT VARIOUS TEMPERATURES

In this series of experiments, Al/concrete mixtures were heated under inert atmosphere to 1250, 1350, or 1450 °C before exposure to air. The behavior during the temperature ramp under inert gas was similar for all samples. The results summarized in Table 4 show the effect of varying the oxidation temperature. The energetics of reaction and the magnitude of the accompanying mass change due to oxygen uptake increase with oxidation temperature.

Table 4. TGA and DTA results for a 1:1 by mass mixture of (Al + concrete) heated under Ar to 1250, 1350, or 1450 °C, then exposed to air for 2 hr.

Oxidation temperature / °C	Mass gain during oxidation / %	Energy output upon exposure to air / J g^{-1}
1250	18.8	3630
1350	26.7	4108
1450	41.1	10627

TGA/DTA USING CARBON DIOXIDE AS OXIDANT

The TGA/DTA runs were performed on binary mixtures of (Al + environmental sample) under an inert ramp to the desired oxidation temperature, followed by exposure to CO_2 at 1350 or 1500 °C. The oxidation by CO_2 is expected to lead to formation of CO, and this was verified during a TGA/DTA experiment by analyzing the vent gas using gas chromatography. Carbon monoxide was detected upon exposure of the sample at high temperature to carbon dioxide, and the evolution of CO continued as long as there was an increase in mass of the sample.

Analysis of mass increases during oxidation, magnitude of oxidation exotherm, and rates of reaction were determined for each combination of reactants under each set of experimental conditions, as summarized in Table 5. The exotherm areas were converted to J g^{-1} using the DSC-DTA calibration factor described earlier. An example of a set of data from TGA/DTA is given in Figure 3, where the input values in Table 5 have been identified. In some cases, it was not possible to deconvolute an “initial exotherm” from the overall DTA signal. The terms H-95 and H-10 refer to two batches of Al powder with nominally 95 and 10 micron mean particle size, respectively. Environmental samples were ground to appropriate size ranges for the different Al powder batches (see experimental section). Note that a high degree of variation was noticed in the behavior of concrete-containing mixtures when comparing the different particle size ranges. For instance, the total mass increase after full oxidation by CO_2 varied between 13 wt.-% (H-10 series) and 43 wt.-% (H-95 series); the rates of reaction showed a similar trend. This variance is attributed to the macroscopically inhomogeneous nature of concrete. To illustrate this, three separate specimens were taken at random from the same concrete sample, were ground to a fine powder, and then interrogated using XRF to quantify their chemical composition. The results showed that between the three specimens there are wide variations in the quantities of Si and Ca (the two major constituents of concrete) that were detected. In future experiments, therefore, a more rigorous sampling technique should be used for ensuring a representative and reproducible sampling of concrete.

Post mortem characterization using XRD of the samples oxidized at 1500 °C under CO_2 revealed that the major identifiable compounds present were alumina and mullite where the sample contained a large fraction of silica, as well as calcium aluminate in samples containing a significant amount of calcium. These reactions generally proceeded to completion in the 2 hr oxidation step, thus only oxidized products were detected by XRD.

