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Exothermic surface reactions in alumina–aluminum shell–core nanoparticles with iodine oxide decomposition fragments

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Abstract A pre-ignition reaction (PIR) once thought to be unique to aluminum (Al) and fluorine-based oxidizer reactions is observed for aluminum and an iodine-containing oxidizer. This PIR is exothermic and precedes the main exothermic reaction corresponding to aluminum combustion. For the aluminum and iodine oxide system, exothermic surface chemistry was recently predicted for I O fragments forming bridge bonds with the alumina passivation shell using first principle calculations, but now has been observed experimentally. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) were used to assess aluminum and iodine pentoxide (I_2O_5) powder mixtures. Various equivalence ratios were examined and found to affect the PIR onset temperature. Prior to this work, the PIR was attributed solely to surface reactions of the halogen with the Al_2O_3 surface, but, results shown here indicate that both the alumina surface and aluminum core contribute to a PIR and a minimum activation energy is necessary for PIR production.

Keywords Aluminum combustion · Pre-ignition reactions · Alumina surface chemistry · Halogen decomposition fragments · Reaction kinetics

Introduction

The majority of recent interest in halogen-based energetic materials, more specifically iodine-containing formulations, has been motivated by the biocidal effect of iodine and the increasing threats of biological warfare (Clark and Pantoya 2010; Farley and Pantoya 2010; Mulamba et al. 2013). This motivation led to novel findings and potential applications for composites containing iodine (Clark and Pantoya 2010; Zhang et al. 2010; Russell et al. 2011, 2012). Energetic materials containing a mixture of nanoparticles, both fuel and oxidizer, represent a group called metastable intermolecular composites (Miziolek 2002). As the specific surface area of the reactants increases, there is an increase in contact between the fuel and oxidizer particles, which enhances reaction rates and combustion performance (Granier and Pantoya 2004; Bockmon et al. 2005; Plantier et al. 2005). Most of these studies have been performed with aluminum (Al) as the fuel (Kim and Zachariah 2004; Bockmon et al. 2005; Plantier et al. 2005; Dikici et al. 2009; Dreizin 2009). Because Al particles are surrounded by an alumina passivation shell that can range from 2 to 4 nm, the smaller Al particle size leads to increased alumina concentration but significantly increased ignition sensitivity and greater overall reactivity (Aumann et al. 1995; Brown et al. 1998; Dlott 2006; Ahn et al. 2011). Alumina is typically considered a dead weight in propulsion applications because it does not participate in the reaction and acts as a heat sink

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(Trunov et al. 2005, 2006; Dikici et al. 2009; Erickson 2010; Gesner et al. 2012). Yet, overall MICs have higher energy densities in comparison to conventional explosives and so have been extensively studied for their potential uses in primers, explosives, and propellants (Kim and Zachariah 2004; Hlavacek et al. 2005; Valliappan et al. 2005). Information and understanding of their reaction kinetics enable tailoring reactants toward a specific application.

The MIC of interest in this work is aluminum (Al) and iodine pentoxide (I_2O_5). These composites have been documented to attain flame speeds of up to 2,000 m/s, maximum peak pressures reaching 11 MPa ($m = 0.5$ g), and with a substantially high heat of combustion 6.22 kJ/g in comparison to other thermite reactions such as Al/CuO (4.09 kJ/g), Al/MoO₃ (4.72 kJ/g), and Al/Fe₂O₃ (3.97 kJ/g) (Dlott 2006; Martirosyan et al. 2009). Farley and Pantoya (2010) found that for heating rates of 10 °C/min, micron-sized particle composites of Al + I_2O_5 showed no reaction, while the nanocomposite counterpart produced a complex multistep reaction. The nanoscale particles with increased specific surface area promoted reaction kinetics that otherwise were not detectable with micron scale particles. Molecular dynamic simulations' results (Farley et al. 2013) show a complex multistep reaction, that is, as a result of I_2O_5 dissociation fragments that exothermically react with Al and its oxide shell. These fragments including IO₂, IO₃, and I₂O₃ require specific adsorption energies (i.e., -211 kJ/mol per bond) to form bridge bonds with the Al fuel (Farley et al. 2013). These calculations suggest that exothermic surface chemistry in Al + I_2O_5 reactions should be observable.

