



Titanium enhanced ignition and combustion of Al/I₂O₅ mesoparticle composites

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ABSTRACT

Aluminum (Al) is widely used in thermites, and iodine pentoxide (I₂O₅) is a strong oxidizer that can release gas phase iodine. The result is a potentially very powerful and effective energetic composite with biocidal properties. However, the alumina coating on the Al presents a diffusion barrier that increases the ignition temperature. In this paper, nano titanium powders (nTi) were added at various mass ratios to Al/I₂O₅ and a composite mesoparticle was assembled by electrospray. Combustion studies showed that nano Ti can enhance the reactivity of Al/I₂O₅ thermites significantly with increases in pressure, pressurization rate and dramatic decreases in burn time. Part of this behavior can likely be attributed to less sintering enhancing the completeness of reaction in the Ti added cases. Addition of titanium to aluminum was found to have a significant impact on ignition and when Al is replaced with Ti, the ignition temperature was ~300 °C below that of the corresponding aluminum thermite. These results show that titanium can be used as a fuel to tune energetic behavior and iodine release temperature and in some ways superior to aluminum.

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1. Introduction

Thermites are a class of energetic materials composed of metal and metal oxide with greater stored potential energy than traditional CHNO based systems. The most common fuel used in thermites is aluminum due to its high reaction enthalpy and low cost. However, the native oxide coated on aluminum can increase the ignition delay [1]. For some applications, it may be desirable to lower the ignition temperature. Wang et al. found that ammonium perchlorate (AP) can lower the ignition temperature of aluminum because the oxide shell can be corroded by the acid released from the decomposition of AP [1].

Others have added metals to Al-based thermites, such as titanium, nickel, zinc, boron, magnesium to tune either the ignition or combustion behavior [2–6]. Shoshin and Dreizin investigated the ignition temperature of Al–Ti alloys and found that the ignition temperature decreased from 1877 °C (for neat Al) to 969 °C (for a Al_{0.75}Ti_{0.25} alloy) [2]. Aly et al. showed that Al–Ni and Al–Zn composites made by short term milling ignited at a lower temperature than unmilled aluminum [3]. Similarly, AlMg-based thermites

show significant decrease in ignition temperature compared to Al-based ones [4]. Combustion behavior can also be moderated with the additive of other fuels. For example, a 20 mol% addition of boron to Al/CuO increases the pressurization rate ~3 X [5]. Adding 2 wt% nano Ag into Al/CuO has been shown to increase combustion speed by over 60% [6].

For Al NPs-based thermites, traditional oxidizers include CuO, Fe₂O₃, Bi₂O₃, WO₃, etc. [7–11]. Other oxidizers including KIO₄ [12], K₂S₂O₈ [13], Ag₂O [14,15], AgIO₃ [16], I₂O₅ [15,17,18], B₂O₃ [19–21], some metal iodates [22,23], etc. have also been explored for their high reactivity. Among them, Ag₂O, Ca(IO₃)₂, Cu(IO₃)₂ and I₂O₅ are example oxidizers that have been considered as possible biocidal oxidizers because they leave a biocide (silver or iodine) as a reaction product [13–17,22–24]. I₂O₅ has attracted considerable interest because of its high iodine content, ~76% iodine mass fraction. Wu et al. showed that Al/I₂O₅ is extremely effective as oxidizer and iodine generator, and thus as biocidal energetic material [25]. And in fact Martirosyan et al. found that the maximum peak pressure produced by Al/I₂O₅ is comparable to Al/Bi₂O₃ system which is a particularly violent thermite mixture [18].

In this paper, we explore the use of titanium as an additive to tune the ignition and combustion performance of Al/I₂O₅. Based on our previous work, we incorporated small amounts of nitrocellulose (NC) into the system by electrospray considering that fuel

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and oxidizer can be mixed more uniformly and the sintering of Al can be inhibited by the gas release from NC [26]. I_2O_5 particles were synthesized via an aerosol spray pyrolysis (ASP) technique [17] and the mesoparticles of Al/Ti/ I_2O_5 with varying amounts of Al and Ti content were prepared by electrospray. The peak pressure, pressurization and burn time during the combustion were measured by a constant volume combustion cell. The ignition temperature and species released from the thermites were measured by time-resolved temperature-jump time-of-flight mass spectrometer (T-Jump/TOFMS). We found that adding Ti to Al/ I_2O_5 system can increase the pressurization rate, i.e. reactivity, by a factor of 1000, and the ignition temperature can be reduced from $\sim 610^\circ\text{C}$ to $\sim 300^\circ\text{C}$.

