



Tailoring energy release of nano-Si based thermites via incorporation of Ti nanoparticles

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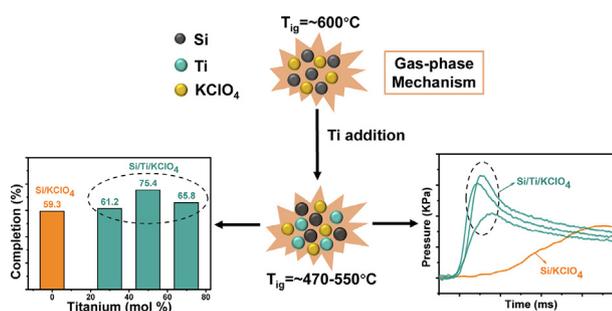
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HIGHLIGHTS

- The combustion behavior and ignition mechanism of several Si-based thermites were investigated.
- The incorporation of Ti nanoparticles reduced the ignition temperature of Si/KClO₄.
- The enhanced reactivity of Si/KClO₄ has been shown via adding Ti nanoparticles.
- The combustion efficiency of Si/Ti/KClO₄ has been improved compared to Si/KClO₄.

GRAPHICAL ABSTRACT



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ABSTRACT

This work explores the ignition mechanism of silicon (Si) based thermites, and it is supposed that the phase change of silica (SiO₂) coating on the Si core producing fractures may play a crucial role in the ignition of Si-based thermites. Several Si-based thermites were evaluated by the combustion test and calorimeter, and potassium perchlorate (KClO₄) is turned out to be a promising oxidizer given the high reactivity and considerable heat release. Titanium (Ti) nanoparticles with a lower onset oxidation temperature than Si were incorporated into Si/KClO₄ system via a facile sonicating method. The ignition temperature of Si/KClO₄ has reduced markedly by ~80–130 °C with significant increases of ~5–8x in pressurization rate and decreases by a factor of ~2–3 in burn time when adding 30–70% Ti by mole into the fuel. The combustion efficiency is improved dramatically from ~59% to ~73%. The enhanced combustion performance could be attributed to the lower ignition temperature of Ti/KClO₄ leading to the initiation reaction of the ternary composites, thus promoting energy release and the reactivity of the ternary system. This work not only investigates the ignition mechanism of Si-based thermites but also sets a stage for tuning the ignition and combustion of Si-based thermites via facile incorporation of Ti nanoparticles.

1. Introduction

Thermites are energetic composites typically consisting of fuels and oxidizers that can release large amounts of energy rapidly upon

ignition, which are widely used in gas generators, pyrotechnics, and micro propulsion [1–5]. Aluminum (Al) [6] is the most commonly used fuel in thermites due to its low cost and ease of manufacture, and also because that its ignition behavior can be improved by the particle size

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transitions into nanoscale [7]. However, Al nanoparticles are passivated by alumina (Al_2O_3) layer, which is dead-burned materials with a thickness of $\sim 2\text{--}6$ nm and retards the ignition of Al to some degree. Since the Al core could not diffuse from the impervious Al_2O_3 until the phase change of Al_2O_3 or the melting of Al causing the break-up of oxide shell [5,8]. Some novel Al-based thermites with enhanced combustion performance have been developed recently via introducing energetic metal organic frameworks, tea polyphenols, polydopamine, and graphene oxide [9–13]. In addition to Al, silicon (Si) is a particularly attractive fuel candidate due to the comparable heating values of Si (33.9 kJ/g and 78.9 kJ/cm³) [14,15], which are comparable to those of Al (30.8 kJ/g and 83.3 kJ/cm³) [16,17]. The protective shell (silica, SiO_2) thickness of Si nanoparticles ($\sim 1\text{--}3$ nm [18]) is considerably thinner relative to Al nanoparticles [19], leading to higher active metal content. Several studies have been done to investigate the basic properties of Si-based energetic materials. Mason et al. predicted theoretically that among Si/oxidizer systems, the maximum adiabatic combustion temperature was achieved by Si/perchlorate systems (~ 2730 °C), and Si/ NH_4ClO_4 produced the most gas with the fastest burning rate of ~ 530 m/s [20]. Terry et al. characterized the combustion temperatures Si/polytetrafluoroethylene (Teflon)/Viton composites, and the results showed that the measured combustion temperatures varied from ~ 1390 °C to ~ 2140 °C [21]. However, unlike the well discussion about the ignition mechanism of Al-based thermites, few studies about the ignition of Si-based energetic materials were conducted, which will be investigated in this work.

Despite several advantages of silicon, the oxide layer (SiO_2) coating on the core of Si may delay the ignition of silicon and reduce the combustion efficiency [22]. A large body of studies have been performed on Si-based thermites to improve the ignitibility by either decreasing the size of Si or improving the contact area between fuels and oxidizers. Meir et al. reported an effective approach to initiate the reaction of thermites via low-power microwaves [23]. Huang et al. found that the reduction of the Si particle size from 1 to 5 μm to $20\text{--}30$ nm could decrease the onset temperature dramatically from ~ 935 °C to ~ 805 °C [24]. They also studied the structure effect of nanosilicon-based thermites on their ignition properties, and the results indicated that better interfacial contact quality between Si and Fe_2O_3 permitted a lower onset temperature at ~ 550 °C than mechanically mixed Si/ Fe_2O_3 thermites (> 650 °C) [25]. Zuo et al. prepared Si@AP/NC composites by electrospray, and the decomposition of AP transitioned from two stages into one stage, which has improved the heat release properties of Si nanoparticles [22]. Besides tuning the particle size of fuels [24] and promoting the contact between fuels and oxidizers [22,26] to enhance the combustion performance of energetic materials, adding a ternary component is another helpful and facile way. Other fuels such as boron (B), silver (Ag), carbon black (CB), and magnesium (Mg) have been employed as an additive for Al-based thermites by sonicating mixing or ball-milling [16,27–29]. Sullivan et al. found that adding < 50 mol% nanoboron (nB) led to ~ 3 times improvement in reactivity compared to Al/CuO [16]. The combustion rate of Al/CuO increased from ~ 740 m/s to ~ 940 m/s by incorporating 2 wt% Ag [27]. The incorporation of CB and Mg could reduce the initiation temperature of Al-based thermites by over 100 °C and ~ 200 °C respectively [28,29]. Besides, nanotitanium (nTi) has also attracted increasingly interests for acting as a fuel in nanoenergetic composites. When reacting with potassium perchlorate (KClO_4), the ignition event occurred at ~ 450 °C, and the nanostructure of Ti could be preserved without losing nanostructure under rapid heating rates [30]. Shoshin et al. found that the ignition temperature of AlTi alloy for processing the aerosol flame was ~ 900 °C lower than neat Al [31]. Even though that several fuels have been added into Al-based thermites, few works are about efforts to improve the energetic performance of Si-based thermites via this method.

