Reaction mechanisms of potassium oxysalts based energetic composites

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ABSTRACT

Ignition temperature is a simple and important parameter that pertains to both the practical aspects of thermite usage as well as a key to exploring reaction mechanisms. In this study, nine aluminum-fueled oxysalt-containing thermites including $K_2S_2O_8$, K_2SO_4, KIO_4, KIO_3, $KClO_4$, $KClO_3$, $KBrO_3$, KNO_3 and K_3PO_4, were investigated. Results from combustion cell tests show that these thermites can be divided into two groups, with the reactive thermites (e.g., Al–$K_2S_2O_8$) generating $\sim 10\times$ higher of pressure and $\sim 10\times$ shorter of burn time than the less reactive thermites in the aforementioned list (e.g., Al–K_2SO_4). Thermal decomposition analysis of these oxysalts at both slow and fast heating rates (0.17 K/s v.s. 10^5 K/s) demonstrates that these oxysalts have a wide range of oxygen release and melting temperatures. On the other hand, the ignition temperatures of the reactive thermites (in Ar and air) are consistent with the temperature of polymorphic phase change of alumina (close to the melting point of Al), indicating that the limiting initiation step of these thermites is the acceleration of outward diffusion flux of Al. In addition, the ignition temperatures of these reactive thermites in vacuum are much higher than those in Ar, suggesting that ignition is based on the interaction between outwardly diffused Al, and generated gas phase O_2. In contrast, the ignition temperatures of the two less reactive thermites are insensitive to pressure. They ignite at temperatures much higher than the melting point of Al, although lower than the decomposition temperature of the corresponding oxysalts, indicating a condensed phase reaction mechanism. Finally, by employing carbon as a non-melting, non-oxide coated fuel, we found an essentially direct correlation between the oxygen release temperature and the ignition temperature.

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1. Introduction

Since the thermite reaction was first named by Goldschmidt in 1908 [1], the concept has been currently broadened to a variety of exothermic reactions involving a metal reacting with an oxide (metal or non-metal) or an oxysalt [2–5]. Due to its extremely high energy density, the thermite system has been employed in a wide array of applications in the pyrotechnic, metallurgical, and ceramic industries [2–5], which has prompted studies to improve their utilization by tailoring their combustion and ignition behaviors [6–10]. The latter property also involves practical safety concerns related to the large-scale industrial use [11,12]. One important research direction is to improve the ignitibility of thermites, which is affected by many factors (contact area, chemical composition, hygroscopicity, etc.). The most common method is by increas-ing the contact area between the fuel and oxidizer, which can reduce the diffusion distance of reactive species to permit ignition at lower temperatures [13–17]. This higher degree of intimacy can be achieved by either decreasing the particle size [14–17], better mixing [13,18,19], or increasing the particle porosity [20].

For the most common aluminum-fueled thermite systems, ignition was proposed to be initiated by a solid-state reaction [21]. Subsequent reaction requires movement of reactive species towards each other, although the nature of this movement is subject to considerable debate [22–28]. However, it was previously reported that the prerequisite for ignition is the availability of molten aluminum [21,29]. Based on this speculation, ignition temperatures for a plethora of thermites should be around the melting point of aluminum. However, a recent study by Jian et al. [30] shows that there can be large differences in ignition temperatures among different nano-thermite formulations involving aluminum and metal oxides. For instance, some formulations (e.g., Al–Bi_2O_3, Al–SnO_2) have ignition temperatures lower than both the melting point of aluminum, and the decomposition temperatures of oxidizers, suggesting another condensed phase reaction

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mechanism that is not governed by melted aluminum [31]. Similarly, Dean et al. [32] examined another nano-thermite formulation (Al–NiO), which produces minimal gas upon ignition, with a much lower ignition temperature ($\sim$400 °C) [33] than either the melting temperature of Al or the decomposition temperature of NiO. Sullivan et al. [34] implemented in situ rapid heating microscopy to monitor the nano-thermite reaction of Al–WO$_3$ and found a reactive sintering phenomenon [35] in which no gas was released, and the reactants deformed to maximize intimate surface contact. While several thermites appear to react via this condensed phase route [32–37], ignition temperatures of some other formulations may exceed the decomposition temperature of metal oxides, suggesting a different reaction mechanism [30].

To date, discussions on ignition mechanism of thermites have been limited to formulations containing various metal oxides (CuO, Fe$_2$O$_3$, *etc.*), whereas the ignition mechanism for thermite formulations containing oxysalts (nitrates [38–40], (per)chlorates [41–44], (per)iodates [45–47], *etc.*) have not been explicitly studied from a mechanistic standpoint. Typically, Al–oxysalt thermites exhibit lower ignition temperatures and higher reaction rates [44,47–49], which are associated with the low oxygen release temperatures of the corresponding oxysalts. An initial exothermic decomposition of some oxysalts during heating may also contribute to the low ignition temperature [41,47]. Recently, a new formulation based on persulfates was found to be more reactive when compared to other oxysalts [50]. The superiority of oxysalts in thermite performance can likely be attributed to the higher oxygen content, and the lower bond energy of the nonmetal-oxygen pair in oxysalts when compared to the metal–oxygen pair in metal oxides [50]. Of particular interest is whether the ignition temperature (T_{ig}) is a predictable function of the oxygen release temperature (T_{O_2}), the melting temperature of aluminum ($T_{Al-melt}$), and the melting temperature of oxidizer ($T_{oxidizer-melt}$).