2. Experimental section

2.1. Chemicals

Iodic acid (HIO_3) (99.5 wt%) was purchased from Sigma-Aldrich and the nano-aluminum powders (nAl) (Alex, ~ 80 nm), with ~ 81 wt% active aluminum, confirmed by thermogravimetry analysis, were purchased from Novacentrix. The nano-titanium (nTi) (50–80 nm) powders, with ~ 70 wt% active titanium, were purchased from US Research Nanomaterials Inc. Anatase titanium dioxide (TiO_2) nanoparticles (< 50 nm) and aluminum oxide (Al_2O_3) nanoparticles (< 50 nm) were purchased from Sigma Aldrich. Collodion solution (4–8 wt% in ethanol/diethyl ether) was purchased from Fluka Corp and a diethyl ether (99.8%)/ethanol (99.8%) mixture (volume ratio: 1:3) was used to dilute the collodion solution.

2.2. Preparation of iodine pentoxide via aerosol spray pyrolysis

Submicron particles of I_2O_5 were obtained via ASP [17]. Typically, 1 g HIO_3 dissolved in 50 mL deionized water (20 mg/mL) was sprayed into aerosol droplets with ~ 1 μm size by an atomizer (~ 35 psi pressure air). The atomized droplets passed through silicon diffusion dryer, where most of the water was absorbed and then passed into a tube furnace at 400°C where the chemical decomposition was complete and I_2O_5 particles were obtained.

2.3. Preparation of the Al/Ti/ I_2O_5 meso-particles

To explore the influence of the titanium on Al/ I_2O_5 thermites, different molar percentages of Ti were varied from 10% to 100% relative to Al. The samples will be referred to in terms of the molar percentage of Ti in the fuel. A corresponding amount of I_2O_5 is added to make the overall mixture stoichiometric assuming the fuel reacts with the oxidizer completely. The composites were made by an electrospray method as described elsewhere [26]. Typically, the fuel and oxidizer were dispersed in ethanol and ether, and 5 wt% nitrocellulose (NC) was added as a binder and the solid particle loading was 100 mg/mL. In a typical experiment (e.g., 50% Ti contained case), 116 mg I_2O_5 was dispersed in 1.2 mL ethanol and sonicated for 1 h. Then 18 mg Al, 32 mg Ti, 0.4 mL ether and 0.15 mL NC collodion solution were added successively. The detailed formulations are shown in Table 1. The mixture was stirred for ~ 5 min and sonicated for 1 h and stirred for additional 24 h. In the electrospray process [26], we employed a feed rate of 2 mL/h, a needle to substrate distance of ~ 15 cm, and an applied voltage of 20 kV.

2.4. Characterization

The ASP prepared I_2O_5 particles were characterized by scanning electron microscopy (SEM, Hitachi, SU-70 FEG-SEM) and powder X-

Table 1

Thermite formulations (fuel/oxidizer equivalence ratio = 1.0).

Thermites	Al (wt%)	Ti (wt%)	I_2O_5 (wt%)	NC (wt%)
Al- I_2O_5	23.8	0	71.2	5
90%Al-10%Ti- I_2O_5	20.7	4.1	70.2	5
70%Al-30%Ti- I_2O_5	15.2	11.6	68.2	5
50%Al-50%Ti- I_2O_5	10.3	18.3	66.4	5
30%Al-70%Ti- I_2O_5	5.9	24.3	64.8	5
Ti- I_2O_5	0	32.3	62.7	5

ray diffraction (XRD, Bruker D8 Advance using $\text{Cu K}\alpha$ radiation). X-ray photoemission spectrometry (XPS, Kratos AXIS 165 spectrometer) and XRD were used to determine the nature of the oxide layer of nTi particles. Morphology and elemental analysis of electrosprayed Al/Ti/ I_2O_5 thermite composites were measured by SEM and energy dispersive spectrometer (EDS) conducted on a Hitachi SU-70 instrument. Thermogravimetry/mass spectra (TG/MS) results of I_2O_5 , Al/ I_2O_5 , Ti/ I_2O_5 , TiO_2/I_2O_5 and Al_2O_3/I_2O_5 were obtained with a TA Instruments Q600 at a heating rate of $10^\circ\text{C}/\text{min}$ up to 700°C in argon connected by a heated micro-capillary ($\sim 300^\circ\text{C}$) to the MS to obtain the simultaneous MS of gaseous product.

