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Influence of Titanium Addition on Performance of Boron-based Thermites

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Abstract: Boron (B) is an attractive fuel for its high energy density, however, the native oxide shell retards boron ignition/combustion. In this study, nano titanium (nTi) powders were added into nano boron (nB)/copper oxide (CuO) and micron boron (μB)/CuO mixtures at various molar ratios. The reactivity for both nB/CuO and μB/CuO were increased significantly by ~3-6 times with the addition of nTi. The possible mechanism for the enhanced reactivity have been investigated via the direct addition of the native oxide of titanium (TiO_2). Enhancement in reactivity is partly attributed the interaction of TiO_2 with the melting boron oxide (B_2O_3) shell. The TiO_2/B_2O_3 mixture in non-liquid phase creates pathway for oxygen to diffuse and thus enhances the boron oxidation rate. In addition, the higher flame temperature due to reaction of Ti and CuO promotes the volatilization of B_2O_3 and melting of boron, resulting in faster reaction between B and CuO.

Keywords: Titanium, Boron, Thermites, Reactivity, Reaction mechanism

1 Introduction

Aluminum (Al) is by far the most common fuel used in energetics including propellants, explosives and pyrotechnics because of its high reaction enthalpy and low cost [1-3]. Boron (B) has always remained an aspirational alternative fuel because of its higher energy density, however, it has only seen limited use due to its kinetic constraints [4-7]. Since the naturally-occurring boron oxide (B_2O_3) shell has a much lower melting temperature than that of the core (~450°C vs. ~2076°C, respectively) [8], the oxide layer on the surface significantly impedes the ignition of boron particles by forming a liquid barrier to oxidation [9, 10]. Additionally, the formation of metaboric acid (HBO_2) in the presence of any hydrogen lowers the energy release [11]. It is generally accepted that boron combustion occurs in two steps [12-15]: (1) the slow oxidation of B core due to the existence of the molten oxide shell, constitutes a significant portion of the whole burn time and (2) subsequent burning of the boron core after the removal of the B_2O_3 at higher temperature. To improve the combustion performance of boron, several efforts have been made including incorporating fluorinated compounds [16, 17], metals [18-22], carbides [23, 24], and others [25-28]. Ulas et al. [17] investigated the ignition and combustion of boron particles in fluorine-containing environments to eliminate HBO_2 formation, and as expected no apparent two-stage combustion was observed. Incorporating magnesium (Mg) into B increased the oxidation rate due to the absence of the oxide layer and decreased the initiation temperature [18]. Cheng et al. [19] incorporated the nitrocellulose (NC) and iron (Fe) particles into B via electrospraying, and the results show that the oxidation temperature of B/NC/Fe particles is lower than pure boron, which could be attributed to iron reaction with oxygen which is then reduced by boron. Sullivan et al. [20] reported that the addition of nanoboron (nB, < 50% in mole of the fuel) to nanoaluminum (nAl)/copper oxide (CuO) thermites can enhance the reactivity ~3x compared to Al/CuO, whereas the addition of micron boron (μB) showed no such effect. Thermochemical calculations show that Al and CuO reaction raises the temperature above the boiling point of B_2O_3 and melting point of boron in mixtures, thus enhancing reactivity of the composites. The reason that nB but not μB lead to enhancement is that the melting of boron is also important in this system and the melting time of nB is significantly shorter than μB. Trunov et al. [21] compared the combustion characteristics of B-Titanium (Ti) composites in different nitrogen (N_2)/oxygen (O_2)/methane (CH_4) mixtures and found that the burn rates and the efficiency of the combustion outperformed Al and efficient combustion of B-Ti nanocomposites can be achieved in both wet gaseous and dry environments because of the exothermic boron-titanium reaction.

