

ABSTRACT

Metal powders such as aluminum are commonly used as fuel additives to propellants, explosives, and pyrotechnics because of the improved performance they offer due to their high combustion enthalpies. However, heterogeneous oxidation of metals may cause long ignition delays, high ignition temperatures, low burn rates, and premature extinction leading to an incomplete combustion. Metal-based, mechanically alloyed materials have been proposed to improve ignition and combustion rates as a result of the metastable phase transitions that occur at low temperatures before, and sometimes during combustion. It is of interest to characterize these materials, and specifically, to explore how they behave under inert and oxidative environments upon heating. In this project, high-energy density, Al-based materials (i.e., Al-Mg, Al-Ti, etc.) are prepared by mechanical milling. Differential scanning calorimetry (DSC) is used to identify and characterize reactions that occur upon their heating in different environments, including subsolidus phase changes, eutectic and pure metal melting, and formation of various oxidized products. Thermogravimetric analysis (TGA) measurements are used to help identify and quantify decomposition and oxidative behaviors. Exothermic reactions observed in DSC are correlated to oxidative weight gains observed in TGA. Kinetic correlations are found using isoconversion processing to identify the reactions that cause or contribute to ignition of the materials. Results of such correlations will be presented in the paper.

INTRODUCTION

High combustion enthalpy metal additives to propellants, explosives, and pyrotechnics may enhance their performance. The main challenge with metal additives is that their reactions are hindered by slow kinetics that give way to high ignition temperatures, long ignition delays, slow burn rates, and incomplete combustion. Metal-based reactive materials, including Al-based alloys have been developed, capable of exothermic reactions preceding combustion, and thus accelerating ignition of these materials. These reactions include sub-solidus, intermetallic phase transformations.

Al-based alloys are particularly interesting enabling one to reduce ignition delays and accelerate burn rates while still taking advantage of the high combustion enthalpy of Al. The work presented here involves the preparation and characterization of Al-Mg and Al-Ti powders prepared by mechanical milling. Mechanically alloyed powders experience intermetallic, sub-solidus phase changes when heated, which promote their ignition, e.g., by generating an

additional fresh surface. Thermal analysis techniques such as thermogravimetric analysis (TGA) along with differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are used to identify and quantify these reactions. Correlations are then made to identify which reactions lead to powder ignition.

MATERIALS

Starting materials used in the synthesis of the composites included elemental powders of Al (Atlantic Equipment Engineers, 99.8% pure, -325 mesh), Mg (Alfa-Aesar, 99.8% pure, -325 mesh), and Ti (Alfa-Aesar, 99%, -325 mesh). For Al-Mg powders, the material compositions varied systematically with the Al concentration ranging from 47 to 90 at.%. Powders were ball-milled using a Retsch PM-400 MA planetary mill. As described elsewhere [1], the first stage of milling involved the preparation of a coarse, mechanically alloyed Al-Mg powder. Powders of Al and Mg were loaded in steel milling vials in argon. The powder charge was 30 g per vial and the ball to powder mass ratio (BPR) was 10. 9.5 mm-diameter hardened steel milling balls were used. A rotational speed was set to 350 rpm for 120 min. 50 ml of hexane (C_6H_{14}) was added to each milling vial as a process control agent (PCA). The second stage of milling involved the addition of iodine (I_2 , chips, Sigma Aldrich, 99% pure), at 4 wt. % of the initial powder load. The 9.5-mm balls were removed and replaced with the same mass of 3-mm hardened steel balls, which allowed for a softer milling necessary for particle size reduction. Milling for the second milling step was continued for 60, 120, and 180 min. depending on powder composition.

For Al-Ti powders, compositions varied between 75 to 90 at. % Al as described elsewhere [2]. Powders were ball-milled for 15 h using an 8000D series SPEX Certiprep shaker mill. Powders of Al and Ti were loaded in zirconia vials in 5 g batches with a BPR of 10, with 2 wt. % of stearic acid added as PCA.

EXPERIMENTAL

Scanning electron microscopy (SEM) was used to study powder morphology using a Phenom Tabletop Microscope by FEI Technologies Inc. Backscattered electron images were taken to inspect particle shapes and sizes. Thermal stability and temperature-dependent phase transformations were studied using TGA, DSC, and DTA. A TA Instruments Q5000IR thermogravimetric analyzer (TGA) was used to help identify and quantify decomposition and oxidative behaviors of the composites. 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. For oxidation experiments, the balance was purged with argon at 10 mL/min and the furnace was purged with oxygen at 25 mL/min. A Netzsch Simultaneous Thermal Analyzer STA409 PG was used for DSC and DTA experiments. For DSC experiments involving Al-Mg powders, corundum sample crucibles were used. For Al-Ti powders, DSC experiments were performed using aluminum pans and DTA experiments used corundum crucibles. Oxidation experiments were performed in a mixed 1:1 ratio of oxygen (50 ml/min, Matheson, 99.98% purity) and ultra-high purity argon (50 ml/min, Matheson, 99.99%) at various heating rates between 5 and 40 K/min. Decomposition experiments shown were performed in argon only and at a heating rate of 5 K/min.

