COMPOSITE REACTIVE MATERIALS COMBINING METALS WITH VOLATILE ADDITIVES

ABSTRACT

Several composite reactive materials of powdered Aluminum (Al) combined with a volatile additive, such as iodine, iodoform, or cyclooctane, were prepared by mechanical milling at cryogenic temperatures. Room temperature milling was also explored by combining Aluminum-Boron (Al-B) alloy with iodine. Initial thermo-gravimetric measurements show that the volatile components remain in the prepared materials at higher temperatures than known compounds, i.e., iodides, decompose. Such materials are of interest as additives to energetic formulations in propellants, explosives, and pyrotechnics. The presence of volatile components can affect ignition and combustion of the resulting energetic formulations. Changing the nature and amount of the additive enables one to customize the formulation, e.g., achieve biocidal effects for explosives or improve mixing of reactive particles with surrounding environment for propellants and pyrotechnics. The nature of a bond achieved by cryogenic milling between the volatile additives and metal is not understood; decomposition and oxidation of these new materials must be characterized and described quantitatively in order to predict their behavior in practical systems. In this project, thermo-gravimetric measurements were performed to study both heat induced release of volatile additives and oxidation when the prepared materials are heated respectively in inert and oxidizing environments. For each reaction, multi-step mechanisms are identified and the kinetics for each step along with activation energies are determined using Kissinger analysis. An extrapolation of the measured kinetic trends to the range of high heating rates characteristic of ignition enables one to identify ignition mechanism for the prepared materials. It is observed that release of iodine stabilized in the metal matrix upon its heating triggers ignition of the prepared aluminum-iodine and aluminum-iodoform composite materials.

INTRODUCTION

In recent years, there has been an interest in developing energetic composite materials with volatile additives to alter the ignition and combustion performance of pure metals. Specifically for explosives, the focus was on reactive metal composites containing volatile additives capable of generating biocidal combustion products. In the case of propellants and pyrotechnics, volatile additives are commonly used to improve mixing of reactive particles with surrounding environment. Selecting the type and composition of the volatile additive allows one to customize the formulation for specific applications.

Stability, oxidation rates, and ignition kinetics of new materials are of interest. Thermo-gravimetric measurements at low heating rates were used to study these composites in both inert and oxidizing environments. The multi-step kinetic trends identified from thermo-gravimetric measurements are extrapolated and compared with ignition kinetics studied at high heating rates. Kissinger analysis is used to determine the process responsible for ignition of the composites.

MATERIALS

A model 01HD attritor mill by Union process was used to prepare mechanically alloyed powders at the temperature of liquid nitrogen (-196 °C). The starting materials, aluminum powder and volatile additives, iodine, iodoform or cyclooctane, were ball-milled inside a 750 mL milling vial for 24 hours at 400 rpm using a rotating impeller. The cryogenic milling produced a 50-g batch of powder. The ball to powder mass ratio was 36. Additional information regarding the cryogenic milling process in the attritor mill is provided elsewhere [1]. Composite materials prepared by cryogenic milling include $Al \cdot I_2$ [2], $Al \cdot CHI_3$, and $Al \cdot C_8H_{16}$.

$Al \cdot B \cdot I_2$ [2] composite was synthesized by mechanical milling of metal powders, Al and B, with elemental iodine at room temperature inside a shaker mill (SPEX Certiprep, 8000 series) with two vials cooled by an air jet. Each vial contained 6 g of powder. Ball to powder mass ratio was 10. The vials were loaded with metal powders and volatile additives and sealed inside an argon-filled glovebox. The milling time was 4 hours.

EXPERIMENTAL

A TA Instruments Q5000IR thermo-gravimetric (TG) analyzer was used to investigate both the decomposition and oxidation of each composite. The powders were loaded into an alumina crucible with a sample mass of 2 – 4 mg. For decomposition experiments, the balance and furnace were purged with argon at 20 and 50 mL/min, respectively. The volatile additive release and stability in the metal-matrix were quantified using TG measurements in argon. For oxidation experiments, the balance was purged with argon at 10 mL/min and the furnace was purged with oxygen at 25 mL/min.

Ignition of the milled powder was characterized in air using a heated filament experiment described in detail elsewhere [4, 5]. A slurry with milled material and hexane was made to prepare a thin, 1-cm long coating on a 4.5 cm long, 0.5 mm diameter nickel-chromium alloy heating wire. The coated wire was heated by a DC current. Varied applied voltage

and adjustable resistors connected in series with the wire were used to vary the heating rates in the range of 1000 – 10,000 K/s. The temperature of the filament was measured using a high-speed infrared pyrometer (DP1581 by Omega Engineering, Inc.) focused on an uncoated filament surface adjacent to the powder coating. The emission from the powder coating was visualized using a high speed video camera (MotionPro 500 by Redlake), operated at 500 fps. Prior to ignition, the coating surface was darker than that of the heated filament. The ignition instant was registered when the powder became brighter than the heated filament.