In this study, we explored the effect of the addition of nano titanium (nTi) on nB and μB based thermites. The combustion performance and the ignition temperature of the B/Ti/CuO mixtures were obtained and compared. We found that the reactivity increased by a factor of ~6 and ~3 when adding nTi to the nB and μB based thermites, respectively. The enhanced performance was investigated via the addition of titanium dioxide (TiO_2) into boron and evaluating their thermal behavior. The mechanism to promote the combustion was proposed. The interaction between the TiO_2 shell and B_2O_3, which is in non-liquid phase until the temperature exceeds 1400°C, exposes the pure boron core to an oxidizer by reducing the amount of liquid B_2O_3 coating and thus decreasing kinetic constraints. In addition, the flame temperature during combustion for different samples have been measured and compared.

2 EXPERIMENTAL SECTION

2.1 Chemicals

CuO (< 50 nm) nanopowders were purchased from Sigma Aldrich. Nano boron used in this study has an average particle size of about 60 nm, with 60 wt. % active boron. Micron boron powders, labeled SB95, with 96 wt. % active boron has particle sizes ranging up to ~700 nm. Both boron samples were obtained from the SB Boron Corporation. Nano titanium (~50-80 nm) powders were obtained from US Research Nanomaterials Inc., with ~70 wt. % active titanium. The active metal contents of the above powders was confirmed by thermogravimetry analysis (TGA). Anatase titanium dioxide nanoparticles (< 50 nm) were also obtained from Sigma Aldrich. All the chemicals were used as received without any further processing.

2.2 Sample preparation

Thermite compositions used CuO as the oxidizer in stoichiometric amounts, and the formulations for nano and micron boron are shown in Table 1. For example, nB/30% Ti/CuO signifies that the molar percent of Ti in the fuel is 30%, the remainder of the fuel is nB, and the oxidizer is stoichiometric CuO.

Table 1. Stoichiometric thermite formulations

Thermites	B (wt. %)	Ti (wt. %)	CuO (wt. %)
nB/CuO	13.3	0	86.7
nB/30% Ti/CuO	7.8	12.5	79.7
nB/50% Ti/CuO	5	18.8	76.2
nB/70% Ti/CuO	2.7	24	73.3
μB/CuO	8.7	0	91.3
μB/30% Ti/CuO	5.7	10.7	83.6
μB/50% Ti/CuO	3.8	16.8	79.4
μB/70% Ti/CuO	2.2	22.5	75.3
Ti/CuO	0	30.2	69.8

Thermites were prepared by physical mixing. Firstly, CuO powders were weighed and ~5 mL hexane was added to a plastic vial. Then the corresponding fuel and another ~5 mL hexane was added. The mixture was sonicated for ~30 min to ensure good mixing and then dried in a hood overnight. The resulting dry powder was subsequently broken apart for use.

2.3 Measurement of reactivity

Reactivity was determined using a constant volume combustion cell, and obtained via calculating the pressurization rate, which has been described in previous work [29, 30]. Typically, ~25 mg of loose thermites powder is loaded in a combustion cell of ~20 cm^3 volume. The mixture is ignited via joule heating from a nichrome wire on the top of the powder. Pressure and optical signals were obtained with a piezoelectric pressure sensor and a photodetector, respectively. The pressurization rate was obtained by calculating the slope of the initial pressure rise, and the burn time was evaluated from the width at half-max of the optical emission. Measurements were repeated in triplicate, and the average values were presented. The error bars represent the calculated standard deviation.

2.4 Measurement of ignition temperature

The ignition temperature of the mixtures was measured using hot-wire time-resolved temperature-jump (T-Jump) coupled with a Vision Research Phantom v 12.0 high-speed camera (67056 frames/s) [31]. Typically, thermites were loaded onto 76 μm diameter platinum wire and joule heated to ~1200ºC at a rapid rate ~4×10^5 ºC/s in argon. From the recorded current and voltage signals, the temporal temperature of the wire was determined based on the Callender-Van Dusen equation [32]. The detailed description of the experiment could be found in our previous works [33, 34].