2.5. Combustion cell test

A constant-volume combustion cell was used to measure the combustion behavior of thermite samples [27]. In a typical experiment, 25 mg of loose thermite powders was loaded into the combustion cell with a constant volume of ~ 20 cm^3 and ignited with a resistively heated nichrome coil. The pressure and optical emission from the thermite reaction were recorded by the attached piezoelectric pressure sensor and a photodetector, respectively. The peak width at half height of the optical emission was defined as the burn time.

2.6. T-jump ignition and time-resolved mass spectrometry measurement

The ignition of thermites and oxygen release of the oxidizer were investigated by temperature-jump/time-of-flight mass spectrometry (T-jump/TOF-MS) coupled with a high-speed camera (Vision Research Phantom v12.0, 67,056 frames/s) [28]. Typically, a thin layer of the thermite sample was coated onto a platinum wire (76 μm in diameter, 10 mm in length). And the coated wire was inserted into the ionization region of a TOFMS and resistively heated to $\sim 1200^\circ\text{C}$ in 3 ms with a heating rate of $4 \times 10^5^\circ\text{C}/\text{s}$. The temporal temperature of the wire was determined from the detected current and voltage according to the Callender–Van Dusen equation [12]. Time-resolved mass spectra were used for characterization of gaseous species produced during the rapid heating. The ionization/extraction region of the TOFMS was pulsed at 10 kHz resulting in a full mass spectrum every 100 μs . A 600 MHz digital oscilloscope was used for data acquisition with a sampling rate of 100 mega sample per second. A detailed experiment description could be seen in ref. [29].

2.7. Flame temperature measurement

A high-speed camera (Vision Research Phantom Miro M110, 77,000 frames/s) was used to estimate the flame temperature of Al/ I_2O_5 and Ti/ I_2O_5 coated on the wire by performing color ratio pyrometry. The acquired wavelength and intensity were calibrated with a Blackbody Infrared Light Source (Newport Oriel 67000 Series) and the collected data was substituted into Planck's Law [30]. MATLAB was used to recover values for red, green and blue channels at each pixel and three color ratios (green/red, blue/green, and

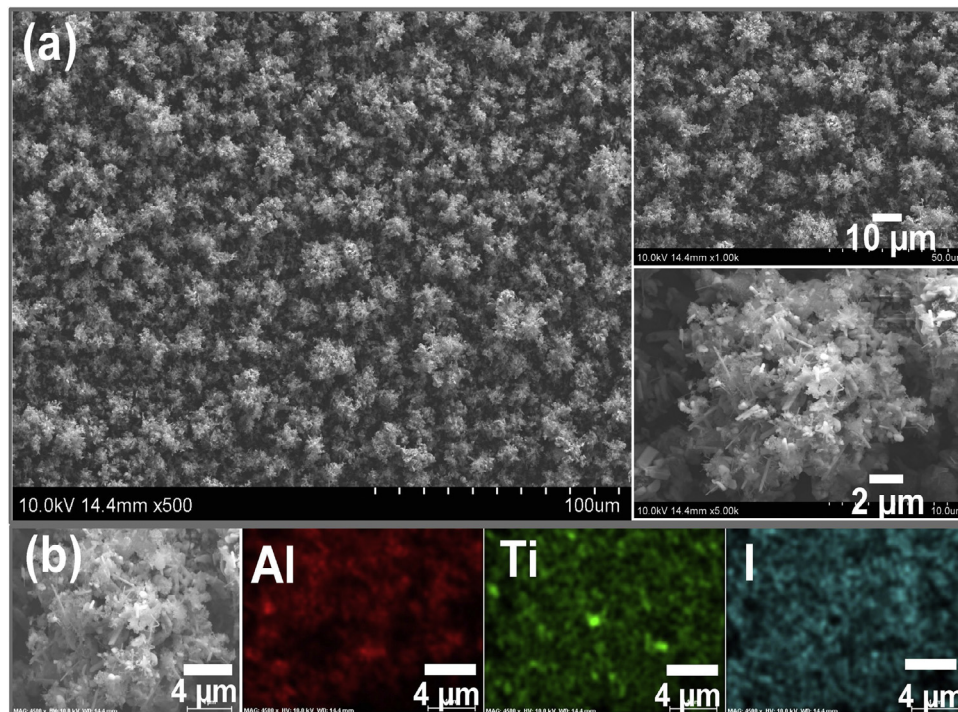


Fig. 1. SEM (a) and EDS (b) of 30% Ti by mol (in fuel) mesoparticle composites. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

blue/red) were simultaneously used to estimate the temperature. Then the mean and median temperature vs. time profile was obtained by collecting the frames with at least 10 contiguous, unsaturated pixels that were above the black level and within the error threshold being used.