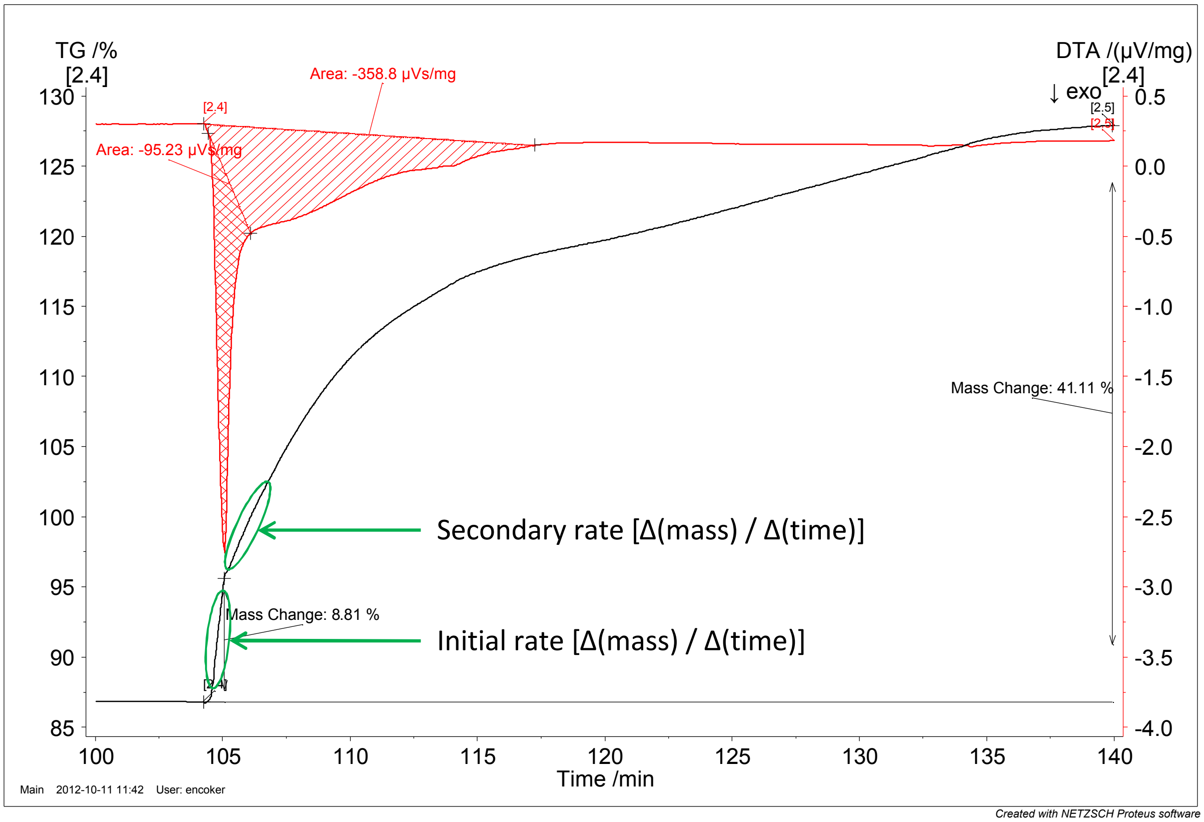

Figure 3. An expanded view of a representative TGA/DTA data set where the input values for Table 5 have been identified. Note that there is an inflection point in the mass curve, shortly after mass increase begins. The “initial mass increase” value is the increase in mass measured from just before CO_2 exposure to the inflection point, and the “initial rate” is also calculated from this near-linear portion of the mass-increase curve. The “secondary rate” is taken from the gradient of the mass curve shortly after the inflection point. The areas of the exotherm are as indicated: “initial exotherm” = hashed area; “total exotherm” = hashed + striped areas.

Table 5. Summary of TGA/DTA data for CO_2-oxidation of mixtures containing Al powder, environmental sample, and optionally, alumina. The exotherm quantities are normalized to the total sample mass; for mixtures containing added alumina Al metal constitutes ⅓ of the mass, and for all other mixtures Al metal is ½ of the mass.