2.5 Characterization

The B/Ti/CuO mixtures were characterized by scanning electron microscopy (SEM, Hitachi, SU-70 FEG-SEM), and the results shown in Figure 1 demonstrate that the nB/50% Ti/CuO are well mixed. The SEM images of other nB/Ti/CuO mixtures are shown in Figure S1, which also indicate the well mixing of the fuels and oxidizers. The B/Ti/CuO mixtures, were heated to different temperature, and their combustion products have been characterized via powder X-ray diffraction (XRD, Bruker D8 Advance using Cu Kα radiation) and X-ray photoelectron spectroscopy (XPS, PHI QUANTERA-II SXM). Thermogravimetry/ differential scanning calorimetry (TGA/DSC) tests of fuels including B and Ti, and some mixtures of B and Ti, B and TiO_2 were conducted in a TA Instruments Q600 at a heating rate of 25°C/min up to 1000°C under an oxygen atmosphere with a flow of 100 mL/min.

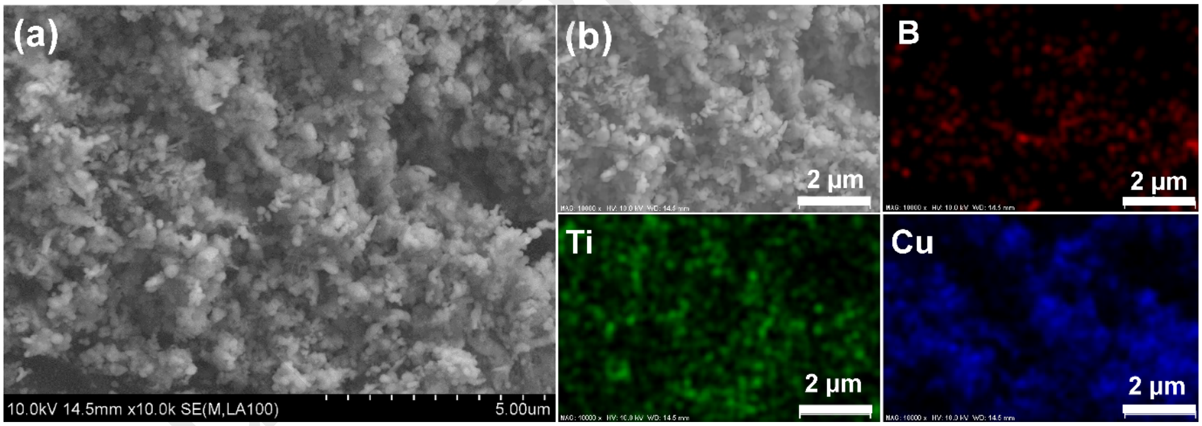

Figure 1. SEM (a) and EDS (b) of nB/50% Ti/CuO mixture.

2.6 Measurement of flame temperature

A high speed 32-channel spectrometer previously developed was used to measure the combustion temperature [35, 36]. The spectrometer consists of an optical fiber receiver, coupled to a 500 mm spectrometer (Acton SP 500i) with a 150 groove/mm grating. The collected spectrum was focused onto a 32 channel Photo Multiplier Tube (PMT) array (Hamamatsu H7260), which is interfaced with a high-speed data acquisition system (Vertilon IQSP 580), over a spectral range of 513-858 nm. The wavelength and intensity calibrations were performed via a HgNe pencil lamp (Newport) and a calibrated tungsten halogen lamp (Avantes). Each channel collected light over a band of wavelengths with the width of ~13 nm in this configuration. The sampling rate was ~40 kHz that produced a temperature every 25 μs. To obtain the time-solved temperature profile, the collected data was fit to Planck's law [37].

3 Results and discussion

3.1 Enhanced reactivity of B/CuO with the addition of Ti and ignition characterization

Combustion cell results as a function of Ti content are summarized in Figure 2. Peak pressure shown in Figure 2a clearly show the enhancement for both nano and micron B with addition of Ti. It is clear that compared to B/CuO, an enhancement in the peak pressure is achieved when adding Ti, and up to a factor of two enhancement at 50 % Ti. Pressurization rate (Figure 2b), reflects the reactivity [20], which is obtained via calculating the average pressure rise rate as shown in Figure S2. Figure 2b shows an enhancement of ~6 times and ~4 times for nB and μB with Ti addition. This reinforced reactivity is also reflected in lowered burn times (Figure 2c). For the nB/Ti/CuO system, the burn time of nB/30% Ti/CuO reduced by around 3x relative to nB/CuO. Similarly, the burn time of μB/CuO also decreased from ~14 ms to ~4 ms after adding 30% Ti. Based on these results we can conclude that reactivity has been significantly enhanced by the addition of nTi into both nB/CuO and μB/CuO mixtures. The mechanism of this enhancement will be discussed in later sections.