Osborne and Pantoya (2007) studied Al combined with polytetrafluoroethylene (PTFE) and observed a pre-ignition reaction (PIR) associated with the formation of fluorine radicals that react with the Al₂O₃ shell at high temperatures, forming as part of its products aluminum fluoride (AlF₃). They deduced that the fluorine played a role in the promoting exothermic surface reactions in the Al₂O₃ shell. Fluorine and iodine are highly electronegative elements and may exhibit similar halogen-related behaviors when interacting with aluminum particles. The objective of this study is to resolve functional reaction kinetics associated with the Al + I_2O_5 system. This will be achieved by characterizing a baseline behavior of the composite and then studying the composite behavior

at varying heating rates and equivalence ratios (ERs). With the majority of previous Al + I_2O_5 studies using slower heating rates (Clark and Pantoya 2010; Farley and Pantoya 2010; Zhang et al. 2010; Farley et al. 2013) coupled with the predictions of exothermic surface chemistry (Farley and Pantoya 2010), examining higher heating rates may lead to the identification of exothermic surface chemistry. Also, varying ERs allow for an observation of the effects of fuel concentration on the behaviors of these composites and an improved understanding of the composites thermal kinetics.

Materials and methods

The aluminum (Al) powder was supplied by Nova-Centrix (Austin, TX), with an average particle diameter of 80 nm with 80 % Al purity and 20 % alumina (Al₂O₃) passivation shell. The iodine pentoxide (I_2O_5) was procured from Sigma Aldrich (St. Louis, MO) at 99 % purity. The Al + I_2O_5 mixtures were prepared at varying ERs ranging from 0.8 to 1.2 (i.e., fuel lean to fuel rich). The measured powders were suspended in hexanes and sonicated in a Misonix S3000 sonicator for 1 min cycling 10 s on and 10 s off. The cycling program avoids damage to the oxide shell during this intimate mixing process. Post sonication, the mixtures were poured into a Pyrex[®] dish and the hexane evaporated while in a fume hood. The mixed powder was then reclaimed for further experimentation.

Reaction kinetics

Simultaneous thermal analysis (STA) was performed using a Netzsch STA 409 differential scanning calorimeter and thermogravimetric analyzer (DSC/TGA). The samples were programmed to be heated from 30 to 800 °C at a rate of 25 °C/min in an argon environment. Temperature calibrations for the instrument were performed using melting of a set of metal standards resulting in a temperature accuracy of ±1 °C. Platinum crucibles with alumina liners were used and contained 3 mg of sample during testing. Tests were performed in an argon environment where the STA column was evacuated to 1×10^{-4} atmospheres using a Pfeiffer model TMU turbo pump and then backfilled and purged with argon at a flow rate of

70 mL min⁻¹ for the remainder of the cycle. Sintering can occur during heating and melting, ultimately affecting heat transfer in the DSC measuring head. To insure consistency, repeatability, and minimize artifact alterations of results, three experiments were performed for each sample. The data were analyzed using the NETZSCH Proteus Thermal Analysis software package.

Further, STA experimentation was performed analyzing samples heated to 800 °C at 10, 20, and 40 °C/min. Activation energy was calculated using an isoconversion method presented by Starink (Nixon et al. 2011) and shown in Eq. (1).

$$\ln\left(\frac{B}{T_p^{1.95}}\right) = \frac{E_a}{RT_p} + \ln A \quad (1)$$

From Eq. (1), B is the heating rate, T_p is the exothermic peak temperature, A is a pre-exponential factor, E_a is activation energy, R is the universal gas constant, and $B/T_p^{1.95}$ approximates the reaction rate.

The activation energy E_a (kJ/mol) can be found by plotting $\ln(B/T_p^{1.95})$ as a function of $(1/RT_p)$ and taking the slope of the line.