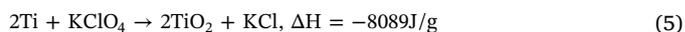
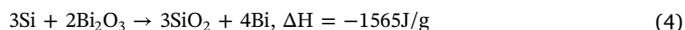
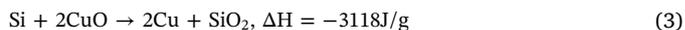
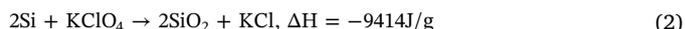
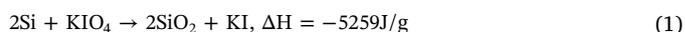
In this paper, the ignition of several Si-based thermites composed of Si and oxidizers with various oxygen release temperatures was characterized via temperature-jump (T-jump)/time of flight mass (TOF-MS)

to investigate their ignition mechanism. Besides, the combustion performance of them was evaluated by combustion cell tests and calorimeter, and KClO_4 was found as an optimized oxidizer for Si-based thermites. Ti nanoparticles were employed as an additive, considering that the lower heating value per mass (19.7 kJ/g) of Ti than Si, to Si/ KClO_4 composites with varying molar content (in the fuel) from 30% to 70%. The ignition of Si/Ti/ KClO_4 has been characterized by T-jump. Then, the combustion behavior including reactivity and combustion efficiency of Si/Ti/ KClO_4 nanocomposites has also been evaluated.

2. Experimental section

2.1. Materials and sample preparation

Nanosilicon (nSi) ($\sim 20\text{--}30$ nm) and nanotitanium (nTi) ($\sim 20\text{--}50$ nm) were purchased from Aladdin Industrial Corporation. The oxidizers including KIO_4 , KClO_4 , CuO, and Bi_2O_3 were purchased from Sigma-Aldrich. Composites studied in this work were prepared by sonication dispersion. The stoichiometric ratio of fuels and oxidizers was determined based on their reaction equations as shown in Eqs. (1)–(5), accompanied by the expected energy release.



The weighed amount of fuels and oxidizers were put into a vial and sonicated in 10 mL hexane for 30 min. After drying the samples overnight in the hood, the powders were broken apart gently by a spatula to obtain loose powders for further measurements.

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

The ignition and produced gaseous species during the combustion process were characterized by T-jump/TOF-MS [32], which has been shown in Fig. S1 and described in detail in ref. [33]. Typically, a layer of thermites was loaded onto the platinum wire with a width of 76 μm and a length of 10 mm. Then thermites were rapidly joule heated to 1200 °C in 3 ms with a heating rate of $\sim 4 \times 10^5$ °C/s. The temporal temperature of the wire can be obtained according to the Callender-Van Dusen equation from recorded voltage and current signals [34]. The mass spectra of gaseous species were obtained every 0.1 ms.

2.3. Combustion cell test

The reactivity was characterized via the combustion cell test. Typically, ~ 25 mg thermites powders were put into a combustion cell with a constant volume of ~ 20 cm³. Then thermites were joule heated and ignited by the nichrome, which is on the top of the sample. With the existence of a piezoelectric pressure sensor and a photodetector, pressure and optical signals were obtained. By calculating the slope of the initial pressure rise, the pressurization rate can be obtained, and the full width at half maximum (FWHM) of the optical curve represents the burn time. The pressurization rate measured via constant-volume combustion cell test has been used to determine the reactivity of thermites by several authors [16,35,36]. Thus, the definition of reactivity in this study is the measured pressurization rate. The combustion test of each sample was conducted in triplicate, and the average values were presented with error bars representing the calculated standard deviation. The detailed experiment description can be found in ref. [37,38].

2.4. Calorimeter measurement

The heat release during the combustion of Si-based thermites was measured in a calorimeter [39]. Generally, ~200 mg thermites were put into a steel crucible, and the calorimeter was sealed. The sample was ignited at 1 atm pressure of air by the nichrome filament via joule heating. The nichrome bridges two electrical pins and bents into the samples. The released heat from the reaction dispersed into the water bath within the calorimeter and caused the temperature of the system to increase. Thus, the heat release can be obtained. The experimental setup for the calorimeter could be found in Fig. S2.

2.5. SEM and XRD characterization

The morphology of Si-based thermites and Si/Ti/KClO₄ composites was characterized via scanning electron microscopy (SEM, Hitachi S-4800), which has been shown in Figs. S3–S4. Elemental distribution and elemental mapping were obtained by energy-dispersive X-ray spectroscopy (EDS), and the EDS images of Si/70% Ti/KClO₄ composites were shown in Fig. S5. The combustion products of Si-based thermites and Si/Ti/KClO₄ composites have been collected and characterized by powder X-ray diffraction (XRD, Bruker D8 Advanced using Cu K α radiation).