RESULTS

For TG measurements, heating rates were varied from 2 to 20 K/min and the samples were heated up to 1000 °C. Both TG traces and their derivatives are shown in Figure 1 for decomposition experiments at 5 K/min. Derivatives of the TG traces, dm/dT, were used to identify individual stages of volatile additive release during the temperature ramp. Individual stages indicate different types of encapsulations of the volatile additive into the metal achieved during mechanical milling.
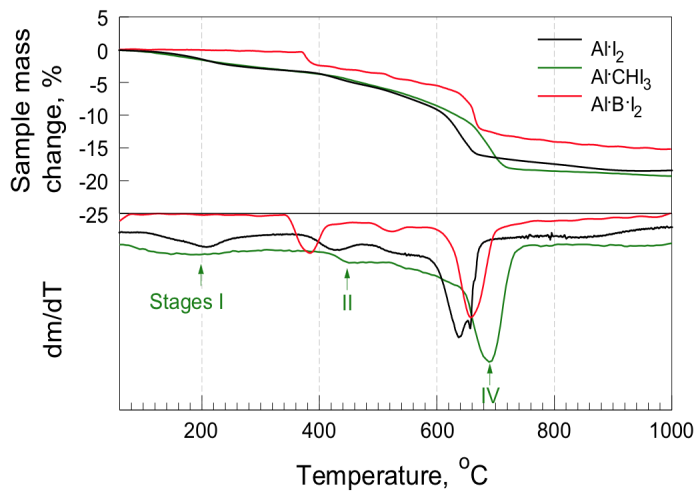

Figure 1: Mass change and derivative traces of composites at a heating rate of 5 K/min.

Results on the oxidation of the composites at 5 K/min are shown in Figure 2. A stepwise mass increase is observed for all composites during the temperature ramp. It is clear from the TG traces that volatile additives alter the oxidative behavior of aluminum. All composites start to oxidize at much lower temperatures compared to the reference Aluminum powder.
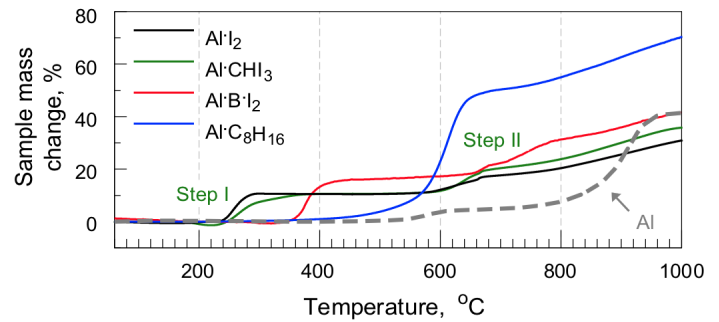

Figure 2: Oxidation of composites at a heating rate of 5 K/min.

Figure 3, shows the ignition temperatures as a function of heating rate. The data are scattered in a relatively narrow range of temperatures. A very weak trend of increasing temperatures at greater heating rates may be observed. The ignition temperatures of the composites are much lower compared to the reference aluminum.
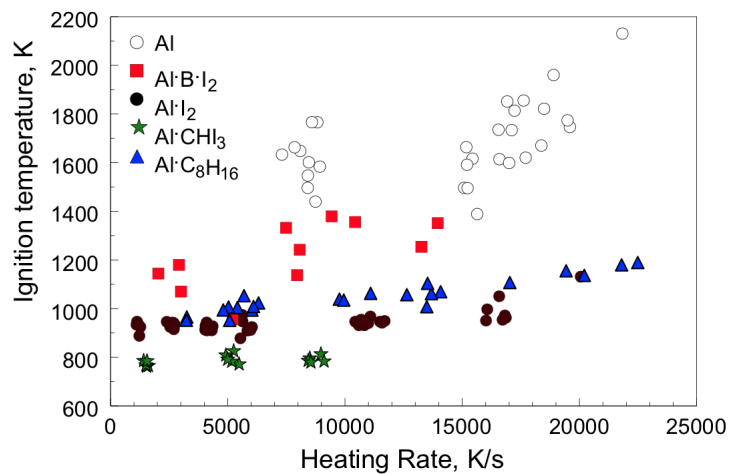

Figure 3: Ignition temperature of composites in air at various heating rates

An example of identifying the kinetic mechanism responsible for the ignition of composite using Kissinger analysis is illustrated using thermo-gravimetric measurements for $Al \cdot CHI_3$ in Figure 4. Temperatures marking positions of individual stages of iodine release (minima in the TG derivative traces), oxidation steps, and ignition temperatures are shown in the Kissinger plot. The vertical axis shows $\ln(T^2/\beta)$, where β is the heating rate and T is the specific event temperature; the horizontal axis is the reciprocal temperature, 1/T. Iodine release stages I and II do not correlate with the first oxidation step. In contrast, the iodine release stages III and IV correlate with the second oxidation step occurring near the Al melting point.

Comparing events observed in low-heating rate TG experiments with ignition, it becomes apparent that ignition is well correlated with the iodine release stage II. Extrapolation of the kinetic trend for the first oxidation step into high heating rates also points to the temperature range close

to that observed for ignition; however, the effect of heating rate on oxidation during iodine release stage I appears to be noticeably stronger than that observed for ignition temperatures.