Sample	Temperature of exposure to CO_2 / °C	Initial mass increase / %	Initial rate / mass-% min^{-1}	Initial exotherm / $J\ g^{-1}$	Total mass increase / %	Secondary rate / mass-% min^{-1}	Total exotherm / $J\ g^{-1}$
H-95 + Asphalt	1350	2.584	12.502		27.44	4.4106	1041.3
H-95 + Concrete	1350	3.495	14.047	472.6	28.56	5.3343	1180.4
H-95 + Martyte™	1350	7.274	15.559		14.89	2.2878	531.0
H-95 + Sand-soil	1350	1.594	9.388		29.67	3.0767	351.5
H-95 + Asphalt	1500	9.47	18.655	358.7	42.522	4.3631	1729.8
H-95 + Concrete	1500	4.619	14.886	162.0	42.929	3.7966	2517.6
H-95 + Martyte™	1500	15.036	18.857		24.826	2.4235	882.2
H-95 + Sand-soil	1500	5.073	14.474	339.6	41.837	3.3916	2636.0
H-95 + Al_2O_3 + Asphalt	1500	7.46	15.761	495.1	27.757	3.8717	1379.0
H-95 + Al_2O_3 + Concrete	1500	7.365	15.632		28.584	4.4194	1336.1
H-95 + Al_2O_3 + Martyte™	1500		18.586		19.95	2.4812	733.5
H-95 + Al_2O_3 + Sand-soil	1500		14.778		26.445	3.069	959.0
H-10 + Asphalt	1500	21.92	17.033	1114.5	39.794	14.69	2071.4
H-10 + Concrete	1500	3.485	2.2229		13.482	2.0729	220.6
H-10 + Martyte™	1500	25.08	19.728	1542.9	35.705	16.536	1940.3
H-10 + Sand-soil	1500	29.424	20.899	1629.4	42.127	17.079	2504.2
H-95 + Concrete flake	1500	1.19	5.0	118.0	37.32	2.3	1617.0
H-95 + Al_2O_3 + Concrete flake	1500	1.80	3.0	87.1	25.86	2.2	1172.3

ALUMINUM (H-95) + CONCRETE FLAKE; EXPOSURE TO CO_2 AT 1500 °C.

Since powdered environmental samples represent a “worst case” scenario in determining the energetics and rate of reaction with Al propellant, some experiments were also conducted using fragments of concrete block in place of the concrete powder. Figure 4 summarizes the TGA/DTA data for Al (H-95) surrounding a piece of bulk concrete (flake) during heating under argon to 1500 °C, then exposing the sample to CO_2. Data for powdered concrete is included for comparison. As expected, the lower available surface area of the concrete flake resulted in a lower overall rate of reaction with Al powder, as reflected in the slower increase in mass and broader exotherms upon exposure to CO_2 than the corresponding powdered concrete mixtures. The total mass increases of the flake samples after 2 hours of exposure to CO_2 approach those of the powder samples, indicating that over time the reaction front is able to proceed into the bulk of the flake.