3. Results and discussion

3.1. Ignition and combustion performance of nSi-based thermites

3.1.1. Ignition characterization and mechanism investigation

To figure out the ignition mechanism of nSi-based thermites, KIO₄, KClO₄, CuO, and Bi₂O₃ with various oxygen release temperatures ranging from ~450 °C to ~860 °C [40,41] have been mixed with Si, and the ignition was characterized by T-jump/TOF-MS. The formulation for Si-based thermites could be found in Table 1.

According to the relationship between the ignition temperatures of thermites (T_{ig}) and the oxygen release temperatures of corresponding oxidizers (T_{O_2}) (Fig. 1), Si-based thermites could be divided into two groups. The first group including Si/KIO₄ and Si/KClO₄ has $T_{ig} > T_{O_2}$, which suggests that thermites ignite after the oxygen release of corresponding oxidizers. The ignition of these thermites is driven by the reaction between the released oxygen from oxidizers and the Si, thus undergoing a gas-phase mechanism [41]. The remaining ones ignite before the oxygen is released from CuO and Bi₂O₃, which means no gaseous oxygen appears prior to the initiation of thermites reaction, and the ignition of thermites begins with the interaction of the Si and oxygen ions diffusing from oxidizers. Therefore, these thermites follow a condensed phase route [41].

The mass spectrometry of gaseous species during the rapid heating has been analyzed to further explore the nSi-based thermites reaction. For Si/KIO₄ (Fig. 2a), the oxidizer decomposes first to release oxygen with the appearance of O₂⁺ before the ignition point. The oxygen reacts with Si to form SiO₂, and K⁺ and I⁺ can be found in the gaseous products decomposing from KIO₄. Similarly, in the gaseous products of Si/KClO₄ (Fig. 2b), O₂⁺ and K⁺ appear before the ignition event. For condensed-phase-mechanism based thermites, SiO⁺ appears after the ignition of Si/CuO and Si/Bi₂O₃ in Fig. 2c and d. It makes sense because Si reacts with

the oxygen ion diffusing from oxidizers in the condensed phase, thus SiO⁺ can be detected by the mass spectrometry. Then, SiO⁺ is further oxidized and transformed into SiO₂, which is supposed to be the final product. In addition, there is no O₂⁺ appearing before the ignition of Si/Bi₂O₃ since the ignition temperature is ~300 °C lower than the oxygen release temperature of Bi₂O₃. For Si/CuO, the appearance of O₂⁺ is likely due to the proximity of the oxygen release of CuO and the ignition of Si/CuO. The gaseous species with corresponding m/z values have been summarized in Table S1.

However, it seems like that there is a threshold for the ignition temperature of Si-based thermites from Fig. 1, which is near the phase change of SiO₂ (~573 °C, from α -SiO₂ to β -SiO₂) [42]. Even if KIO₄ releases oxygen at ~450 °C, the corresponding thermites ignite at ~600 °C, which is different from nanocarbon (nC)/KIO₄ [41] igniting upon the oxygen release of KIO₄ since there is no oxide shell for nC. It reveals that nSi has a different ignition mechanism from nC owing to the oxide shell of Si. For Si, the melting points of the nascent oxide shell (SiO₂) and Si are 1715 °C and 1414 °C respectively, which are much higher than the measured ignition temperatures. This suggests the initiation of the ignition must be related to the change of oxide shell (SiO₂) coating on the Si that allows the diffusion of gaseous oxygen and the ignition event, which leads to the self-sustained oxidation of the Si core like Al and tantalum [41,43].

Furthermore, it is well documented that the α -SiO₂ transforms to β -SiO₂ abruptly at ~573 °C [42,44]. The fracturing can be easily induced since a significant change in volume occurring with the transformation [44,45]. Thus, it is reasonable to conjecture that the cracks caused by the transformation of α -SiO₂ into β -SiO₂ provide a low-resistance pathway for the oxygen to react with the Si core across the SiO₂ boundary. Therefore, the phase change of SiO₂ on the core of Si becomes the prerequisite for the ignition of Si-based thermites either with a gas-phase mechanism or condensed-phase mechanism, resulting in a threshold ignition temperature of ~573 °C as shown in Fig. 1.

3.1.2. Reactivity characterization

Table 2 shows the wide range in combustion performance of nSi-based energetic materials with calculated adiabatic flame temperature (AFT) and peak pressures via REAL Version 3.0 (Computer Modeling of Complex Chemical Equilibrium at High Pressure and Temperature). The calculations via REAL are conducted based on the Minimum Free-energy Law. The calculations are done assuming a 25 mg mass in a 20 cm³ combustion cell, and constant-volume combustion is used to evaluate the peak pressure of the system.

The experimental highest peak pressure is achieved by Si/KClO₄, which is ~40 kPa higher than Si/KIO₄ and is ~5 and ~2 orders of magnitude greater when compared to Si/CuO and Si/Bi₂O₃, respectively. The trend of measured peak pressure aligns with the calculated ones. The peak pressure of Si/KIO₄ is comparable with Si/KClO₄, indicating that Si/KClO₄ and Si/KIO₄ composites generated more gas than Si/CuO and Si/Bi₂O₃ during the combustion accompanied with relatively higher AFT. Since the peak pressure is related to the amount of gaseous products and the achieved flame temperature during the combustion. No experimental data for flame temperature is available, thus the calculated AFT values are adopted in this study [46,47].