Results and discussion

The heat flow and mass change results for pure I₂O₅ are presented in Fig. 1. The heat flow DSC scale axis is representative of the energy change as a function of temperature and measured in units of mW/mg. The mass loss TG % axis is representative of the mass change as a function of temperature. Mass loss is usually associated with drying, phase change, or gas produced during reaction. Iodine pentoxide is extremely reactive and known to react with moisture in air upon exposure (Farley and Pantoya 2010). Iodic acid, HIO₃, is formed as a result and this process is reversed during heating as indicated by the endotherm observed at 200 °C (Farley and Pantoya 2010). The various stages of dissociation are marked on Fig. 1 at the points where the heat flow slope changes (i.e., Stages A–D).

The hydroxyl decomposition process can be described by Eq. (2).



The mass loss at ~220 °C coincides with an endotherm, and is indicative of the loss of bonded hydroxyls from I₂O₅. There is a slight dip in the heat

flow that begins at ~300 °C, corresponding to the initial stages of I₂O₅ decomposition. Further I₂O₅ decomposition is observed at ~400 °C, where I₂O₅ dissociates into the gas phase and 100 % mass loss is observed. As shown in Fig. 1, dissociation for this material is a complex multistage process. It is initiated in Stage A where 70 % of mass is lost and the process is endothermic. This is followed by Stage B where a slight exothermic process causes plateauing in the heat flow, while the mass loss rate remains constant. Stage C shows a sharp endotherm that is exactly coincident with a significant increase in mass loss rate. A substantial change and increase are observed in Stage D representative of an exothermic reaction. This complex process has been previously observed yet it is not well understood or thoroughly explained (Farley and Pantoya 2010). The I₂O₅ global decomposition reaction is shown by Eq. (3).



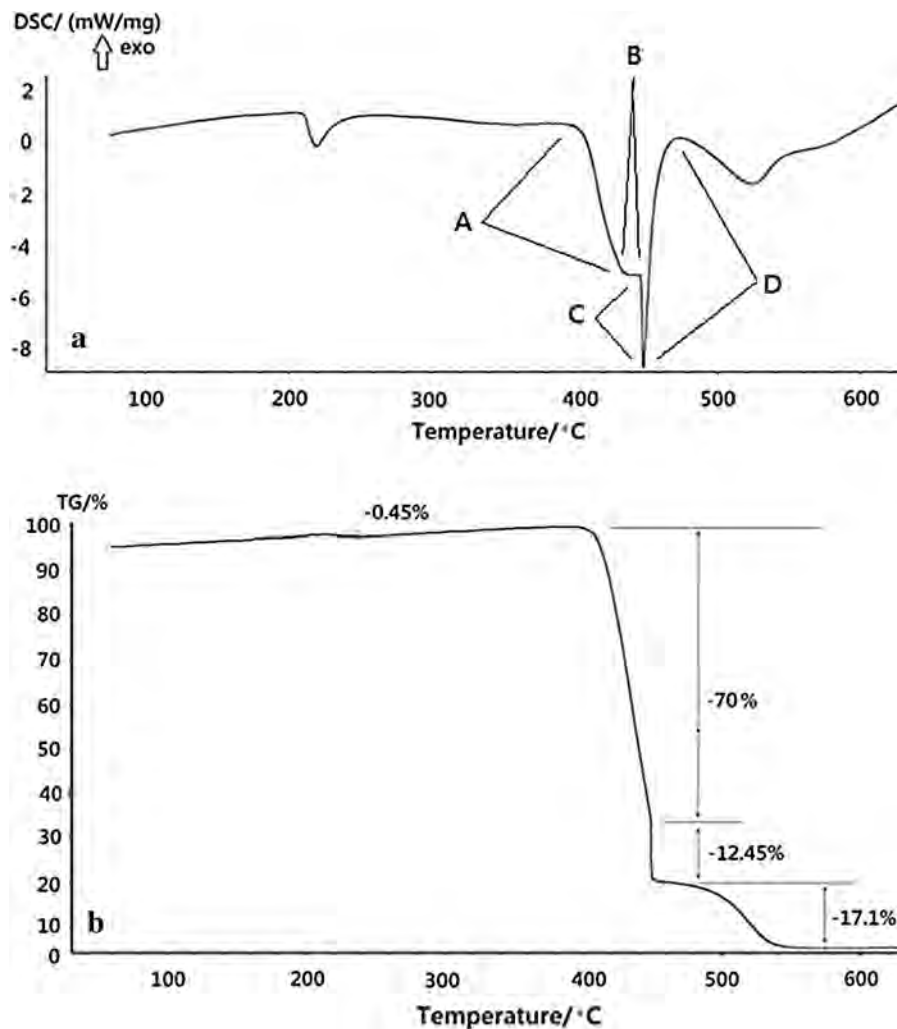
The elementary reactions and stages in Fig. 1 may be explained using first principles and condensed-phase periodic density functional theory (DFT) analyses performed by Farley et al. (2013). Their simulations analyzed both the gas and solid phases of Al I₂O₅ elementary reactions under the assumption Al particles were encapsulated with an Al₂O₃ shell and that exothermic interface reactions were taking place upon activation (Farley et al. 2013). Interface adsorption (exothermic) and I-transfer (endothermic) processes were also calculated. Some decomposition kinetics are summarized in Table 1 and can be applied here to explain the exothermic and endothermic behaviors seen in Fig. 1. The reactions in Table 1 where O₂ is produced post dissociation are all exothermic and have a negative enthalpy.