3. Results and discussion

3.1. Characterization of Ti nanoparticles

It is well known that the oxide shell of nano-particulate fuels such as Al and B, has a significant effect on ignition and combustion [1,31]. Here we evaluate the nature of the native oxide shell of nTi via XRD and XPS. Combining the XRD (Fig. S1) and XPS results (Figs. S2 and S3), we conclude that the major materials on n-Ti is mainly amorphous TiO_2 and 20% of the oxide shell is TiN, and perhaps some TiO, with a small amount of TiON. It is reported [32] that TiN can be oxidized by oxygen, which means the oxide shell of Ti is reactive to some degree.

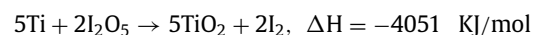
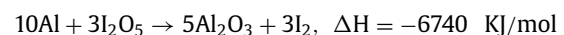
3.2. Size and morphology of electrospayed Al/Ti/ I_2O_5

The synthesized I_2O_5 particles by aerosol-spray pyrolysis have a size distribution ranging from 200 to 700 nm, as shown in Fig. S4 and were confirmed to be I_2O_5 by XRD (Fig. S5). SEM images and EDS mapping results (Fig. 1) of electrospayed composite mesoparticles containing 30% Ti by mol (in fuel), as a representative, show that the Al/Ti/ I_2O_5 composites are equiaxial porous agglomerates with a size distribution of 5–10 μm in which the needle-like crystals are I_2O_5 (confirmed by EDS). EDS mapping (Fig. 1(b)) indicates that the nAl, nTi and I_2O_5 are homogeneously dispersed. SEM images of other samples can be seen in Fig. S6.

3.3. Bulk combustion analysis

Bulk combustion of composites was evaluated in a confined pressure cell where the pressure and optical emission (from which

burn time is obtained) are temporally recorded and shown in Fig. 2(a)–(c) as a function of Ti content. Thermochemical calculations for pressure and the adiabatic flame temperature (AFT) were obtained using CHEETAH 5.0 [33] as shown in Fig. 2(a) and (d), respectively. The calculations are done based on the following equations, assuming a 25 mg mass in a 20 cm^3 combustion cell, in which constant volume combustion is used to estimate the peak pressure of the system.



The peak pressure of thermites with different Ti content in Fig. 2(a) indicates that Ti addition significantly improves performance (by 6 X). However, the difference in calculated peak pressure by CHEETAH is not significant. According to Fig. 2(a), the calculated peak pressure is over predicted in the aluminum dominating cases but is much lower at high Ti loadings (>50 mol%) than measured, since the kinetics dominates in these cases. In prior work we have shown that aluminum sintering can result in incomplete reaction, leading to lower heat release. Ti presumably will be less affected due to its high sintering temperature and thus it is likely it is a better fuel from a completion of reaction point of view [34].

Similar behavior is seen in the pressurization rate as seen by the semi-log plot, which is a measure of peak reaction rate and is shown in Fig. 2(b). In this case pressurization rate is increased by a factor of 1000 over the range of Ti addition. This higher reaction rate is also reflected in burn time shown in Fig. 2(c), which monotonically decreases with Ti addition. Burn times monotonically decrease with Ti addition, with burn times of a pure Ti thermite a factor of 20 smaller than the corresponding pure Al based thermite.

The pressurization rate, which depends on the reactivity, correlates with oxygen release rate [27]. It has been shown that the oxygen release from pure I_2O_5 occurs prior to the reaction of Al and