One non-intuitive result is the higher peak pressure observed in the μB/Ti/CuO cases even though the kinetics are clearing favoring the nano cases (Figure 2 b, c). We attribute this to the lower dead weight of the B_2O_3 (4 wt. % vs 40 wt. %) in the micron boron case as shown in Table S1. Since each combustion test is conducted on a quantitative amount of thermites, the higher the active fuel content the more gas produced and thus a higher peak pressure. Thermochemical calculations based on free energy minimization [38, 39] are shown in Figure S3 confirm that the enhancement is more for the micron case. This is presumably because as we add more Ti, we are effectively having a smaller mass fraction of boron oxide which makes it seem that the micron is a better performer.

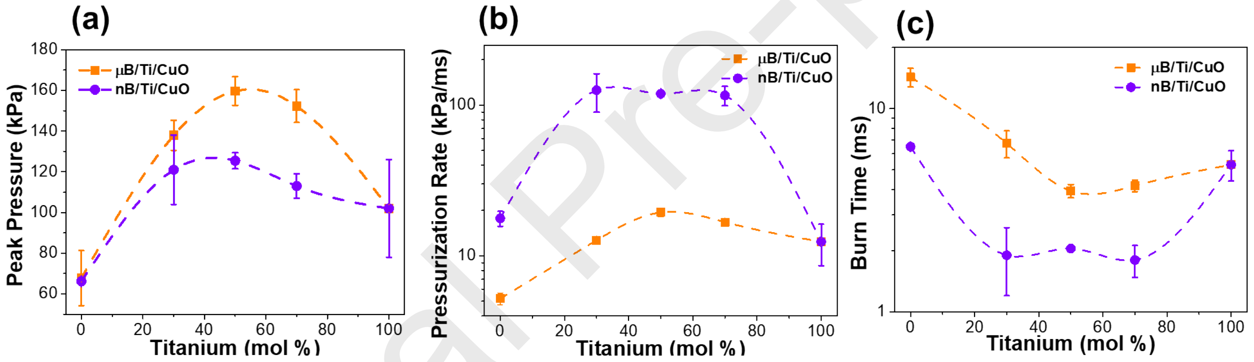

Figure 2. (a) Peak pressure, (b) pressurization rate, and (c) burn time as a function of titanium mol % in B/Ti/CuO thermites.

The ignition properties characterized via T-jump are shown in Figure 3 for T-Jump ignition indicate a lack of sensitivity to the addition of Ti nanoparticles for nB/Ti/CuO thermites, and that their ignition temperature is ~600ºC (±50ºC). For μB/Ti/CuO mixtures, the ignition temperature gradually decreases with the increasing Ti molar percent. In detail, the ignition temperature of Ti/CuO is ~70ºC lower than μB/CuO. However, the lower ignition temperature of nB/CuO than

Ti/CuO presents a different situation. Therefore, we can conclude that the enhanced combustion performance is not nominally related to ignition temperature.