In this paper, we systematically investigated the ignition of thermites that involve Al and a variety of potassium oxysalts, in relation to the physiochemical changes of these components during heating. These studies involved using constant-volume combustion cell tests, thermal decomposition tests for oxysalts under both slow heating (10 K/min) and ultrafast heating ($\sim$10^5 K/s) conditions, and ignition tests for both microscale and nanoscale thermites in air, in Ar and in vacuum. Nano-carbon-fueled thermites containing similar oxysalts were also used as controls to tweeze out the role of liberated oxygen.

2. Material and methods

2.1. Materials

Nano-sized aluminum was obtained from Argonide Corporation, and nano-sized carbon black was obtained from Cobot Corporation. Both materials have an average size of $\sim$50 nm. Micro-sized potassium persulfate (K$_2$S$_2$O$_8$) powders were purchased from Fluka. All of the other micro-sized oxysalt powders, namely potassium sulfate (K$_2$SO$_4$), potassium nitrate (KNO$_3$) potassium chlorate (KClO$_3$), potassium perchlorate (KClO$_4$), potassium bromate (KBrO$_3$), potassium iodate (KIO$_3$), potassium periodate (KIO$_4$), and potassium phosphate (K$_3$PO$_4$) were purchased from Sigma-Aldrich. Scanning electron microscopy (SEM, Hitachi, SU-70 FEG-SEM) analysis shows that these as-received potassium oxysalts powders have a wide range of sizes from 1 μm to 100 μm.

The corresponding nine nano-sized potassium oxysalts were prepared by an aerosol spray drying process, as is shown in Scheme 1. In short, 0.02 mol/L water solution of oxysalt was prepared in the atomizer and sprayed into 1 μm droplets by a pressured air flow. Droplets flowed through a diffusion dryer to remove most of the water, followed by complete dehydration by a tube

furnace at 150 °C for K$_2$S$_2$O$_8$ and at 180 °C for the other oxysalts. The dehydrated nanoparticles were finally collected on a Millipore membrane filter with a pore size of 0.4 μm. The average size of nine nano-oxysalts is $\sim$0.5 μm. Particle sizes were measured by SEM and statistically analyzed from a random selection of 60 particles in SEM images.

To prepare the thermite composite, nano-fuels (Al or C) were mixed with oxysalts (microscale or nanoscale) in a stoichiometric ratio. Accounting for the alumina shell (30%) on the nano-Al, the actual weight of nano-Al added was 1.4 times higher. The mixture was then sonicated in hexane for 30 min and then the solvent was evaporated at room temperature.

2.2. Constant-volume combustion characterization

The analysis of nano-Al/micro-oxysalt thermite reactions was conducted in a constant-volume combustion cell (Scheme 1). Prior to tests, all the thermite samples were dried in vacuum for hours in order to mitigate the adverse influence of hygroscopicity. 25 mg of thermite sample was loaded inside the combustion cell that has an internal spacing of $\sim$13 cm^3. After igniting the sample with a heated nichrome coil, the temporal pressure and optical emission from the thermite reaction were electronically recorded.

2.3. TG-DSC analysis of the decomposition of oxysalts

Thermogravimetry and differential scanning calorimetry (TG-DSC) tests of microscale oxysalts were conducted simultaneously in a SDT Q600 from TA Instruments, USA. Around 2 mg of as-received oxysalt powders was loaded into the sample crucible inside the apparatus and heated at 10 K/min in 100 L/min Ar flow. The TG and DSC heat flow calibrations were conducted prior to tests. For the TG calibration, two calibration weights were used to calibrate the beam and weight correction factors. For the DSC heat flow calibration, the capacity curve of sapphire over the range of 500–1800 K, as well as the heat of fusion of high purity zinc metal, were analyzed and compared with the standard values to generate a calibration cell constant. In the analysis of the TG-DSC results, the onset temperatures of physicochemical changes (including phase and chemical changes) are defined as the crossing points of extrapolated curves.

2.4. T-jump TOF-MS analysis of the decomposition of oxysalts

The decomposition of oxysalts (microscale or nanoscale) at ultrafast heating rates of 4×10^5 K/s was investigated via temperature-jump time-of-flight mass spectrometry (T-jump TOF-MS, in-house assembled). A concentrated oxysalt powder suspension in hexane was deposited onto a 76 μm Pt wire uniformly, to a thickness $<$ 10 μm so that the temperature of the deposit is approximated by the wire temperature. The loaded Pt wire was then inserted into the MS chamber and rapidly joule-heated to $\sim$1400 K by a 3 ms pulse. The temporal temperature of the wire was measured from the detected current and voltage according to the Callender–Van Dusen equation [51]. TOF-MS spectra was collected every 0.1 ms. A detailed experimental description can be found in Ref. [52]. In the analysis of the MS results, the onset temperature of a specific species is defined based on 5% of the maximum intensity of its MS peak.

2.5. Ignition tests of thermite reactions

A Vision Research Phantom v12.0 high speed camera (14.9 μs per frame) was employed to determine the onset of ignition on the wire. By mapping the temporal optical emission from the high-speed imaging, and the temporal wire temperature, the ignition