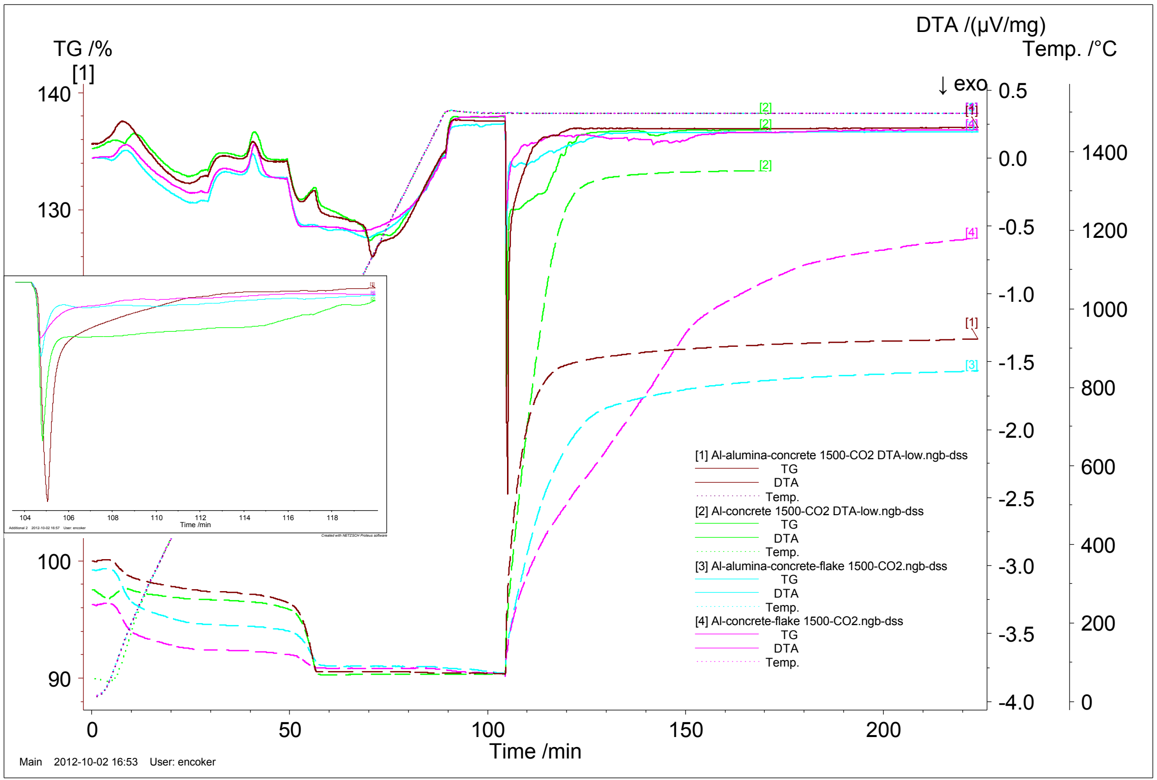

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Figure 4. TGA/DTA data for a series of experiments comparing concrete powder to bulk concrete (flake) during heating under argon to 1500 °C, then exposing the sample to CO_2. Curves 1 and 2 show concrete powder with either Al + alumina (1), or Al only (2), and curves 3 and 4 show the corresponding samples where a piece of concrete flake replaces the concrete powder. All mass curves have been normalized at the point just before CO_2 was introduced. Exposure to CO_2 coincides with the rapid mass increase and exotherm at 105 minutes into the experiment. The inset figure is an expansion of the first 15 minutes of the exothermic peaks, normalized at the point just before CO_2 exposure.

ALUMINUM (H-95) + CONCRETE; LIMITED EXPOSURE TO CO_2 AT 1500 °C.

Figure 5 summarizes the TGA/DTA data for Al (H-95) intimately mixed with concrete, during heating under argon to 1500 °C, then exposure to CO_2 for either 2, 4, or 8 minutes followed by 120 minutes soak under flowing argon. Data for a sample including added alumina at 4 minute exposure to CO_2 is included for comparison. Figure 6 shows the linear relationship between the total CO_2 exposure during the 1500 °C soak and the sample mass increase and exotherm area. The best fit line does not cross through the origin of the graph, and this is a consequence of the experimental setup wherein there is a consistent delay between the time CO_2 flow is commanded by the software and when the CO_2 flow actually begins. The calculated CO_2 exposure in Figure 6 is based upon the software-commanded flows, not actual flows.

The conclusions from Figure 6 are that CO_2 is responsible for the oxidation of reactants (i.e., not background oxygen, or other species), and that the reaction exotherm is proportional to the total amount of CO_2 to which the specimen is exposed. If one considers the reaction sequence to involve a thermite reaction, then it seems that, at the temperatures studied, the extent of the thermite reaction that occurs is mediated by the capacity to re-oxidize the products of the thermite reaction. (CO_2 acts to initiate the thermite reaction, but does not participate in the thermite reaction itself). On the other hand, if the reaction sequence is one involving oxidation of Al to Al_2O_3 and mullite formation through reaction with SiO_2, then a correlation of the reaction exotherm to the amount of CO_2 is to be expected.