The endothermic behavior observed in Stage A of Fig. 1 is associated to the first I₂O₅ decomposition stage as shown in Table 1, followed by an exothermic Stage B, endothermic Stage C, and a final exotherm at Stage D.

Figure 2 presents the heat flow (DSC) and mass loss (TG) results for Al + I₂O₅ at an ER of 1.0 (i.e., stoichiometric).

Consistent in Figs. 1 and 2, the initial hydroxyl loss at 220 °C is observed as a small endotherm. Following, Fig. 2 presents a small exotherm at ~320 °C, followed by a bigger exotherm at ~405 °C, and then a small endotherm at 450 °C. It is noted that the heat

Fig. 1 Graphs show STA data of pure I_2O_5 in an argon environment at a heating rate of 25 °C/min: **a** heat flow reaction stages are marked A D; and, **b** mass loss behavior



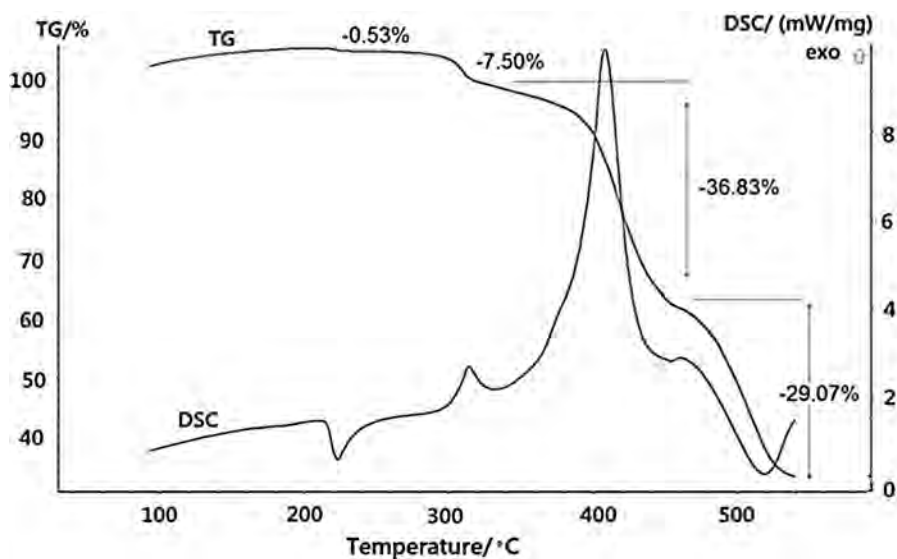
flow curves in Figs. 1 and 2 are essentially inverted above 300 °C such that areas showing exotherms in Fig. 1 are showing endotherms in Fig. 2 and vice versa. Therefore, reactions occur at the stages of I_2O_5 dissociation. The main exotherm appears to include Stages A B dissociations, while Stages C D correspond to the endotherm and exotherm at ~447 and 450 °C. These reactions all occur below the melting temperature for Al (660 °C) such that Al is in the solid phase. The Al + I_2O_5 mass loss pattern in Fig. 2 is similar to the pure I_2O_5 mass loss pattern in Fig. 1. Specifically, the initial hydroxyl mass loss is shown at ~220 °C and the changing rates of mass loss between 400 and 500 °C are repeated. All other heat flow behaviors result from adding Al to the mix. For example, a small exotherm occurs at 300 °C where no I_2O_5 dissociations were observed. This exotherm