Activation energies, ΔE, of individual iodine release stages and oxidation steps shown in Table 1 are directly proportional to the slopes of the linear-regression lines in the Kissinger plots presented in Figure 4. No activation energy value is shown for the iodine release stage III, which appears to directly correlate with the Al melting. The activation energies are determined for both Al·CHI$_3$ and Al·I$_2$. Although TG traces for both Al·CHI$_3$ and Al·I$_2$ look qualitatively similar to each other, a difference in activation energies for both individual iodine release stages and oxidation steps is observed. Activation energies of iodine release are generally lower for Al·CHI$_3$. If the decomposition rate is limited by diffusion, then this lower activation barrier suggests a lower diffusion resistance in the case of the iodoform composite, possibly due to particle disintegration and therefore increased creation of new surface during decomposition

For oxidation, the activation energies for the first step are similar for both Al·I$_2$ and Al·CHI$_3$. For the second step, the activation energy for Al·CHI$_3$ is lower.

Table 1: Activation energies, ΔE (kJ/mol), for Al·CHI$_3$ and Al·I$_2$ for various kinetic mechanisms

Iodine release	stage I	stage II*	stage IV*
Al·CHI$_3$	80±15	330±110	250±30
Al·I$_2$	130±10	530±100	530±90

Oxidation	step I	step II
Al·CHI$_3$	76±12	260±15
Al·I$_2$	65±6	380±39

*In Ref. [1] the iodine release stages corresponding to stages II and IV for Al·I$_2$ are referred to as "additional" and stage II, respectively.
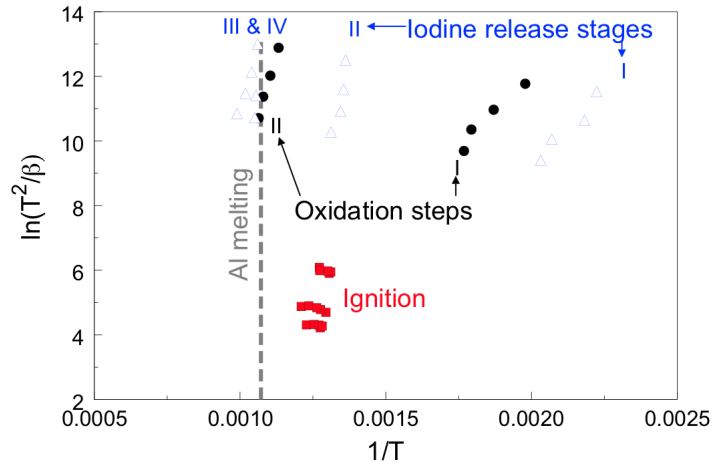

Figure 4: Kissinger plot of Al·CHI3 with ignition temperatures (squares), iodine release stages (triangles), and oxidation steps (circles) measured at different heating rates. Al melting point (dashed line) is also shown.

DISCUSSION

From the TG traces, it was evident that the materials prepared using cryogenic milling were more stable than same materials prepared at room temperature (not shown in this paper). Al·B·I2 was the only composite prepared by the room temperature ball milling that successfully stabilized a volatile component. TG traces were used to compare composites made with different milling conditions, i.e. ball-milling at liquid nitrogen temperature vs. room temperature. Furthermore, comparisons are made with a quantitative relative measure of material stability, S, defined as the percentage of weight loss observed from decomposition TG trace at temperatures exceeding 400 °C (673K). The values of S are 83% for both Al·I2 and Al·CHI3 whereas for Al·B·I2, it is 84%. Thus, both Al·CHI3 and Al·I2 prepared by cryo-milling are similar in stability to each other, and slightly less stable compared to Al·B·I2.

The individual release stages observed in the TG traces can be attributed to different ways the volatile additive is bound inside the Al-matrix. For example, in the case of Al·I$_2$, stages I and II are corresponding to two types of loosely bound iodine, that are released at the decomposition temperature of elemental iodine and dissociation temperature of AlI$_3$, respectively [2]. A significant iodine release occurs at stage IV, around the aluminum melting point, 660 °C, indicating that part of the iodine was confined within the aluminum crystal lattice or its defects, which are destroyed during melting. The ignition for this composite occurs at the aluminum melting point where iodine release is substantial. A similar approach can be used for other composites to identify their ignition mechanisms.

CONCLUSION

Thermo-gravimetric analysis was used as a tool to characterize metal composites containing volatile additives. The stability of the encapsulation of volatile component inside the Al-matrix

was quantified. Cryogenic milling was a necessity to stabilize high amounts of volatile additives. With thermo-gravimetric measurements in both inert and oxidizing environments, the individual release stages of volatile additives and stepwise oxidation of the composites were identified. The kinetic mechanism triggering the ignition of the prepared materials, $Al \cdot I_2$ and $Al \cdot CHI_3$, was associated with the release of iodine encapsulated inside the metal matrix.

ACKNOWLEDGEMENT

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