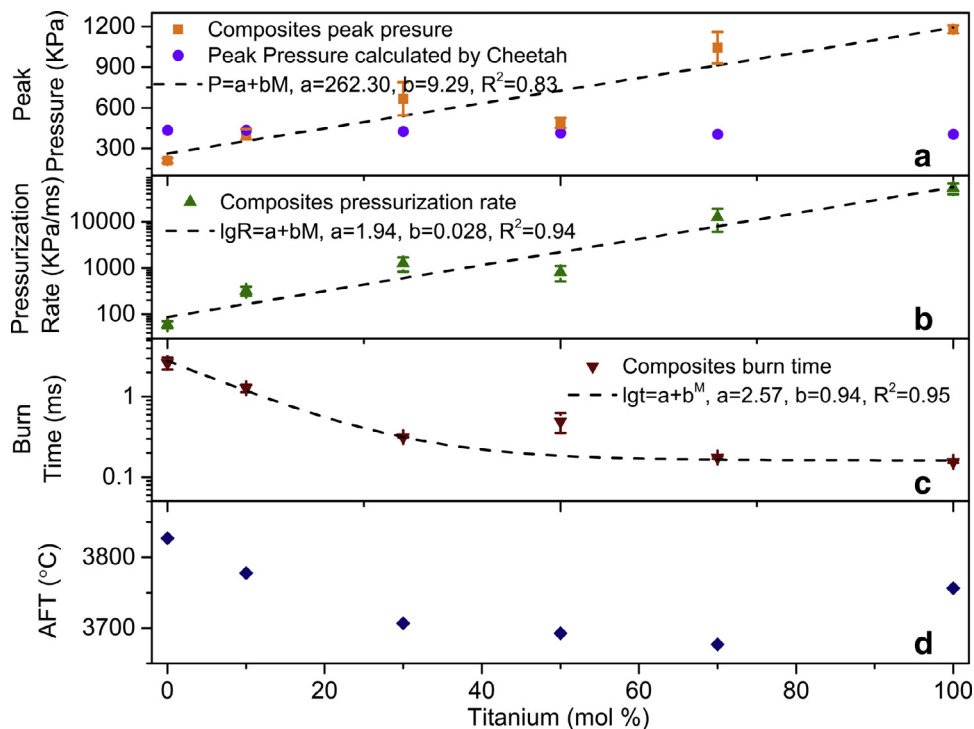


Fig. 2. (a) Peak pressure in experiments and calculated by CheetaH, (b) pressurization rate, (c) burn time, and (d) adiabatic flame temperature calculations as the function of the Ti molar percent in the fuel and the corresponding fitting curves. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

I_2O_5 [25]. However, for Ti and I_2O_5 , we infer that oxygen release in Ti/ I_2O_5 is activated by the reaction. Thus, the oxygen release rate of Al/ I_2O_5 is significantly lower than that of Ti/ I_2O_5 and the pressurization rate of Ti/ I_2O_5 is much higher than that of Al/ I_2O_5 . And has been previously shown, sintering while important in slowing the combustion of aluminum [35], is not observed to the same extent with titanium nanoparticles which has a much higher melting point [36].

Figure 2(d) shows that the AFT of Al/Ti/ I_2O_5 composites ranging slightly from $\sim 3700^\circ\text{C}$ to $\sim 3800^\circ\text{C}$. But the experimental flame temperature ($\sim 2700^\circ\text{C}$) is lower than Al/ I_2O_5 ($\sim 3500^\circ\text{C}$) shown in Fig. S7 due to incomplete reaction as evidenced by the existence of TiO product (Fig. S8). Thus the experimentally observed decreases in burn time are likely much more to do with the completeness of reaction and inherent kinetics of Ti vs. Al rather than thermodynamics. To conclude, the additive of Ti in Al/ I_2O_5 increased the peak pressure, pressurization rate and lowered the burn times significantly.

3.4. Ignition characterization and analysis

3.4.1. T-jump/TOFMS analysis of Al/Ti/ I_2O_5

The ignition temperature and the temporal evolution of gaseous species were characterized by T-jump/TOFMS [29]. The iodine and O_2 release intensities vs. temperature at high heating rate are plotted in Fig. 3(a) and (b). As shown in Fig. 3(a), the onset temperatures of iodine release are similar for all thermites, but the release rate is highly sensitive to Ti loading and increases with Ti loading such that the iodine release peak shifted from $\sim 640^\circ\text{C}$ (without Ti) to $\sim 400^\circ\text{C}$ (100% Ti). As Fig. 3(b) shows, the onset temperature of oxygen release decreases slightly from $\sim 400^\circ\text{C}$ to $\sim 320^\circ\text{C}$ and the oxygen release peak also moves to lower temperature with increasing Ti content. It indicates that the release of iodine and O_2 in Al/ I_2O_5 system is facilitated by adding Ti. Further the iodine and O_2 release temperature from thermite composites are even lower

than that of pure I_2O_5 when Ti loading is higher than $\sim 30\%$. Addition of fuel in all cases broadens the release time and temperature when compared to neat I_2O_5 (orange curve), which is due to reactions between I_2O_5 and the oxide shell of the fuel and will be discussed in Section 3.4.2. The peak in iodine is delayed by almost 200°C with the 100% Al and dropped by $\sim 150^\circ\text{C}$ at 100% Ti relative to neat I_2O_5 . Effectively similar trends are seen for oxygen release. This indicates it is possible to tune the I_2 and O_2 release temperatures by adding different fuels.