Ignition of the prepared materials was analyzed using a heated filament ignition apparatus [3, 4]. A thin layer of powder was coated onto a nickel-chromium alloy wire. The wire was heated electrically and its temperature was monitored using an infrared pyrometer focused on its uncoated surface adjacent to the powder coating. Concurrently, a photodiode sensor identified a sharp onset of light emission from the coating at the ignition instant. The temperature measured by the pyrometer at that instant was assumed to be the ignition temperature. Such experiments were conducted in air for a range of heating rates between 10^3 and 10^5 K/s. Ignition instant was also identified from videos recorded using a high-speed camera (MotionPro500 by Redlake) at 500 fps.

RESULTS

Fig. 1 shows SEM images for prepared Al-Mg powders. For all compositions, the images show fine, equiaxial particles with rounded shapes. No apparent detached Al and Mg particles are visible, indicating a homogeneous mixing between the two phases. Particle sizes for each composition are comparable to each other.

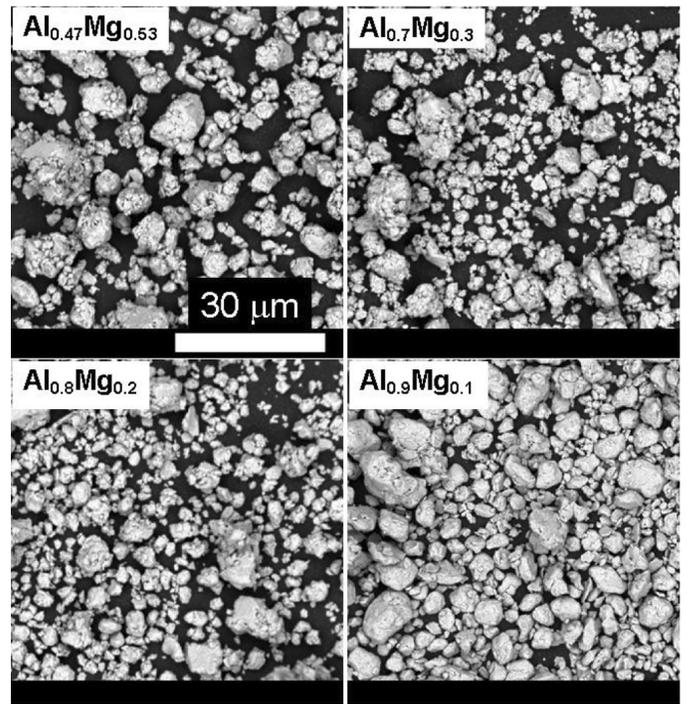


Figure 1: Back-scattered SEM images of powders of different Al-Mg compositions.

DSC and TGA traces for the oxidation experiments for Al-Mg are shown in Fig. 2. Exothermic features are observed in DSC between 200-400 °C where sub-solidus reactions are expected to occur. An inset is shown to magnify this low-temperature region discussed in more detail elsewhere [5-7]. For the $\text{Al}_{0.47}\text{Mg}_{0.53}$ powder, an endothermic peak corresponding to the eutectic melting at ~ 450 °C (~ 723 K) is visible, as expected for this composition from the binary Al-Mg phase diagram. For all powders, exothermic peaks corresponding to the strong oxidation steps in TGA are observed.

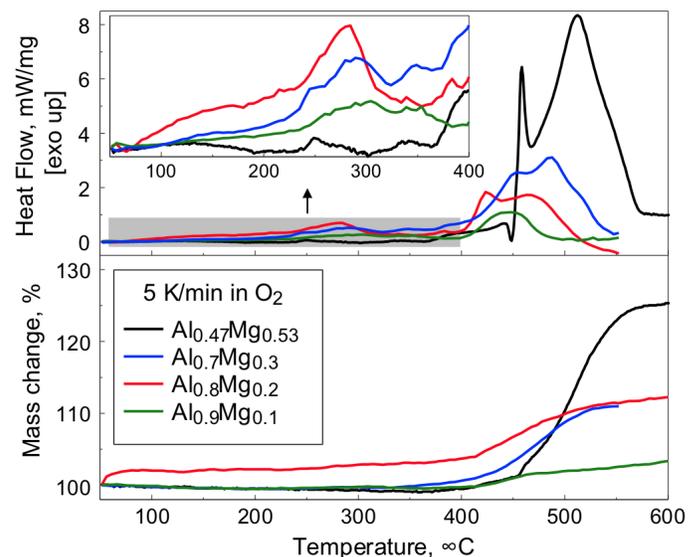


Figure 2: DSC and TGA traces for oxidation experiments performed in O_2 at 5 K/min for different Al-Mg compositions.