Table 1 Dissociation processes reported in (Farley et al. 2013) that correlate with endothermic and exothermic behaviors observed in the I_2O_5 STA (i.e., Fig. 1)

Reaction stage	Dissociation	$\Delta_r H$ (kJ/mol)	Onset temperature
Stage A endotherm	$I_2O_5 \rightarrow IO_2 + IO_3$	37.8	405 °C
Stage B exotherm	$\rightarrow I_2O_3 + O_2$	12.0	432 °C
Stage C endotherm	$\rightarrow IO_2 + IO$	23.2	447 °C
Stage D exotherm	$\rightarrow I_2 + O_2$	25.8	450 °C

resembles an observation by Osborne and Pantoya (2007) who studied fluorine and aluminum. They observed a similar small exotherm prior to the main Al

Fig. 2 Heat flow and mass loss curves from DSC/TG measurements of Al/I₂O₅ in an argon environment at a heating rate of 25 °C/min



reaction and coined it a pre-ignition reaction (PIR). They showed that the alumina shell surrounding the Al particle was fluorinated by the fluoride ions from PTFE decomposition, and that this interaction was responsible for the exothermic PIR. The first exotherm shown in Fig. 2 will now be referred to as a PIR exotherm.

This PIR exotherm corresponds to a reaction involving a halogen and is not the main exothermic reaction as indicated by the 2nd exotherm in Fig. 2. In the temperature region of the PIR, I₂O₅ has not begun dissociation as shown in Fig. 1; therefore, the PIR exotherm would be a result of kinetics associated with aluminum. Farley et al. (2013) found that I₂O₅ and its decomposition fragments adsorb strongly to alumina via bridge bonds and that the adsorption energy is strongly exothermic at 423 kJ/mol for a single I₂O₅ molecule. With the adsorption of iodine to Al₂O₃, the mass loss observed concurrently with the PIR in Fig. 2 is explained by the oxygen released from I₂O₅ dissociation. The adsorption process responsible for the PIR has I₂O₅ exothermically dislodging hydroxyls on the Al₂O₃ surface and forming I O Al bridge bonds requiring an adsorption energy of 211.495 kJ/mol per bond formed (Farley et al. 2013).

To confirm this PIR behavior associated with I₂O₅ fragments reacting with Al₂O₃, a mixture of Al₂O₃ + I₂O₅ was examined for the same conditions as the Al + I₂O₅. This analysis isolates reaction between the Al₂O₃ shell and I₂O₅ and Fig. 3 presents the results.

Figure 3 shows a PIR in the same temperature range as in Al + I₂O₅ shown in Fig. 2. Due to the oxygen inertness of Al₂O₃ at these temperatures, the exotherm can only be attributed to the bridge bonds forming between Al₂O₃ and I O dissociation fragments. Following the PIR, no major exotherm is observed, instead two successive endotherms with the latter being larger than the first. Endothermic behavior in the 420 °C range is consistent with mass loss in all TG figures (Figs. 1b, 2, 3) corresponding to I₂O₅ decomposition. As observed in Figs. 1b, 2, and 3, there is a second endotherm attributed to the final stage of mass loss. This second endotherm is much larger in Fig. 3 in comparison to Figs. 1 and 2. The calculated heats of reaction and melting for Figs. 1, 2, and 3 are presented in Table 2.

Trunov et al. (2005) found that the amorphous Al₂O₃ shell begins significant growth from 300 °C and then undergoes a phase change from amorphous Al₂O₃ to γ Al₂O₃ when it reaches critical thickness (~4 nm) in the 500–550 °C range. This phase change may be responsible for the greater endotherm in Fig. 3 in comparison to Figs. 1 and 2. The higher density associated with γ -Al₂O₃ nanocrystallites may promote enhanced bonding behavior (Trunov et al. 2005).