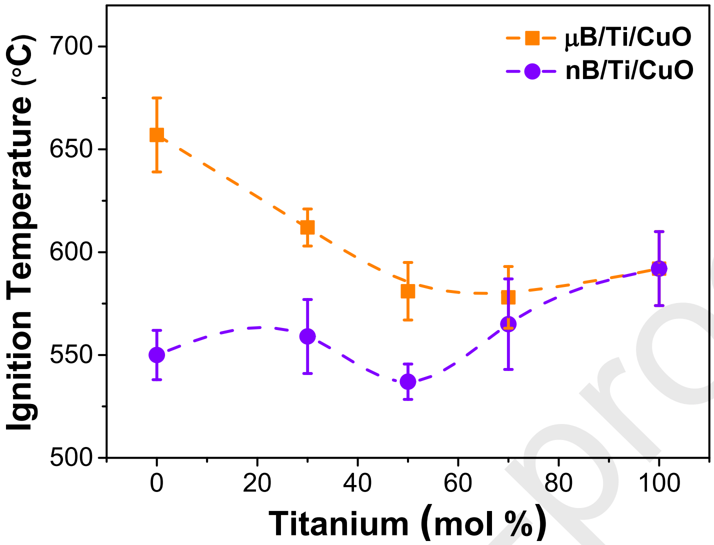

Figure 3. Ignition temperature as a function of titanium mol % in B/Ti/CuO thermites

3.2 Thermal behavior of B/TiO_2 and a proposed mechanism

To investigate the mechanism of the enhanced combustion performance of B/CuO via Ti addition, there are several points that need to be considered in this ternary system: (1) Possible reaction of Ti and B_2O_3 as the initiating step; it is reported [40] that there is no reaction between Ti and B_2O_3 until 1200°C, (2) Only reactions of B/CuO and Ti/CuO were observed. No alloying reaction between B and Ti [41, 42] was found according to DSC (Figure S4), XRD results (Figure S5, S7), and XPS spectra shown in Figure S6 and S8. (3) the reaction between B and TiO_2 is not supported thermodynamically, and (4) the chemical reaction between B_2O_3 and TiO_2 seems not to be supported by TGA/DSC (Figure S9), however, they might have some physical interactions as both B and Ti have oxide shells.

To further explore the possible interaction, we investigated the oxidization behavior of B, Ti, nB/Ti, and nB/TiO_2 in pure oxygen at 1 atm in TG/DSC. The results shown in Figure 4a demonstrate that compared to the pure fuels, the oxidization rate of both nB/Ti and nB/TiO_2 increased rapidly above ~500°C. This observation is mirrored in the DSC (Figure 4b) showing the exotherms of two mixtures occur sooner by as much as a 100°C and are sharper compared to the single metal. We attribute the slightly lower exotherm of nB/Ti (relative to nB/TiO_2) to the heat release from the oxidation of Ti by oxygen, which promotes the reaction of nB with oxygen. The relative oxidation process data has been summarized in Table 2. The oxidation temperature is determined by a 5% mass gain.

Similar phenomena have been seen in the TGA/DSC results (Figure S10) when comparing the oxidization behavior of μB, Ti, μB/Ti, and μB/TiO_2. The mixtures of nB/TiO_2 in different weight ratios have also been characterized by TGA/DSC (shown in Figure 5), which further confirmed the role of TiO_2 i.e. increasing fraction of TiO_2, lowers the temperature of the exotherm.

