Combustion of thermite mixtures based on mechanically alloyed aluminum-iodine material

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Brief Communication

Abstract

Halogen-containing reactive materials could be used for mitigating the spread of hazardous, active biological microorganisms aerosolized as a result of explosion. Here we present experimental results on combustion of mechanically alloyed aluminum-iodine (Al·I₂) powder mixed with Fe₂O₃, CuO, MoO₃, Bi₂O₃, and I₂O₅. The mixtures were compacted into pellets and ignited with a CO₂ laser. High-speed video recording was used for observations. Mixtures of the Al·I₂ powder with Fe₂O₃ did not ignite, while mixtures of this powder with the other oxides exhibited a self-sustained propagation of the combustion front with similar burn rates. Comparison experiments with a finer, micron-sized Al powder have shown a more rapid combustion of mixtures based on metal oxides and, in contrast, a slower and unsteady combustion of Al/I₂O₅ thermite. These observations are interpreted based on the analysis of reaction mechanisms.

Keywords: Heterogeneous combustion; Thermites; Biocidal reactive materials; Laser ignition

1. Introduction

Halogen-containing reactive materials could be used for mitigating the spread of hazardous, active biological microorganisms aerosolized as a result of explosion [1, 2]. Different methods for incorporating halogens in reactive materials have been considered. In particular, reactive compositions including halogen-containing thermites have been explored [3-7]. The tested mixtures included metal powders and halogen-containing oxides such as iodine pentoxide (I_2O_5) and silver iodate ($AgIO_3$).

Recently, a mechanically alloyed aluminum-iodine ($Al \cdot I_2$) powder has been synthesized [8]. Relatively low ignition temperatures of this powder [9, 10] imply that it can substitute aluminum in thermite mixtures, thus serving as a fuel and, at the same time, the source of iodine. It is expected that the use of this material instead of aluminum in thermite mixtures based on iodine-containing oxides would increase iodine yield, while maintaining the mixture's high energy density. Further, thermite mixtures of $Al \cdot I_2$ powder with oxides of metals such as iron, copper, bismuth, and molybdenum could be used for iodine generation when relatively small amounts of iodine are sufficient and the use of unstable and hygroscopic iodine-containing oxides is not desired.

The objective of present paper is to investigate combustion of thermite mixtures that include the mechanically alloyed $Al \cdot I_2$ powder and the following oxides: Fe_2O_3 , CuO , MoO_3 , Bi_2O_3 , and I_2O_5 . It was also desired to compare combustion characteristics of these mixtures with those of thermites based on commercial, micron-sized Al powder.

2. Experimental

Mechanically alloyed $Al \cdot I_2$ (20 wt% I_2) powder was fabricated by ball milling at the liquid nitrogen temperature. Details are given elsewhere [8]. A commercially available aluminum powder (97.5% pure, spherical, Alfa Aesar) was used in experiments conducted for comparison. Bismuth (III) oxide (Bi_2O_3 , 99.9% pure), copper (II) oxide (CuO , >99.0% pure), and molybdenum (VI) oxide (MoO_3 , 99.5% pure) were obtained from Alfa Aesar, while iron (III) oxide (Fe_2O_3 , >99% pure) and iodine pentoxide (I_2O_5 , 98% pure) were supplied by Sigma Aldrich.

Particle size distributions of the used powders were determined using a multi-laser particle size analyzer (Microtrac Bluewave) with isopropyl alcohol as the carrier liquid.

Both Al and $Al \cdot I_2$ powders were mixed with the oxides according to the stoichiometries of Al-oxygen reactions, i.e., I_2 was considered as an inert additive. The mixing was conducted in an acoustic mixer (Resodyne LabRAM) with an intensity of 40% for 2 min. Wet (hexane) mixing was used. The mixtures were compressed into pellets (diameter 6 mm, height 6-14 mm) using a uniaxial hydraulic press (force 9.8-14.7 kN).

The pellets were ignited by an infrared (wavelength 10.6 μm) beam of a CO_2 laser (Synrad Firestar ti-60). The experiments were conducted in air at atmospheric pressure. Figure 1 shows the experimental setup. A sealed aluminum chamber (inner diameter 70 mm, length 160 mm) is equipped with two removable window ports and a zinc selenide ($ZnSe$) window. The pellet is installed vertically on a brass pedestal. The laser beam enters the chamber through the $ZnSe$ window and heats the pellet at the top. To prevent damage by high-temperature combustion products, the $ZnSe$ window is installed at the top end of a long (30 cm) vertical tube. The beam diameter at the pellet top is about 3 mm. The pellet is aligned with the infrared beam using a diode pointer (Synrad), which emits a visible red laser beam aligned with the CO_2 laser beam.