In Fig. 3, one exothermic onset at ~318 °C is found which coincides with the PIR in Fig. 2 but was not observed in Fig. 1. The element present in composites showing PIR in Figs. 2 and 3 that is not in the composite for Fig. 1 is Al₂O₃, such that the PIR is a result of iodination of alumina and the formation

Fig. 3 Heat flow and mass loss curves from DSC/TG measurements of $\text{Al}_2\text{O}_3 + \text{I}_2\text{O}_5$ in an argon environment at a heating rate of $25\text{ }^\circ\text{C}/\text{min}$

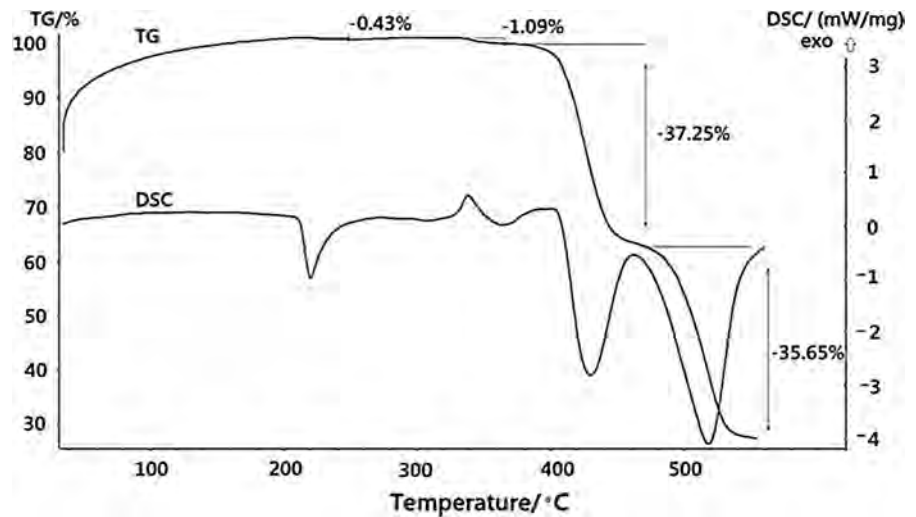


Table 2 Quantitative assessment of the heating and melting peaks in Figs. 1, 2, and 3

	PIR $\Delta_r H$ (J/g)	Main exotherm $\Delta_r H$ (J/g)	1st endotherm $\Delta_r H$ (J/g)	2nd endotherm $\Delta_r H$ (J/g)
Figure 1	0	0	501	106
Figure 2	20	434	0	151
Figure 3	14	0	179	307

of I O Al bonds in coherence with calculations by Farley et al. (2013).

Further experiments were performed for varying ERs to observe an effect on the PIR. A fuel rich 1.2 mixture was studied along with a fuel lean 0.8 mixture, and the heat flow results are presented in Fig. 4.

Figure 4 shows a PIR in all cases. A difference is observed in the onsets of these PIRs: the fuel rich mixture has the lowest onset temperature (i.e., $281.3\text{ }^\circ\text{C}$), while the fuel lean mixture has the highest onset temperature (i.e., $309.1\text{ }^\circ\text{C}$). This leads to a potential concentration-dependent behavior similar to observations by Pantoya and Dean (2009) who found similar correlations between fluorine concentration and PIR onset. The fuel rich mixtures have more Al and, therefore, more Al_2O_3 which may allow for increased surface area induced reaction between the alumina shells and I_2O_5 leading to earlier observed PIRs. Therefore, there appears to be a concentration factor coupled with the adsorption of I_2O_5 dissociating