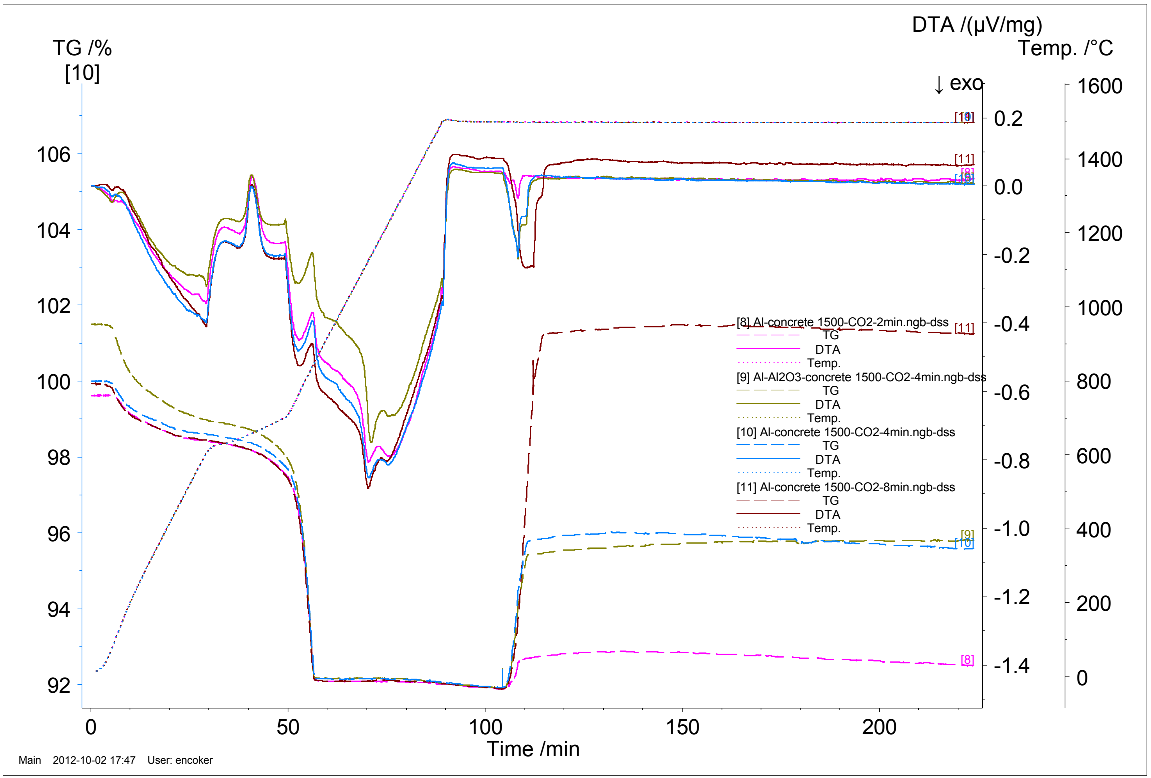

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Figure 5. TGA/DTA data for a series of experiments using concrete powder mixed with Al (curves 8, 10, and 11) or Al + alumina (curve 9) where the sample was exposed to CO_2 at 1500 °C for limited periods of time. All mass curves have been normalized at the point just before CO_2 was introduced. Exposure to CO_2 coincides with the rapid mass increase and exotherm at 105 minutes into the experiment. Curve 8: 2 min exposure; curves 9 and 10: 4 min exposure; curve 11: 8 min exposure to CO_2.

Regardless of the reactions occurring, it is to be expected that alumina and silica will be formed upon oxidation at high temperature. Under the conditions of these experiments, and depending on the stoichiometry of Al_2O_3 to SiO_2, mullite will be formed to some extent; this has been verified by X-ray diffraction of mixtures of Al powder and environmental sample recorded after the TGA/DTA experiments described above.