Figure 4 shows the O_2 release temperature in neat I_2O_5 and the ignition temperature for different Al/Ti/ I_2O_5 composites. Figure 4 shows that adding Ti monotonically lowers the ignition temperature significantly from $\sim 610^\circ\text{C}$ to $\sim 300^\circ\text{C}$.

For the Al/ I_2O_5 composites, the ignition temperature was $\sim 610^\circ\text{C}$, which is often seen since the phase changes in alumina (from amorphous to $\gamma\text{-Al}_2\text{O}_3$) [37] can lead to the initiation of some Al-based thermite reaction. Although O_2 was released before the alumina phase changes, aluminum reacts with O_2 only when aluminum has sufficient mobility. Interestingly all the Ti based thermite systems (Ti ≥ 30 mol%) ignited below the apparent O_2 release temperature from pure I_2O_5 (dashed horizontal green line 420°C). This implies that a condensed phase reaction mechanism dominates for Ti ignition. Above 50% Ti in the fuel the ignition temperature is constant at $\sim 300^\circ\text{C}$. We propose that the ignition of Al/Ti/ I_2O_5 is triggered by the oxidation of titanium and the reactive oxide shell of Ti (confirmed by XRD and XPS) also facilitates the oxidation to some degree [36].

Figure 5 shows snapshots of the combustion of composites at various loading of Ti. As the Ti content increased the reaction initiated earlier, consistent with the trend of ignition temperature. Moreover, the reaction of the composites became more visibly violent and this is not altogether surprising as the enthalpy for oxidation on a per atom of fuel basis is 12% higher for Ti than it is for Al thus we expect that unless that is a significant kinetic barrier Ti should be a good fuel. Both the ignition and combustion behavior

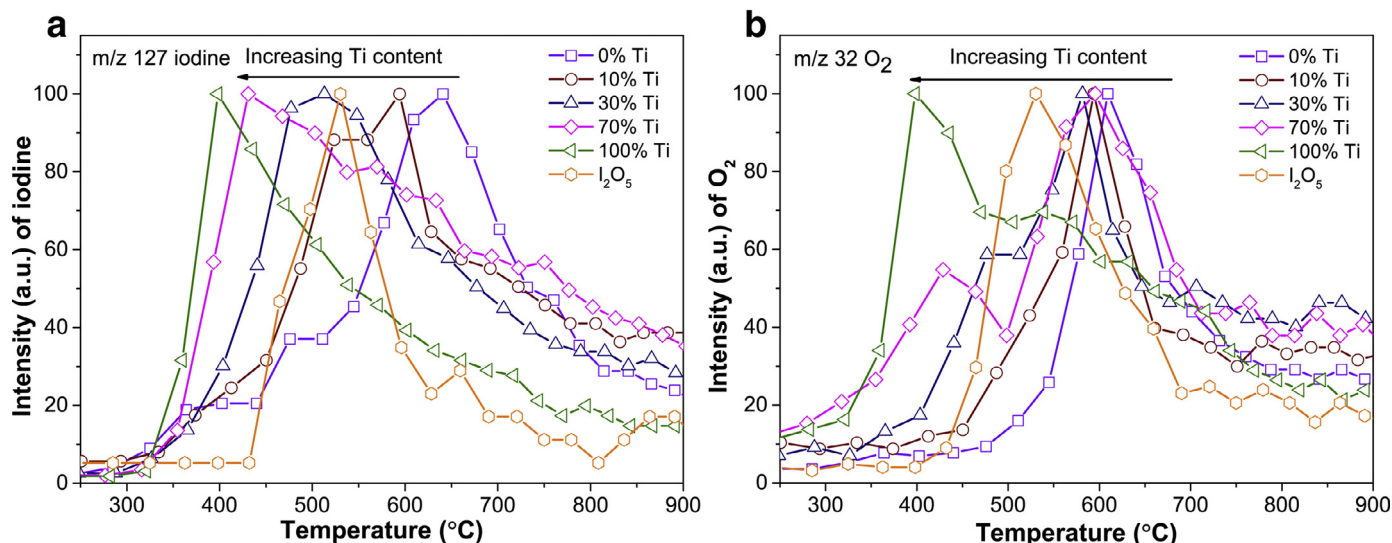


Fig. 3. High heating rate: normalized intensity vs. temperature of (a) iodine and (b) oxygen release from Al/Ti/I₂O₅ thermite mixtures with varying Ti mol% (in fuel) with T-jump/TOFMS. Note: Temperature has been mapped to time. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