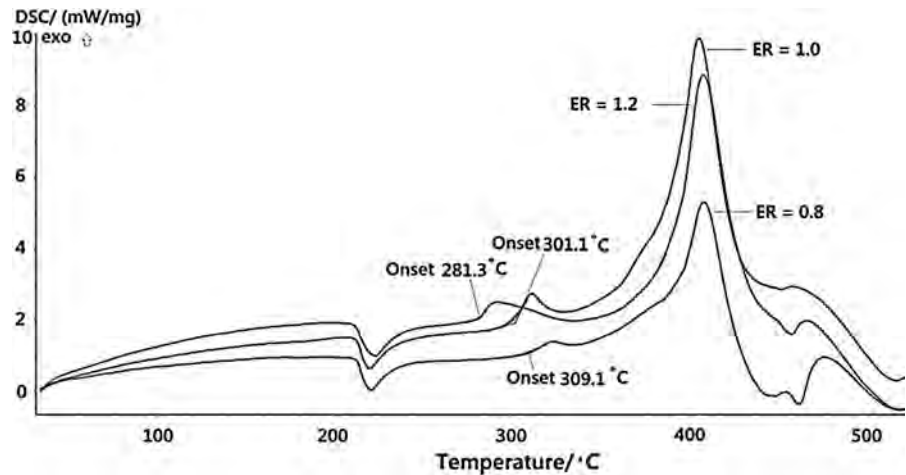
fragments to the Al_2O_3 surface that affects the PIR behavior. To investigate how these parameters both play a role the PIR, further testing was performed with a single stoichiometry analyzed at varying heating rates.

A literature search shows that only a couple of heat flow and mass loss studies of $\text{Al} + \text{I}_2\text{O}_5$ has been performed and all did not observe PIR (Farley and Pantoya 2010; Farley et al. 2013). These studies examined heating rates between 2 and $10\text{ }^\circ\text{C}/\text{min}$. Therefore, similar tests were performed to extend to higher heating rates at 10, 20, 30, and $40\text{ }^\circ\text{C}/\text{min}$ and compared with the $25\text{ }^\circ\text{C}/\text{min}$ results shown in Figs. 1, 2, 3, and 4. Figure 5 presents the results for thermal behavior of $\text{Al} + \text{I}_2\text{O}_5$ at varying heating rates.

Figure 5 shows that no PIR is observed until heating rates $\geq 25\text{ }^\circ\text{C}/\text{min}$. If the PIR was simply a matter of I_2O_5 fragments interacting with the alumina surface then the lower heating rates would exhibit similar behaviors as the higher heating rates, but that is not observed in Fig. 5. Even though surface interactions contribute to the exothermicity of the PIR (Osborne and Pantoya 2007; Farley and Pantoya 2010; Farley et al. 2013), there appears to be more to the PIR than just surface reactions. The varying parameter in Fig. 5 is the heating rate and so its effects could explain the presence or lack of PIR.

For the varied heating rate, the activation energy was calculated as 1.43 kJ/g [from Eq. (1)] correlated to Al_2O_3 and I_2O_5 fragments reaction. The activation energy for Al and I_2O_5 fragments (main exotherm) was calculated and found to be 1.83 kJ/g and is

Fig. 4 Heat flow curves from DSC measurements of Al + I₂O₅ in an argon environment at a heating rate of 25 °C/min and for varying equivalence ratios (ER)



comparable to the value obtained by Farley et al. (2013) of 1.79 kJ/g. For diffusion reactions, Al and oxygen species diffuse toward each other through the oxide shell (Rai et al. 2006; Chowdhury et al. 2010). Three forces take part in this action: frictional force (resistance to moving ion), diffusive force (dependent on concentration), and electrostatic force (interaction between ions) (Laidler 1987). The equations describing these forces are presented in (Laidler 1987) and repeated here in Eqs. (4–6).

$$F_{es} = -\frac{dU_{es}}{dr} \tag{4}$$

$$F_d = -\frac{kTdc_B}{c_B dr} \tag{5}$$

$$F_r = -f_B \frac{dr}{dt} \tag{6}$$

In these equations, U_{es} is the electrostatic potential, c_B is the concentration, f_B is the frictional coefficient, r is the depth into the surface, T is the temperature, k is the thermal conductivity, and dr/dt is the diffusive velocity (Laidler 1987). These forces are combined to form the diffusive flux (J_B) which refers to the number of ions passing through the surface. The equation for J_B is derived in (Laidler 1987) and given by Eq. (7).

$$J_B = \frac{4\pi r^2 kT}{f_B} \left(\frac{dc_B}{dr} + \frac{c_B dU_{es}}{kT dr} \right) = -\frac{dr}{dt} 4\pi r^2 \tag{7}$$

Increasing the heating rate increases the temperature gradient between the outside surface and the core, and higher temperatures cause an increase in molecular kinetic energy represented by Eq. (8).