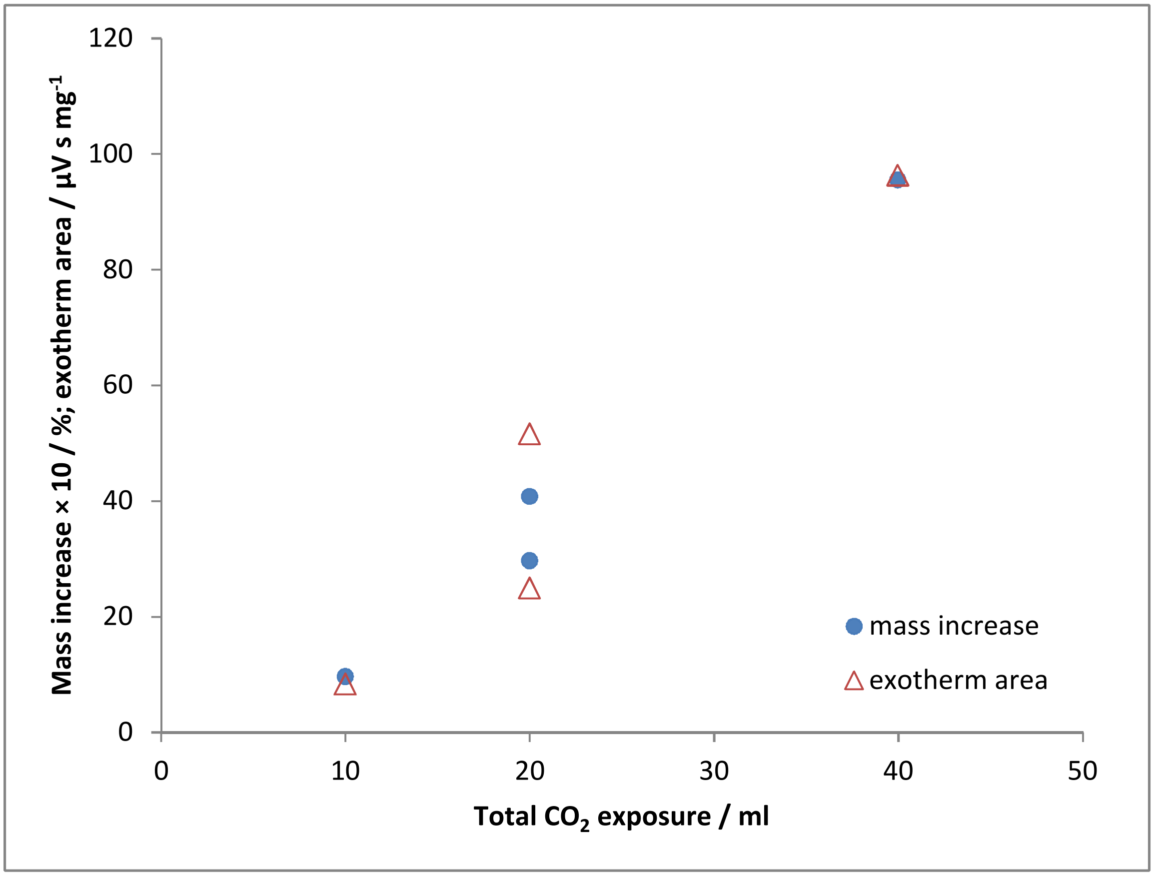

Figure 6. Summary of total mass increase data and total exotherm area data from the TGA/DTA experiments of Figure 5. The total CO_2 exposure takes into account CO_2 concentration, flow rate, and time of exposure. The mass increase and exotherm area values are normalized to the total sample mass.

Similar variations in mass increase and exotherm area were observed when exposing the samples to air or to water vapor in CO_2 for limited periods of time.

The heat of reaction (ΔH) as a function of temperature, and the free energy of reaction (ΔF) as a function of temperature for various thermite reactions were obtained from tabulated data [9] of the heat of formation and the heat capacity as a function of temperature. These data are shown in Figure 7. Reference [9] provides the coefficients for simple polynomial expressions that (piecewise) cover a large range of temperatures. Steps in the calculated data are a consequence of discontinuities in the tabulated data, and/or phase transitions in the materials. It can be concluded from Figure 7 that the driving force for the iron thermite reaction is higher than that for the silica thermite reaction, and that the former has potential to release significantly more energy, particularly at temperatures above 1500 K.