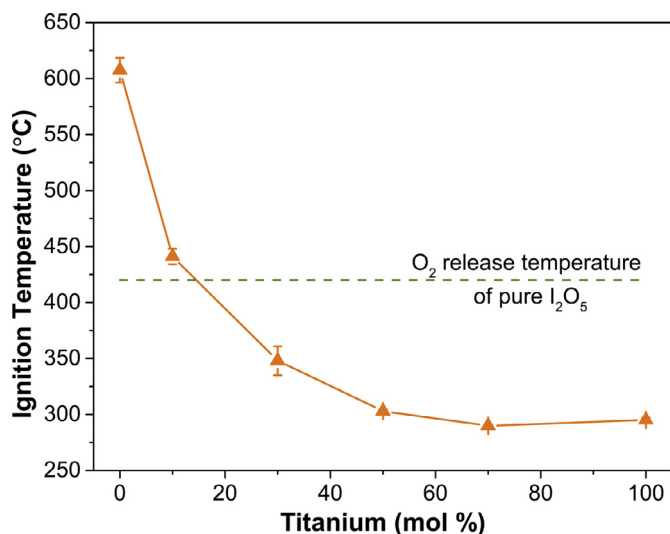


Fig. 4. The ignition temperature of Al/Ti/I₂O₅ thermite mixtures with varying Ti mol% (in fuel). The horizontal line corresponds to the O₂ release temperature in neat I₂O₅. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

show that Ti, although possessing a high temperature native oxide is actually much less of a barrier than Al.

3.4.2. TGA/MS at low heating rate to evaluate the role of native oxide shell

The results presented in Fig. 3 show that the presence of the fuel influences the release rate of iodine from I₂O₅. The decomposition behavior of neat I₂O₅, Al/I₂O₅ and Ti/I₂O₅ has been studied at low heating rate by TGA/MS (Fig. S9) and the results show that the onset of decomposition of I₂O₅ and iodine release is accelerated in the presence of Ti relative to either neat I₂O₅ or Al/I₂O₅. Despite the lower decomposition temperature that actual kinetics of decomposition is considerably faster for the neat I₂O₅, which is consistent with the T-jump/TOFMS results in Fig. 3. This is also consistent with previous studies [38] which show interactions between oxide shell of the metal which spread out the iodine release.

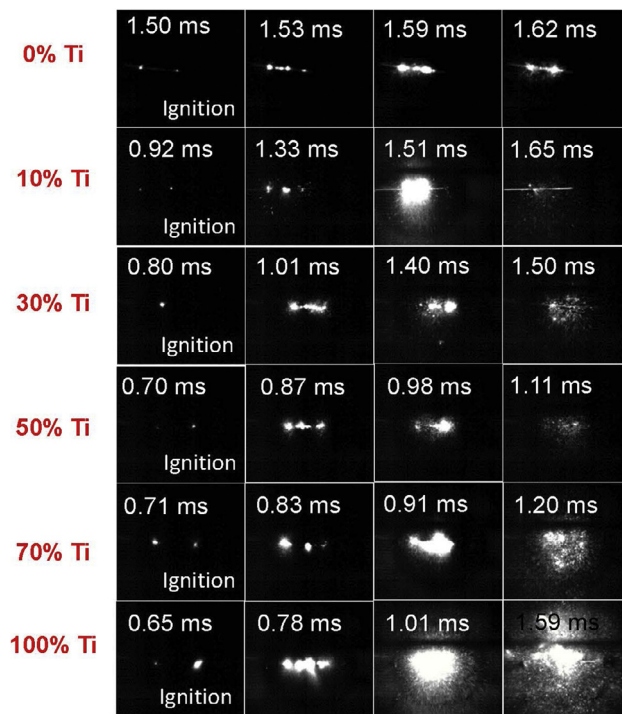


Fig. 5. Temporal images of the wire ignition of Al/Ti/I₂O₅ composites with different Ti content relative to Al. Note: time stamps are measured from trigger. The first images for each sample show the ignition of samples and the three others show the combustion. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