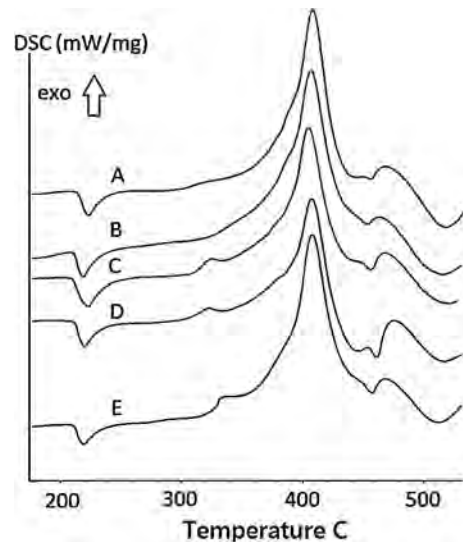


Fig. 5 The effects of vary heating rates: A 10, B 20, C 25, D 30, and E 40 °C/min for composite at 0.8 ER examined in an argon environment

$$K_{energy} = \frac{1}{2} m \left(\frac{dr}{dt} \right)^2 \tag{8}$$

Therefore, if heating rate is increased, kinetic energy is increased, and diffusive velocity is increased in accordance with Eq. (6). An increase in diffusive velocity relates to an increase in diffusive flux and promotes increased reaction of iodine and Al₂O₃. Based on the deductions above, the electrostatic component of diffusive flux and the ionic nature of this composite, I₂O₅ fragments also diffuse into the Al₂O₃ shell. Therefore, the Al₂O₃ surface is not only

interacting with oxygen and the I_2O_5 fragments, but also there is diffusion of oxygen and some ionic I_2O_5 fragments into the oxide layer.

Based on Fig. 5 increasing heating rate beyond the threshold where the PIR is observed (i.e., 25 °C/min) results in a consistent PIR observation. For diffusion controlled reactions, increasing heating rates increases diffusion velocities of the oxygen toward the Al and of the Al toward the oxygen, but it also increases the diffusion flux of other ionic elements. Therefore, there appears to be a balance such that beyond a threshold heating rate, the concentration of ionic elements diffusing into the shell would balance the oxygen to Al diffusion and exhibits a consistent PIR. It is also noted that slower heating rates may reach this threshold such that concentration of I_2O_5 to Al_2O_3 interaction is sufficient for PIR, the reaction may be simultaneous with the main combustion reaction and, therefore, cannot be observed. These observations suggest that not just surface reactions are responsible for the PIR, but core interactions as well.

Conclusion

Exothermic surface chemistry associated with the alumina passivation shell and iodine-containing species was identified prior to the main aluminum combustion reaction. Powder composites composed of nanoscale aluminum particles passivated with an alumina shell and iodine pentoxide particles were examined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). A multistaged endothermic/exothermic behavior unique to I_2O_5 was observed and explained using predicted molecular dynamics models that result from multiple I_2O_5 dissociation fragments. A PIR once thought to be unique to nano-Al/PTFE mixtures was revealed for the Al/ I_2O_5 and Al_2O_3/I_2O_5 mixtures, as well as fuel rich and fuel lean mixtures. Correlations with the diffusive flux showed that PIR is dependent on both the concentration and activation energy. Adsorption of I_2O_5 fragments to the Al_2O_3 surface coupled with diffusion of ionic I_2O_5 fragments into the Al_2O_3 shell was found to play a significant role in the production of PIRs. The effect of varying ERs did not affect the production of a PIR but rather its onset temperature. The fuel rich mixtures show lower onset temperatures and the fuel lean mixtures showed higher onset

temperatures such that the PIR was concentration dependent. These are impactful findings because the alumina passivation shell is typically considered dead weight and a heat sink in combustion reactions, but it is shown here to participate exothermically in the reaction when combined with an iodine-containing oxidizer.

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