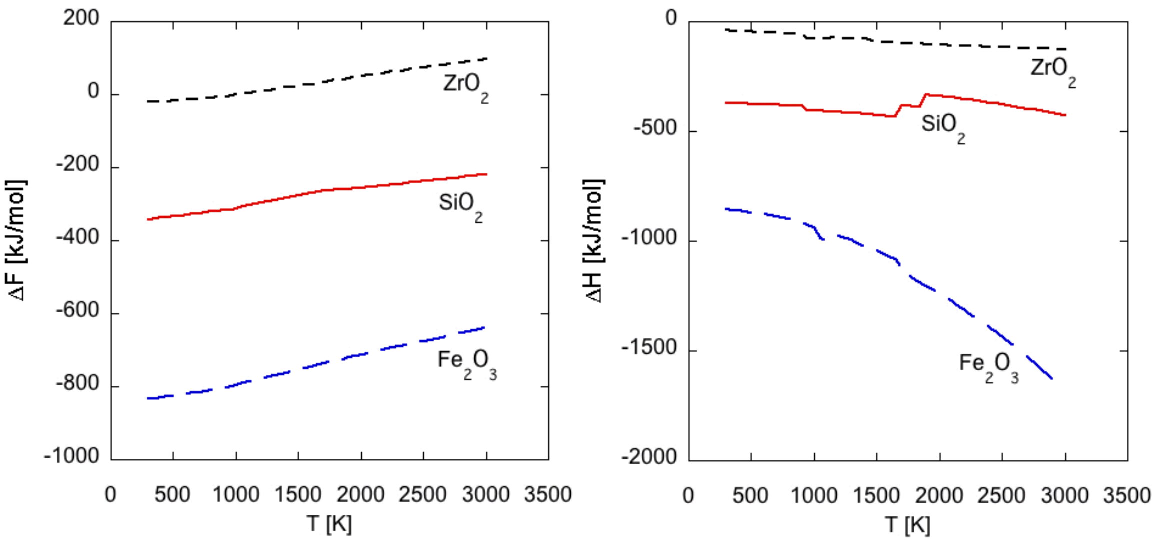

Figure 7. Free energy (ΔF) and enthalpy (ΔH) of the thermite reaction between Al and SiO_2, Fe_2O_3, or ZrO_2 in the presence of oxygen as a function of temperature.

SUMMARY AND CONCLUSIONS

This brief report summarizes an initial study of the interaction of Al powder (simulating solid rocket propellant) with environmental samples harvested at or near launch-pad 17A at Cape Canaveral, Florida. The environmental samples were sand/soil, concrete, Martyte™, and asphalt. Thermogravimetric analysis with differential scanning calorimetry (TGA/DSC), or TGA with differential thermal analysis (TGA/DTA) was used to evaluate decomposition and oxidation reactions as well as the energetics of reaction. Two series of experiments were conducted where the specimen was heated to the desired oxidation temperature and allowed to thermally stabilize under inert atmosphere before introducing air: 1) individual components, and 2) binary mixtures of Al powder + one environmental sample.

When investigating the individual environmental samples, mass losses were recorded upon heating up under inert atmosphere, and exposure to air at 1350 °C caused insignificant change in mass compared to inert atmosphere at the same temperature. The mass of the Al powder remained constant during heating to 1350 °C under inert atmosphere and increased only slowly when exposed to air at 1350 °C, in agreement with data from a study of oxidation of Al foil at various temperatures discussed elsewhere.[8] For the binary mixtures, the behavior during heating under inert atmosphere was as predicted from the superposition of the individual Al powder and environmental sample data, however once exposed to air a large exotherm was recorded and the sample mass increased rapidly. There are two possible reaction sequences considered here which may account for the observed results: 1) a thermite reaction between liquid Al and silica ($4Al + 3SiO_2 \rightarrow 2Al_2O_3 + 3Si$) which is highly exothermic, followed by oxidation of the produced Si back to SiO_2; 2) oxidation of Al to Al2O3, and partial reaction of the formed alumina with silica to form mullite (e.g., $3Al_2O_3 + 2SiO_2 \rightarrow Al_6Si_2O_{13}$). All of the environmental samples interrogated were found by XRF to contain SiO_2. Some other components of the samples may also contribute to the overall exothermicity of the reaction due to other thermite reactions, e.g., iron oxides, and other metal oxides. More than one exotherm were often identified, suggesting that different components of the environmental samples reacted at different temperatures, or at different rates. The observation by XRD of elemental silicon in sample residues after oxidation in the TGA confirms that a thermite-type reaction did occur, even at the low temperature of 1350 °C, and that reactions did not go to completion in the course of the 2 hr oxidation.