The maximum reactivity that refers to the pressurization rate [16] in this paper is achieved by Si/KClO₄, which is ~0.5 times higher than the ones of Si/KIO₄ and Si/Bi₂O₃. Si/CuO system has the lowest pressure rise rate with not surprisingly the longest burn time. The reactivity of Si-based thermites is correlated with the gas generation rate of oxidizers [41]. Based on these results, Si-based thermites can be generally divided into two groups: reactive thermites with higher peak pressure and reactivity (Si/KClO₄ and Si/KIO₄), which ignite in a gas-phase mechanism and the less reactive thermites (Si/CuO and Si/Bi₂O₃) involving a condensed-phase mechanism.

In addition, the calculated peak pressure is dependent on the AFT and the amounts of combustion products in the gas phase [48]. The

Table 1
Stoichiometric thermites formulation of Si-based thermites.

Thermites	Si (wt. %)	Oxidizer (wt. %)
Si/KIO ₄	19.6	80.4
Si/KClO ₄	28.9	71.1
Si/CuO	15	85
Si/Bi ₂ O ₃	8.3	91.7

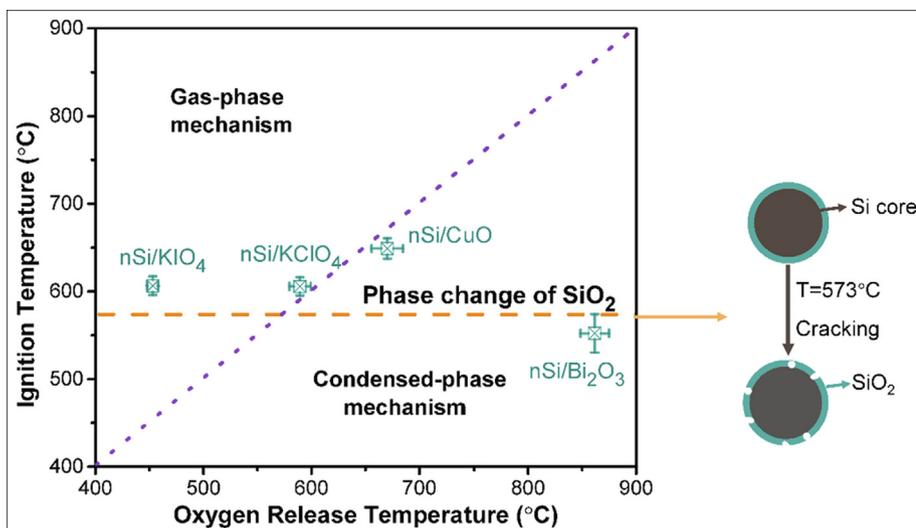


Fig. 1. Ignition temperature of Si-based thermites vs. oxygen release temperature of corresponding oxidizers [41]. Note: The diagonal violet dotted line represents a perfect correlation. The horizontal orange dashed line stands for the transition temperature of α - SiO_2 into β - SiO_2 (573°C) [42]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

high AFT and a large amount of products (~ 1.55 mol/100 g) achieved by Si/ KClO_4 result in a high calculated peak pressure. In comparison, even though the amount of Si/ CuO reaction products (~ 1.60 mol/100 g) is greater than Si/ KClO_4 , the calculated peak pressure is the

lowest due to the relatively lower AFT. As for the discrepancy between the experimental peak pressure and calculated values, the lower experimental values than calculations may be caused by the incompleteness of Si-based thermites reactions or some powders quenching on the walls