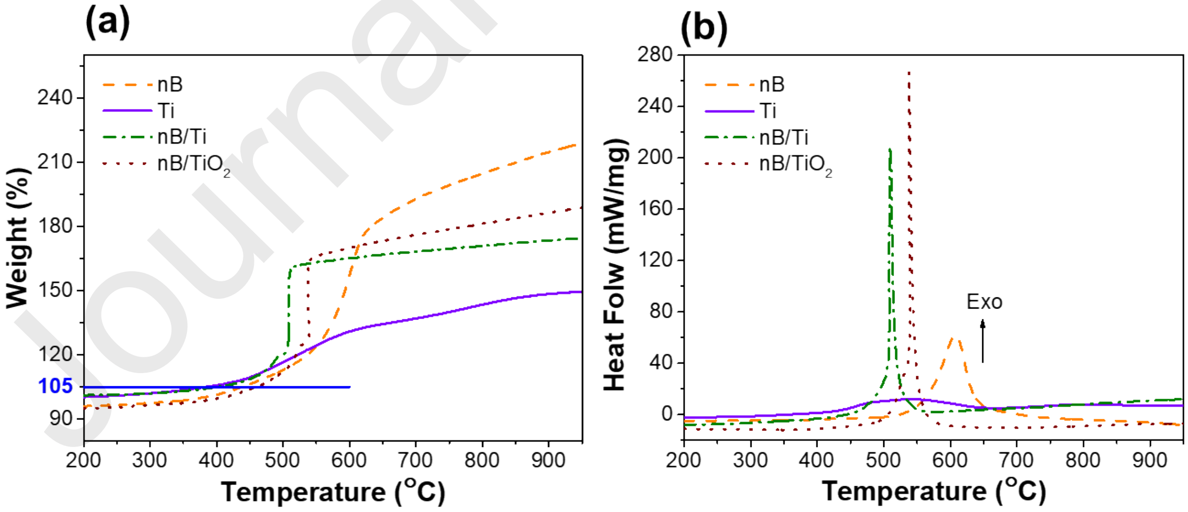

Figure 4. TGA (a) and DSC (b) curves of nB, Ti, nB/Ti and nB/TiO_2 oxidation in oxygen. Note: The mass ratio of nB in nB/Ti and nB/TiO_2 is both 50 wt. %.

Table 2 Key parameters of oxidation process for nB, Ti, nB/Ti and nB/TiO_2

Sample	Onset Temperature/°C	DSC Peak Temperature/°C
nB	445	606
Ti	402	540
nB/Ti	401	509
nB/TiO_2	465	538

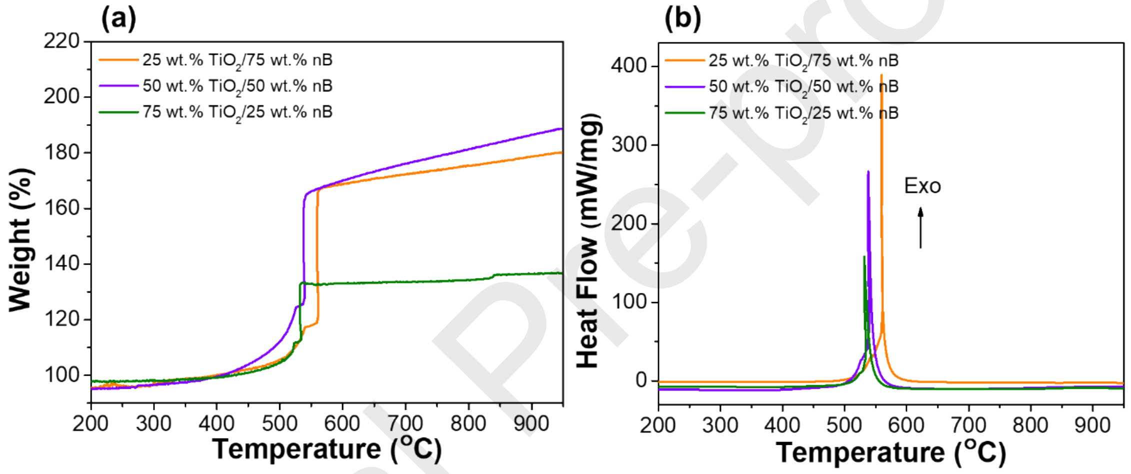

Figure 5. TGA/DSC curves of nB/TiO_2 at different ratios at the atmosphere of oxygen.

The phase diagram of B_2O_3/TiO_2 in Figure S11 [43] confirms that with the presence of TiO_2, the phase status of the mixture at different temperatures will be altered. As we know, B_2O_3 itself will remain as a liquid from ~450°C to 1860°C, which corresponds to its melting and boiling point, respectively. However, when the weight percent of B_2O_3 in the B_2O_3/TiO_2 mixture exceeds ~3 wt.%, the B_2O_3 will not melt until ~700°C. TiO_2 however remains a solid status until >1400°C. Therefore, with the addition of TiO_2, the time duration of B_2O_3 remaining in liquid status is significantly reduced. It is reasonable to speculate that unlike the impervious B_2O_3 shell coating on the B core without TiO_2, the diffusion of TiO_2 may initiate through the melted B_2O_3 layer [44, 45]. As a result, there are some paths created by the phase separation at the interface of B_2O_3/TiO_2 for oxygen to diffuse and react with the B core. The proposed mechanism is shown in Figure 6.