The power of the CO₂ laser beam is controlled by a laser controller (Synrad UC-2000). In the reported experiments, the actual power of the beam after passing the beam delivery system and ZnSe window, measured with a powermeter (Synrad PW-250), was 58–60 W. The duration of the laser pulse is set using LabVIEW (National Instruments) software connected to the laser controller. A custom-made electronic scheme based on a photoresistor turns off the laser pulse upon the ignition. A high-speed video camera (Vision Research Phantom v1210), equipped with a lens for macro shooting (Nikon AF Micro NIKKOR 60mm f/2.8D), is used for observations of the combustion process and measurements of the front velocity. In the present research, the resolution was 1024x768 and the frame rate was varied from 1000 to 7000 fps.

Fig 1. Experimental setup.

3. Results

Table 1 describes particle size distributions measured for the used fuels and oxidizers. Included are the mean volume diameter d_{mv} , the median diameter d_{50} , and parameters d_{10} and d_{90} (the complete particle size distributions are included in the Supplementary material). It is seen that mechanically alloyed Al-I₂ powder is coarser than the commercial Al powder, which is characterized by a mean volume diameter of about 8 μm . The Al-I₂ powder and oxides of Cu and Mo have similar distributions. The mean volume diameters of these three powders are in the range from 20 to 30 μm . Oxides of bismuth and iron are finer (the mean volume diameter is 4 μm for the former and 10 μm for the latter). Iodine pentoxide is the coarsest powder, with the mean volume diameter of about 70 μm .

Table 1. Particle size distribution parameters of the used fuels and oxidizers.

	$d_{mv}, \mu\text{m}$	$d_{10}, \mu\text{m}$	$d_{50}, \mu\text{m}$	$d_{90}, \mu\text{m}$
Al	7.70	3.62	7.15	12.57
Al-I₂	19.76	5.09	16.08	40.34
CuO	28.07	7.09	23.60	53.23
MoO₃	22.58	7.99	17.90	40.27
Bi₂O₃	4.24	1.148	2.621	8.69
Fe₂O₃	10.24	1.264	2.265	31.84
I₂O₅	69.90	4.85	47.53	168.9

Several experiments were conducted with each mixture. Typical videos obtained for mixtures based on mechanically alloyed Al-I₂ powder are included in the Supplementary material, while Figure 2 shows still images from these videos.

Fig. 2. Still Frames from High Speed Videos. These still frames from high speed videos (frame rate: 1000 fps), included in the Supplementary material, show mixtures of mechanically alloyed Al-I₂ powder with (a) Fe₂O₃, (b) MoO₃, (c) Bi₂O₃, (d) CuO, and (e) I₂O₅. The image for iron oxide based mixture is taken from the laser heating phase of the process because this mixture did not ignite. The images for other mixtures are taken from the combustion propagation phase.

Table 2 shows the relative densities of the mixtures and the measured velocities of combustion front propagation. No reliable conclusions were made based on the ignition delays because they varied in the range of 0.01–0.4 s, apparently because of variation of the pellet absorptivity.

Table 2. Characteristics of studied thermite mixtures.

Oxidizer	Al·I ₂		Al	
	Relative density, %	Front velocity, mm/s	Relative density, %	Front velocity, mm/s
Fe ₂ O ₃	59-83	No ignition	No test	No test
MoO ₃	66-74	6	71-72	>100
Bi ₂ O ₃	71-76	10	71-77	>100
CuO	66-85	13-18	72-74	>100
I ₂ O ₅	84-86	13-16	73-90	~ 5

The mixtures of Al·I₂ and Fe₂O₃ powders did not ignite. The luminous zone created by laser heating did not expand, i.e., the reaction did not propagate. The only effect of laser heating was ejection of fragments and gradual destruction of the pellet (Fig. 2-a).

The mixtures of Al·I₂ with MoO₃, Bi₂O₃, and CuO powders ignited and burned in a self-sustained manner with average front velocities varied in the range of 6–18 mm/s. The lowest velocity and unsteady phenomena were observed during combustion Al·I₂/MoO₃ mixtures (Fig. 2-b), while those based on Bi₂O₃ and CuO exhibited a steady front propagation (Figs. 2-c and 2-d).

The mixtures of Al·I₂ and I₂O₅ powders also burned steadily with a front velocity of 13-16 mm/s, but the combustion zone looks different compared to other thermite systems (Fig. 2-e). Instead of a uniform luminous zone, the combustion front consists of numerous hot spots, separated from each other. It is seen how the incandescent fragments are ejected from the pellet, leading to the full dispersion of the material.

In the comparison experiments with mixtures based on commercial Al powder and the same metal oxides (MoO₃, Bi₂O₃, and CuO), a much faster combustion was observed: the front velocities exceeded 100 mm/s. In contrast, combustion of the mixture of Al and I₂O₅ powders was relatively slow (ca. 5 mm/s) and unsteady.