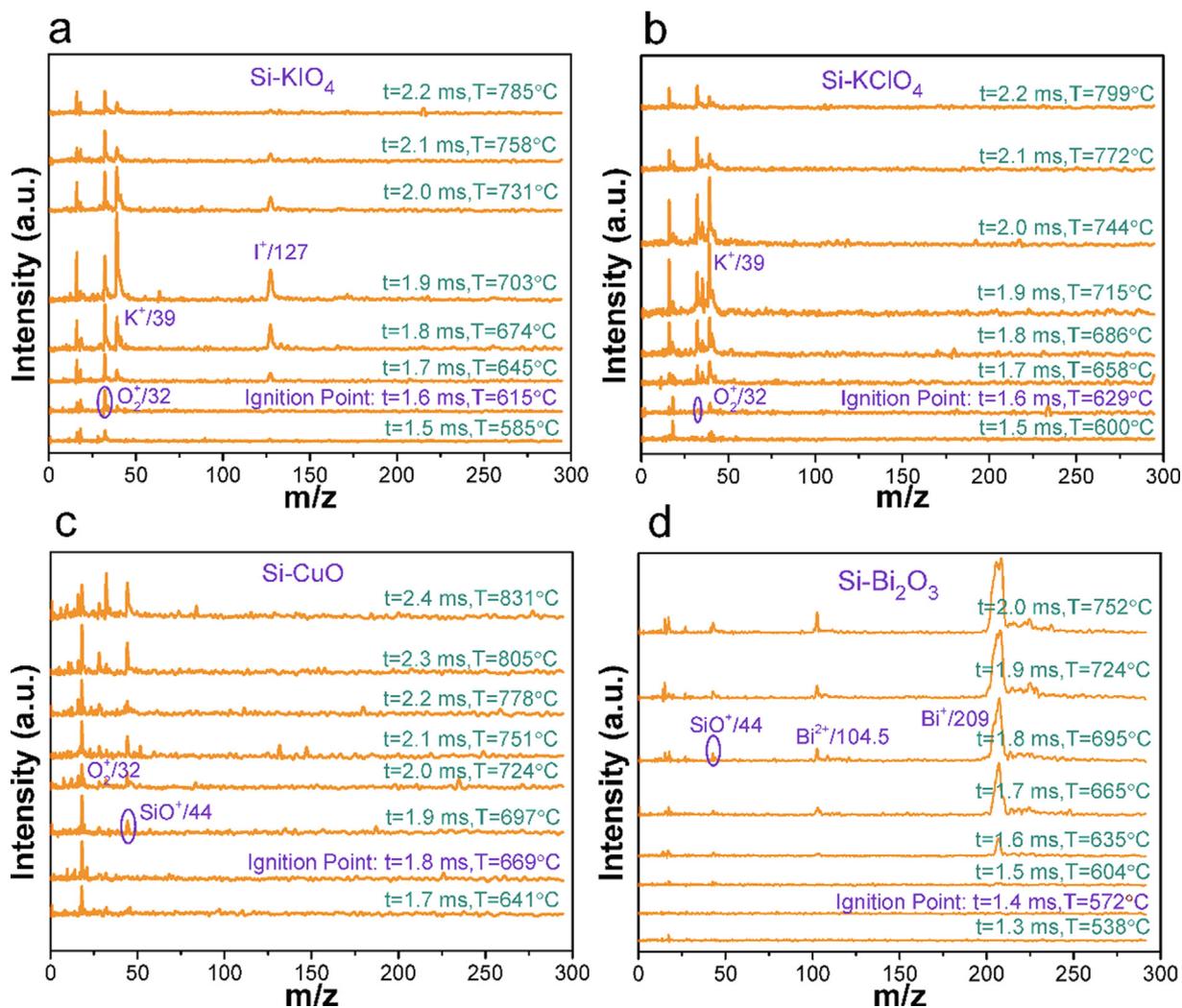


Fig. 2. Time-resolved mass spectra of Si-based thermites: (a) Si/ KIO_4 , (b) Si/ KClO_4 , (c) Si/ CuO , and (d) Si/ Bi_2O_3 . Note: " m/z " represents the mass-to-charge ratio of produced gaseous species.

Table 2
The combustion test and calculations results for Si-based thermites.

Thermites	Peak Pressure (KPa)	Pressurization Rate (KPa/ms)	Burn Time (ms)	AFT (°C)	Calculated Peak Pressure (KPa)
Si-KIO ₄	132.3 ± 9.8	24 ± 1.9	4.1 ± 0.7	3334	360.5
Si-KClO ₄	175.5 ± 11.1	38.7 ± 9.6	5.1 ± 0.6	3475	551.8
Si-CuO	35.3 ± 13.5	0.5 ± 0.2	47.7 ± 15.6	2579	109.5
Si-Bi ₂ O ₃	66.9 ± 8.0	22.1 ± 3.0	4.0 ± 1.0	2286	122.3

Table 3
Heat release of Si-based mixtures measured by the calorimeter and the completion of the reaction.

Thermites	Exp. ΔH (J/g)	Theo. ΔH (J/g)	% Complete
Si-KIO ₄	3380 ± 267	5259	74
Si-KClO ₄	5583 ± 191	9414	59
Si-CuO	1448 ± 79	3118	46
Si-Bi ₂ O ₃	958 ± 37	1565	61

[49,50].

3.1.3. Heat release measurement

The measured heat release results of Si-based thermites shown in Table 3 show that the heat release of Si/KClO₄ is the highest and is ~2200 J/g higher than Si/KIO₄ even though with a relatively lower reaction completion of ~59% compared to Si/KIO₄ (~74%). The lower completion of Si/KClO₄ may be caused by the incomplete decomposition of KClO₄ during the reaction as shown in the XRD characterization of combustion products (Fig. S6). However, for Si/KIO₄, no remaining KIO₄ exists in the products, and part of KIO₄ only underwent the first stage of decomposition to KIO₃ as shown in Fig. S6. Corresponding with the theoretical reaction enthalpy values, the measured heat release of Si/CuO and Si/Bi₂O₃ are significantly lower than ones of Si/KClO₄ and Si/KIO₄. The incompleteness of Si/CuO and Si/Bi₂O₃ reaction is caused by the remaining Si and Bi₂O₃ respectively as shown in Fig. S6.

Combined with the pressure cell test and heat release results, KClO₄ can be a promising oxidizer in Si-based thermites considering the highest reactivity, AFT, and experimental heat release value along with a considerable combustion efficiency.

3.2. Influence of Ti on the energy release of Si/KClO₄

Since we conclude that the ignition of nSi-based thermites may be limited by the phase change of SiO₂ coating on the Si core, and KClO₄ can be an attractive oxidizer for Si-based thermites. Ti nanoparticles whose ignition temperature with KClO₄ [30] is significantly lower relative to Si were incorporated to Si/KClO₄ thermites to explore the influence. The formulation of Si/Ti/KClO₄ composites has been shown in Table 4. Si/30% Ti/KClO₄ signifies that the molar content of Ti and Si in fuels are 30% and 70% respectively, and KClO₄ is stoichiometric.

3.2.1. Ignition measurement of Si/Ti/KClO₄ nanocomposites

The addition of 30 mol% and 70 mol% Ti into the Si/KClO₄ system brings the reaction initiation to ~80 °C and ~130 °C lower temperatures respectively as shown in Fig. 3. When Si is replaced with Ti, the

Table 4
Stoichiometric thermites formulation (Si/Ti/KClO₄).