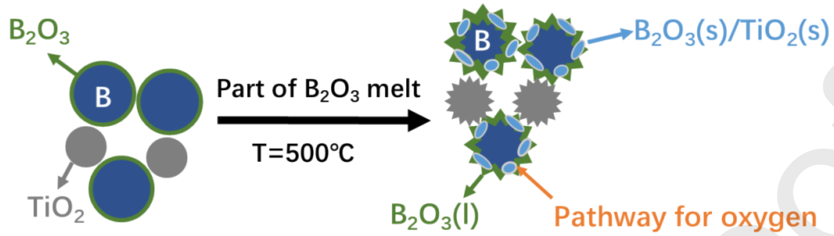

Figure 6. Proposed mechanism of the influence of TiO_2 on the oxidation of boron. Note: "s" means "solid", and "l" represents "liquid".

Therefore, we can conclude that TiO_2 plays an important role in enhancing the performance of B/CuO mixtures. The TiO_2 shell passivating on the Ti core plays a significant role in promoting the contact of the boron core, and the oxidizer by intermixing with the B_2O_3 as confirmed by TGA/DSC (Figure 4, 5, S10) and the phase diagram of B_2O_3/TiO_2 (Figure S11).

3.3 Temporal reaction temperature

To investigate whether adding Ti to B/CuO aids in removing of B_2O_3 and melting boron, we compared combustion temperature temporally. As shown in Figure 7a, the temperature of nB/Ti/CuO ternary system exceeds the melting point of boron (2077°C) and the boiling point of B_2O_3 (1860°C). Figure 7 demonstrates that for the pure nB/CuO system, the combustion temperature exceeded the boiling point of B_2O_3 at ~1.08 ms after ignition, however, the same temperature was achieved in only ~0.08-0.18 ms after ignition upon the addition of Ti. This implies that the addition of Ti's primary function appears to be get the initial temperature sufficiently high so as to aid in volatilizing B_2O_3, and thus kicking on the boron chemistry [9, 20]. Similar behavior was also observed in the ternary system with micron boron as the fuel. The result is an enhanced burn rate and high combustion temperature in the ternary mixture. In addition, we also found that the highest flame temperature during the combustion process for nB/Ti/CuO and μB/Ti/CuO ternary systems are essentially the same. This explain the plateau for burn rate (Figure 2) since the enhancement of reactivity is related to the improved flame temperature.