To further investigate the role of the oxide shell in catalyzing iodine release we evaluate decomposition of neat I₂O₅, Al₂O₃/I₂O₅ and TiO₂/I₂O₅. The ratios of TiO₂/I₂O₅ and Al₂O₃/I₂O₅ are based on the content of oxide shell in the stoichiometric Al/I₂O₅ and Ti/I₂O₅ composites. The results in Fig. 6 shows that alumina clearly catalyzes the decomposition of I₂O₅, but also fixes some iodine, given that some is released late as evidenced both in the TGA as well as a smaller secondary iodine release peak in the MS signal (Fig. 6(b)). The early effect from TiO₂ is not as evident, despite the fact that at both high and low heating rates (Figs. 3 and S9) the on-

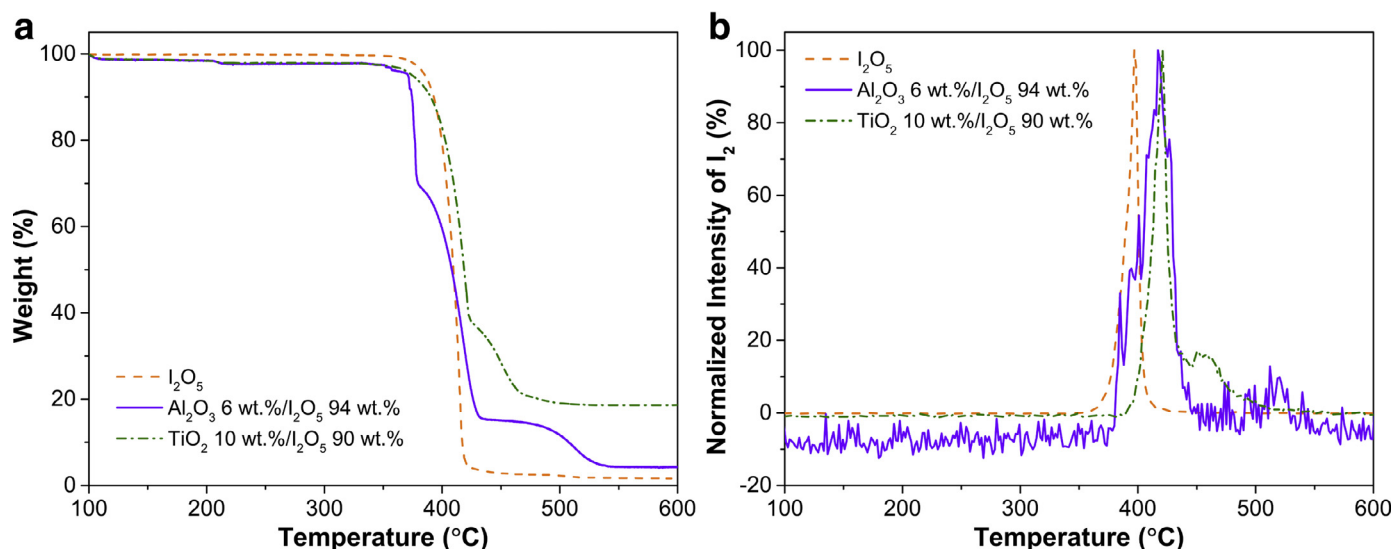


Fig. 6. TGA (a) and mass spectra of I_2 (b) of I_2O_5 , TiO_2 10 wt%/ I_2O_5 90 wt%, and Al_2O_3 6 wt%/ I_2O_5 94 wt%. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

set of iodine release is clearly enhanced by Ti. It is clear however that similar to alumina some of the iodine is fixed as the TGA decomposition step is clearly broader than the neat iodine oxide. All this suggests that there is clear interaction of the oxidizer and the native oxide shell in both fuels. This is different from the results in our previous work where TiO_2 decreased the decomposition temperature of $KClO_4$ [36].

4. Conclusions

In this study, nTi was added to the Al/I_2O_5 and the ignition temperature and combustion behavior of mesoparticles formed by electro spray were evaluated. The combustion behavior showed that nTi can enhance the reactivity of Al/I_2O_5 thermites significantly with increases in pressure, pressurization rate and dramatic decreases in burn time observed. Part of this behavior can likely be attributed to less sintering enhancing the completeness of reaction in the Ti added cases. The ignition temperature was very sensitive to Ti addition and could be decreased by over 300 °C. Both iodine and oxygen release temperatures of Al/I_2O_5 were steadily decreased by the addition of Ti. These results show that titanium can be used as a fuel to tune energetic behavior and iodine release temperature and in some ways superior to aluminum.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2019.04.049.

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