Thermites	Si (wt. %)	Ti (wt. %)	KClO ₄ (wt. %)
Si/KClO ₄	28.9	0.0	71.1
Si/30% Ti/KClO ₄	18.0	18.9	63.1
Si/50% Ti/KClO ₄	11.9	29.2	58.9
Si/70% Ti/KClO ₄	6.7	38.2	55.1
Ti/KClO ₄	0.0	49.8	50.2

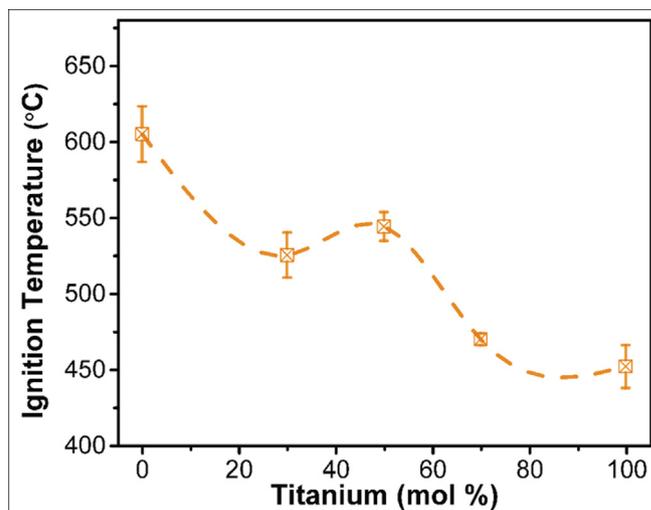


Fig. 3. The ignition temperature of Si/Ti/KClO₄ as a function of the Ti molar percentage in the fuel.

ignition temperature reduces dramatically to ~450 °C relative to Si/KClO₄ (~600 °C). The combustion snapshots in Fig. 4 indicate that the reaction initiated ~0.2 ms earlier with the existence of Ti in the fuel, which is corresponding to the trend of ignition temperature. In addition, in comparison to pure Si and Ti-based composites, Si/Ti/KClO₄ reaction becomes much more violent visibly with stronger light emission. Therefore, the lower initiation temperature of Si/Ti/KClO₄ can be attributed to the low ignition temperature of Ti/KClO₄ that induces the reaction of Si/KClO₄ [28]. The non-linear ignition temperature change is speculated to be related to the different intermetallic reactions between Si and Ti during rapid heating [51,52]. Ti could be used to tune the ignition temperature and the combustion intensity of the Si/KClO₄ system.

3.2.2. Enhanced reactivity of Si/KClO₄ by adding Ti

Pressure signals shown in Fig. 5a indicate that Si/Ti/KClO₄ nanocomposites undergo a faster reaction than Si/KClO₄ and Ti/KClO₄. The peak pressure of Si/Ti/KClO₄ is achieved at ~1–1.5 ms as opposed to ~2.5 ms for Ti/KClO₄ and ~6.5 ms for Si/KClO₄. The summarized peak pressure values in Fig. 5b show that the peak pressures of pure Si-based thermites is slightly higher as a comparison to Ti-based ones, which is consistent with the calculation results from REAL (Fig. S7), indicating more produced gas during the combustion of Si/KClO₄ even though the AFT of Si/KClO₄ is slightly lower than Ti/KClO₄.

However, different from the trend of calculated peak pressure, the peak pressures of thermites with the existence of both Si and Ti are higher than pure Si and Ti-based thermites, which indicates a kinetic dominates more than thermodynamics in these cases. The peak pressure achieved by Si/30% Ti/KClO₄ is twice higher than that of Si/KClO₄. Similarly, the pressurization rates of Si/Ti/KClO₄ composites are higher than Si and Ti-based binary systems as shown in Fig. 5c along with shorter burn times (Fig. 5d). The optical emission of composites and the determination of burn time could be found in Fig. S8. The peak value for the pressurization rate is achieved by Si/30% Ti/KClO₄ and is increased by a factor of ~8 accompanied with ~3X shorter burn time