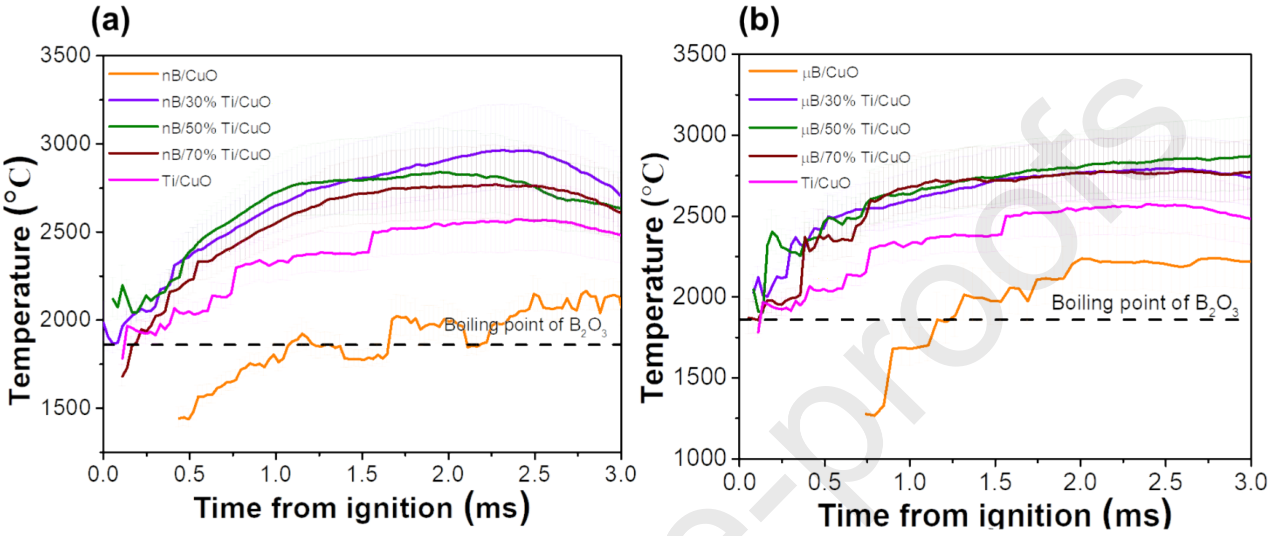

Figure 7. Temporal combustion flame temperature for (a) nB/Ti/CuO and (b) μB/Ti/CuO mixture. The boiling point of B_2O_3 (1860 °C) is shown as the horizontal dotted line.

4 Conclusions

In this study, nTi was used as an additive in nB/CuO and μB/CuO systems, to assess its impact on ignition and reactivity. Combustion test results show that the addition of Ti can enhance the reactivity of both nB/CuO and μB/CuO with higher peak pressure/pressurization rate, and shorter burn time. The ignition temperature did not change significantly, which ranges from ~550°C to ~650°C. To investigate the mechanism, relatively inert TiO_2 is added into boron, and the thermal behavior was characterized, which indicates that the addition of the TiO_2 could promote the oxidation of boron. Thus, we proposed that the interaction between TiO_2 and B_2O_3 shown in their phase diagram suggests a reduction in the amount of liquid B_2O_3 coating on the B core, creating a low-resistance pathway for oxygen to diffuse and react with the B core. Another reason for the performance enhancement could be attributed to the raised temperature achieved by reaction of Ti and CuO, which promotes the evaporation of B_2O_3 and melting of boron core. These results show that Ti can be a useful additive to nB/CuO and μB/CuO mixtures for enhancing and/or tuning their energetic behavior.

Acknowledgements

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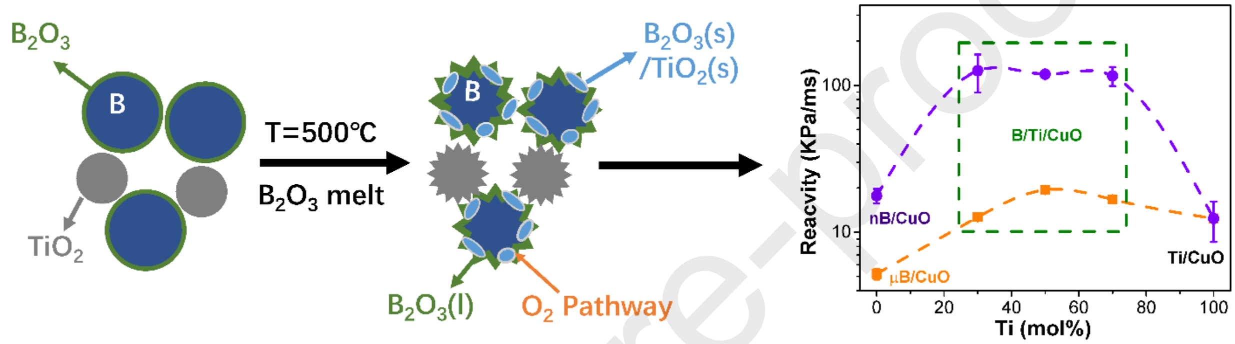
Declaration of Interest Statement

There is no interests to declare.



Highlights

1. Addition of Nano Ti to Nano B results in 3- 6 X enhancement in reactivity.
2. Enhancement in reactivity is partly attributed the interaction of TiO_2 with the melting boron oxide (B_2O_3) shell.
3. The TiO_2/B_2O_3 mixture in a non-liquid phase creates pathways for oxygen to diffuse and thus enhances the boron oxidation rate.