The exotherms measured by DSC upon exposure to air at 1350 °C of binary mixtures of Al powder (H95 grade) and environmental sample (1:1 mass ratio) have been converted to energy released by calibration of the DSC signal. The energetics ranged from about 1100 J g^{-1} (Al + Martyte™) to over 4000 J g^{-1} (Al + concrete). The DTA data, although not as precise, showed a similar trend to that from DSC when running under the same conditions as the DSC experiments.

Binary mixtures of Al and environmental sample, and ternary mixtures including alumina were exposed to oxidant (air, CO_2 or H_2O) at 1500 °C. Comparison of reaction exotherms with sample composition from XRF suggests that the iron thermite reaction may be the dominant energy source at 1500 °C under CO_2 without added alumina. Furthermore, limiting the exposure time to oxidant at 1500 °C of mixtures of Al powder and concrete demonstrated that the overall energy output was proportional to the number of moles of oxidant the sample was exposed to. This suggests that either 1) the extent of thermite reaction occurring, under these conditions, is limited by the amount of oxidant available, i.e., the thermite reaction (e.g., $4Al + 3SiO_2 \rightarrow 2Al_2O_3 + 3Si$) and the subsequent re-oxidation of reduced species (e.g., $Si + 2CO_2 \rightarrow SiO_2 + 2CO$) may be linked rather than two independent reactions, or 2) the reaction sequence involves oxidation of Al to Al_2O_3 and formation of mullite. The reaction of Al powder with low surface area concrete flakes was also investigated. In comparison with concrete powder, rates and extents of reaction were lower for the flakes, however, after 2 hours of exposure to oxidant the mass increases due to oxidation approached those of the powder samples indicating that a reaction front will progress through bulk concrete, given sufficient reaction time.

The rates of reaction with CO_2 at 1500 °C, as reflected in the change of mass of the mixture, showed a distinct inflection point going from a faster initial rate to a slower subsequent rate. While the initial fast rate was similar among most mixtures, the secondary rate was found to be strongly dependent on the average size of propellant and environmental sample particles, i.e., smaller particles resulted in a faster rate of reaction.

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REFERENCES

[1] Price, E. W. and Sigman R. K., "Combustion of Aluminized Solid Propellants," Chapter 2.18 of Solid Propellant Chemistry Combustion and Motor Interior Ballistics, AIAA Progress in Astronautics and Aeronautics, Vol. 185, V. Yang, T. B. Brill, and W-Z Ren, eds., 2000.
[2] Trunov, M.A., Schoenitz, M. and Dreizin, E.L., "Effect of polymorphic phase transformations in alumina layer on ignition of aluminium particles," *Combust. Theory Model.*, **10(4)**, 602-23, (2006).
[3] Levitas, V.I., Pantoya, M.L., Chauhan, G. and Rivero, I., "Effect of alumina shell on the melting temperature depression for aluminum nanoparticles," *J. Phys. Chem. C*, **113**, 14088-96, (2009).
[4] Levitas, V.I., Pantoya, M.L. and Dikici, B., "Melt dispersion versus diffusive oxidation mechanism for aluminum nanoparticles: Critical experiments and controlling parameters," *Appl. Phys. Lett*. **92**, 011921, (2008).
[5] Wang, L.L., Munir, Z.A. and Maximov, Y.M., "Thermite reactions: their utilization in the synthesis and processing of materials," *J. Mater. Sci.*, **28**, 3693-708, (1993).
[6] Chen, Y.F., Wang, M.C. and Hon, M.H., "Transformation kinetics for mullite in kaolin–Al_2O_3 ceramics," *J. Mater. Res.*, **18(6)**, 1355-62, (2003).

[7] Gerardin, C., Sundaresan, S., Benziger, J. and Navrotsky, A., “Structural investigation and energetics of mullite formation from sol-gel precursors,” *Chem. Mater*. **6**, 160-70, (1994).
[8] Coker, E.N., “The oxidation of aluminum at high temperature studied by thermogravimetric analysis and differential scanning calorimetry” SAND report, Sandia National Laboratories, in preparation.
[9] *Handbook of Chemistry of Physics*, 69th edition, CRC press, Boca Raton, FL, (1988-1989).