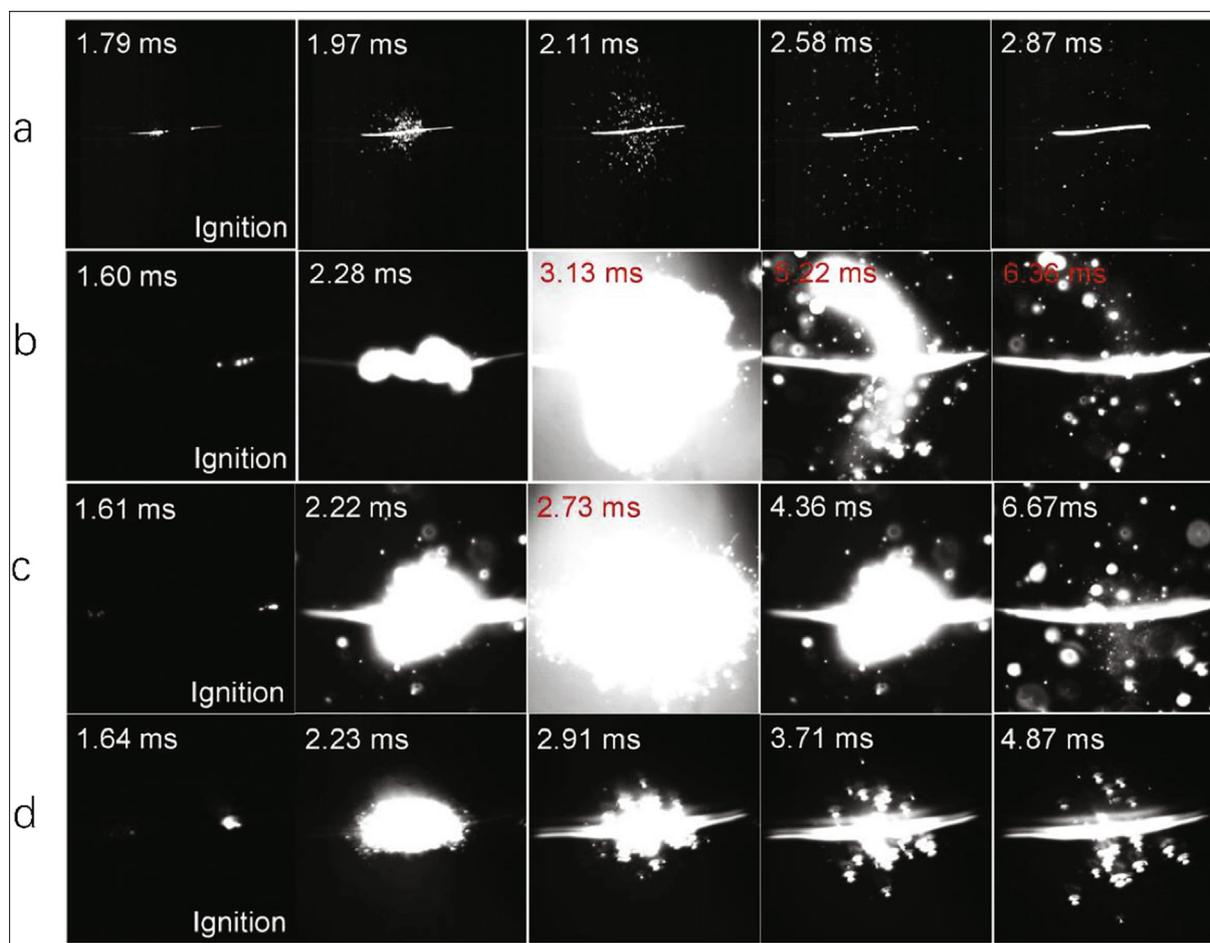


Fig. 4. Combustion snapshots of Si/KClO₄ (a), Si/30% Ti/KClO₄ (b), Si/70% Ti/KClO₄ (c), and Ti/KClO₄ (d) nanocomposites. Note: The time labels represent the time after the trigger. The first images for each sample show the ignition and the others show the combustion.

relative to Si/KClO₄, which is a significant enhancement and is also in good agreement with the peak pressure results (Fig. 5b).

Combined with the ignition measurement (Fig. 3), it is supposed that the reaction between Ti and KClO₄ initiating at a lower temperature triggers and advances the ignition of the ternary Si/Ti/KClO₄ systems [28], accelerating the reaction of Si/KClO₄. The primary reaction (Ti/KClO₄) provides enough energy for a more complete energy release of Si/KClO₄ [16,51], thus resulting in higher peak pressure and reactivity of Si/Ti/KClO₄ composites. The high exothermic intermetallic reaction between Si and Ti may also enhance the reaction of the ternary system [48].

3.2.3. Increased combustion efficiency of Si/KClO₄ via Ti addition

The percentages of completion are estimated and shown in Fig. 6 by comparing the experimental heat release with corresponding theoretical values, which are calculated based on the theoretical enthalpy of Si/KClO₄ and Ti/KClO₄ and their mass percentages in ternary composites. Relative to Si-based thermites, the experimental values of the Si/30% Ti/KClO₄ and Si/70% Ti/KClO₄ are comparable to that of Si/KClO₄ even though the theoretical enthalpy of the Si/Ti/KClO₄ mixtures is lower than Si/KClO₄. As for Si/50% Ti/KClO₄, the heat release measured by calorimeter is $\sim 6300 \pm 577$ J/g, which is ~ 700 J/g higher than Si/KClO₄ and is a significant enhancement in heat release. A higher extent of reaction was achieved by ternary thermites relative to that of Si/KClO₄ ($\sim 59\%$). The completion of Si/50% Ti/KClO₄ is the highest one, which is $\sim 73\%$ overall and $\sim 14\%$ higher than Si/KClO₄. The XRD characterization of the combustion products (Fig. S9) can further confirm it, and a more detailed description can be seen in the

Supplementary Information.

Recent work suggested that a higher combustion efficiency can be achieved by the thermites that release a large amount of gas by prohibiting the active reactants from aggregating [49]. It is consistent with the results shown in this work that the higher peak pressure achieved by Si/Ti/KClO₄ composites (Fig. 5b), which means larger amounts of gaseous products, corresponds to the higher combustion efficiency of Si/Ti/KClO₄ composites as shown in Figs. 6 and S9. It is reasonable to postulate that the more gas production by Si/Ti/KClO₄ composites prevents the coalescence of nSi, thus resulting in the disappearance of nSi in the combustion products and promoting their reaction extent.

Therefore, the ignition temperature of Si/Ti/KClO₄ ternary composites reduced significantly by ~ 80 – 130 °C in comparison to Si/KClO₄. The reactivity and combustion efficiency of Si/Ti/KClO₄ are much greater than ones of Si/KClO₄ and Ti/KClO₄ binary composites, which provides a facile way to improve the combustion performance of Si-based thermites.

4. Conclusion

In summary, the ignition of Si-based thermites is likely to be limited by the phase change of SiO₂. The ignition mechanism of Si/KClO₄ and Si/KClO₄ is the gas-phase mechanism, and Si/CuO and Si/Bi₂O₃ involve a condensed-phase route during the ignition. Among four oxidizers, KClO₄ is found to be an attractive oxidizer for Si-based thermites considering the combustion performance. To lower the initiation temperature, Ti nanoparticles with a lower onset oxidation temperature were added into the Si/KClO₄ system by a facile sonication way. The