4. Discussion

The experiments have shown that the front velocities in all mixtures with Al·I₂ powder are similar to one another, despite different chemical compositions and particle sizes of the oxidizers tested. This indicates that the reaction may be controlled by the processes related to the metal particles. Prior studies [11] have shown that low-temperature oxidation of Al particles is controlled by outward diffusion of Al ions to the exterior of the oxide shell covering the metal. It is possible that this process also controls the reaction between Al·I₂ and metal oxide particles during propagation of the combustion wave over their mixture.

Further, the experiments have shown that the front velocities in the mixtures with Al·I₂ powder and metal oxides are much lower than those for the mixtures of the same oxides with a commercial, micron-sized Al powder. To verify that this effect is not caused by the decrease in the combustion temperature due to the addition of iodine, the adiabatic flame temperatures of all studied mixtures were calculated for 1 atm pressure using THERMO software [12]. The formation enthalpy of I₂O₅, -157.92 kJ/mol [13], was added to the database. It was assumed in the calculations that Al·I₂ material is just a mixture of Al and I₂. The results have shown that the replacement of Al with Al·I₂ decreases the adiabatic flame temperature of all mixtures by 11–80 K (the obtained values are in the range 2800–3800 K and are included in the Supplementary material). Such a small reduction in the temperature cannot explain the significant decreases in the velocity of front propagation observed for thermites based on metal oxides.

The decrease in the front velocity may be associated with a larger size of mechanically alloyed Al·I₂ powder (see Table 1). In a recent study on the ignition mechanisms of thermites [14], the investigated mixtures included nanoscale Al and different metal oxides including the four oxides studied in the present paper. It was shown that at least for thermites based on Bi₂O₃, MoO₃, SnO₂, Sb₂O₃, and WO₃, the ignition is likely a result of direct interfacial contact between fuel and oxidizer, leading to condensed state mobility of reactive species, rather than a result of reaction with gaseous oxygen released from the metal oxides. Apparently, the same mechanism takes place during ignition of all thermites studied in the present work, except for I₂O₅-based mixture. Since Al·I₂ powder is coarser than the tested Al powder, it has a lower area of contact with the oxide, which decelerates the reaction between the metal and oxide particles. The non-ignition of Al·I₂/Fe₂O₃ mixtures correlates with the high ignition temperature of Al/Fe₂O₃ thermite as compared with those of other aluminum – metal oxide thermites [14].

The mechanism of oxygen transport to metal particles during combustion of I₂O₅-based thermites is probably different. It is known that iodine pentoxide decomposes to O₂ and I₂ at a relatively low temperature of about 400 °C [4]. Thus, it is likely that the reaction does not happen at the particle-particle interface, but rather in the gas phase. It has been observed earlier that at such temperatures, mechanically alloyed Al·I₂ powder rapidly reacts with gaseous oxygen [9, 10]. Combustion of the Al·I₂/I₂O₅ mixtures may still depend on the outward diffusion of Al through the particle oxide shells, but the observed different structure of the combustion front (hot spots rather than a uniform luminous zone) supports the hypothesis of a different combustion mechanism.

These considerations also explain the observed slow and unsteady combustion of Al/I₂O₅ thermite. Indeed, oxidation of conventional micron-sized Al powders begins at a higher temperature than for the mechanically alloyed Al·I₂ powder. The temperature at which significant oxidation of Al begins, I₂O₅ is already expected to decompose. Thus, in the prepared powder mixtures, the zones of I₂O₅ decomposition and Al oxidation in the combustion wave may be spatially separated, causing a decrease in the front velocity.

5. Conclusions

Mixtures of the mechanically alloyed Al·I₂ powder with Fe₂O₃ do not ignite. Mixtures of the same powder with other oxides exhibit a self-sustained propagation of the combustion front with similar burn rates. Comparison experiments with a finer, micron-sized Al powder have shown a more rapid combustion for mixtures based on metal oxides. In contrast, a slower and unsteady combustion was observed for Al/I₂O₅ thermite.

Similar burn rates for thermites with $\text{Al}\cdot\text{I}_2$ mixed with different oxides indicate that the reaction is controlled by outward Al diffusion through the oxide shells of metal particles. In mixtures with metal oxides, the reaction requires interfacial contact between the fuel and oxidizer, so that replacing $\text{Al}\cdot\text{I}_2$ with a finer Al powder increases the reaction rate. In contrast, in mixtures with iodine pentoxide, aluminum reacts with gaseous oxygen released by the oxide decomposing at a lower temperature. Since oxidation of $\text{Al}\cdot\text{I}_2$ and decomposition of I_2O_5 occur in the same temperature range, $\text{Al}\cdot\text{I}_2/\text{I}_2\text{O}_5$ mixtures burn rapidly. In contrast, $\text{Al}/\text{I}_2\text{O}_5$ mixtures exhibit a slow and unsteady combustion because the oxidation temperatures of the micron-sized Al powder are higher than the decomposition temperature of I_2O_5 .

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