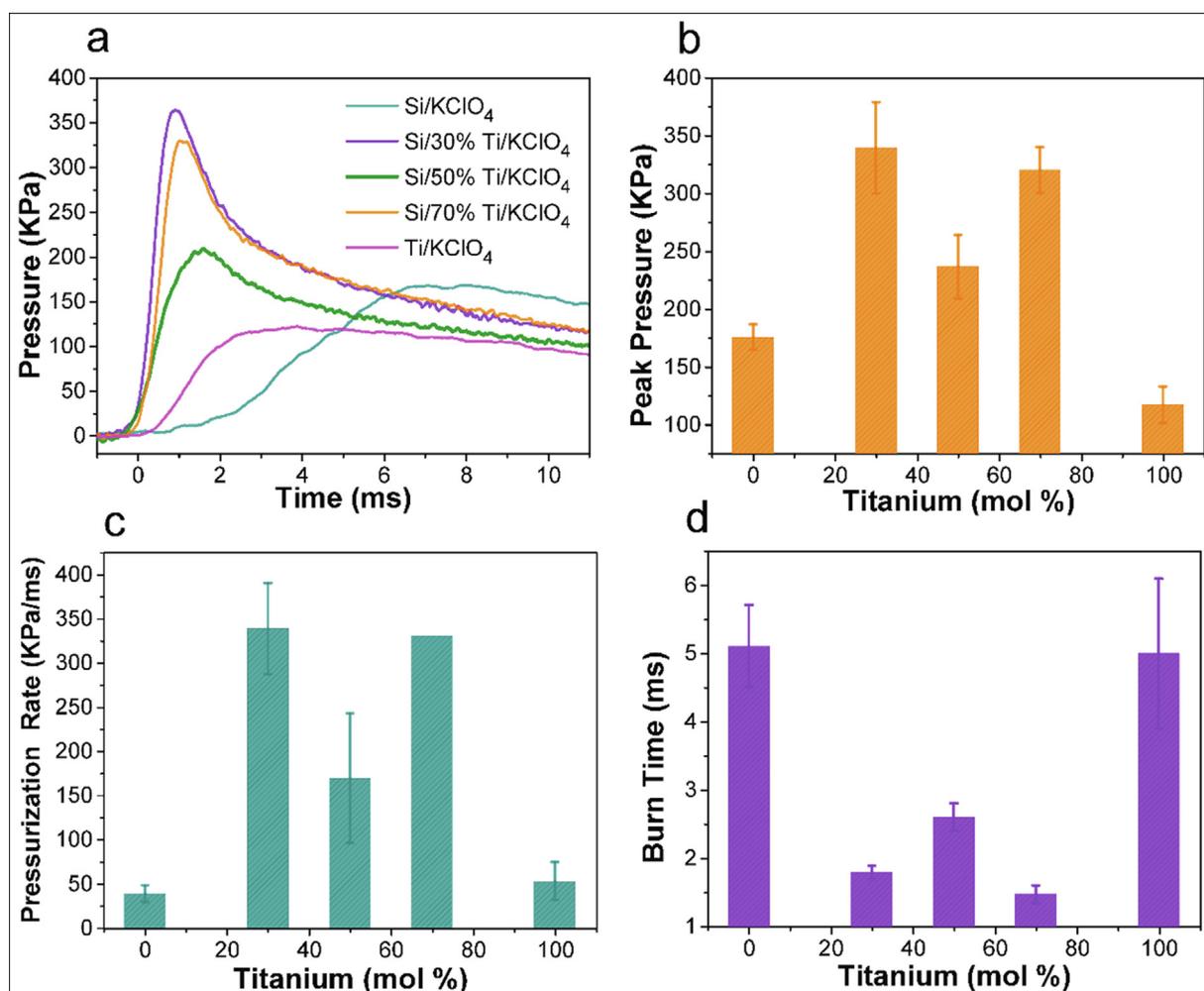


Fig. 5. (a) The pressure trace of Si/Ti/KClO₄ nanocomposites, the trend of (b) Peak pressure, (c) pressurization rate, and (d) burn time of Si/Ti/KClO₄ with varying Ti molar contents.

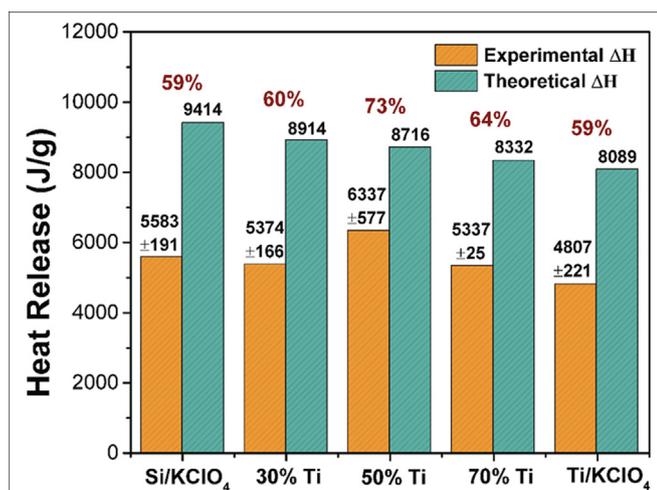


Fig. 6. Heat release of Si/Ti/KClO₄ mixtures measured by the calorimeter and calculated theoretically. Note: the percent above columns represents the reaction extent of thermites.

ignition temperature of Si/KClO₄ can be reduced by ~80–130 °C effectively by adding 30%–70% mol Ti into the fuel. The combustion behavior of Si/KClO₄ has been enhanced significantly via the addition of Ti, including a ~2X peak pressure, ~8X reactivity, and ~3X shorter

burn time. The completion of the reaction increases ~14% compared to Si/KClO₄ mixtures after adding 50 mol% Ti. We propose that upon Ti is added as a second fuel, the reaction between Ti and KClO₄ initiating at ~450 °C could trigger the reaction initiation of Si/Ti/KClO₄ nanocomposites, which accelerates the energy release of Si/KClO₄ and promotes the reactivity. The larger amounts of gaseous products contribute to a higher extent of reaction. Therefore, Ti could be a promising additive to Si-based thermites for tailoring either the ignition or combustion performance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://>

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