Fig. 3 shows DSC and TGA traces for the Al-Mg powders heated in argon. Exothermic peaks at ~250 °C are observed in DSC for all powders, corresponding to the crystallization and growth of Al_3Mg_2 phase identified in earlier work [5, 7]. For the 47/53 and 70/30 compositions, endothermic peaks corresponding to eutectic melting at ~450 °C are also clearly distinguishable. TGA traces show mass loss indicative of the release of I_2 , which begins at higher temperatures as Al content increases. This trend is consistent for all powders except the 80/20 composition. This may be due to a longer milling time experienced by this powder composition and thus, further stabilization of I_2 in the metal.

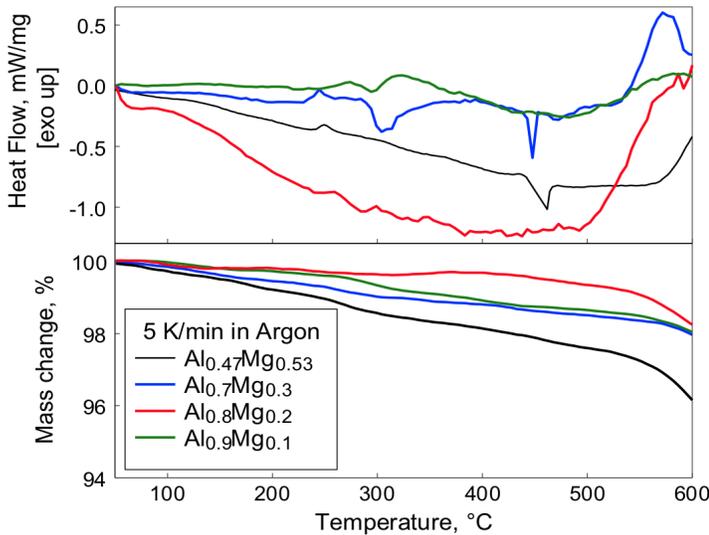


Figure 3: DSC and TGA traces for decomposition experiments performed in Argon at 5 K/min for different Al-Mg compositions.

TGA, DTA, and DSC traces for the oxidation experiments performed for Al-Ti powders are shown in Fig. 4. Oxidation of Al-Ti occurs stepwise, starting after Al melting. Large exothermic peaks corresponding to the two oxidation steps are visible in DTA. Trace amounts of carbon from the stearic acid leads to precipitation of TiC observed by the endotherm in DTA at ~900°C. In the low-temperature, sub-solidus region, exothermic peaks corresponding to formation of a series of less metastable Al_3Ti phases can be observed in DTA and even more clearly in DSC.

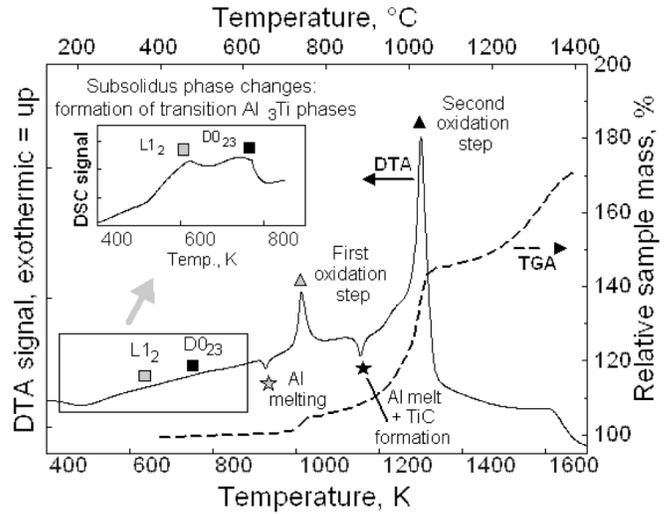


Figure 4: DTA TGA, and DSC experiments for a mechanically alloyed $\text{Al}_{0.9}\text{Ti}_{0.1}$ powder at 15 K/min.

TGA analysis was conducted for both Al-Mg and Al-Ti powders in the same oxidative environment at different heating rates in the range of 5 – 40 K/min. Derivatives of TGA traces (DTG) at varying heating rates were used to construct Kissinger plots using the DTG peak maxima. The resulting Kissinger plots (logarithm of heating rate, β , divided by temperature square vs. inverse temperature) are shown in Fig. 5. Ignition temperatures from the heated filament ignition experiments are also included.

As expected for a thermally activated ignition mechanism, ignition temperatures increase slightly with increasing heating rates. Ignition temperatures are approximately 860 K at lower heating rates and 1060 K for higher heating rates for all Al-Mg powders.

From Fig. 5, it is apparent that the points corresponding to the strong oxidation step do not line up with those of filament ignition. However, the points corresponding to sub-solidus reactions seem to correlate with the ignition points. One must consider that the measured filament ignition temperatures recorded are those of the filament and not of the powder coating, suggesting that the points seen in Fig. 5 could shift more to the right side of the plot, if corrected to represent the actual powder temperature. Considering such a correction, it would be more obvious that the ignition points line up quite well with low-temperature events (formation of intermetallic, sub-solidus phases).

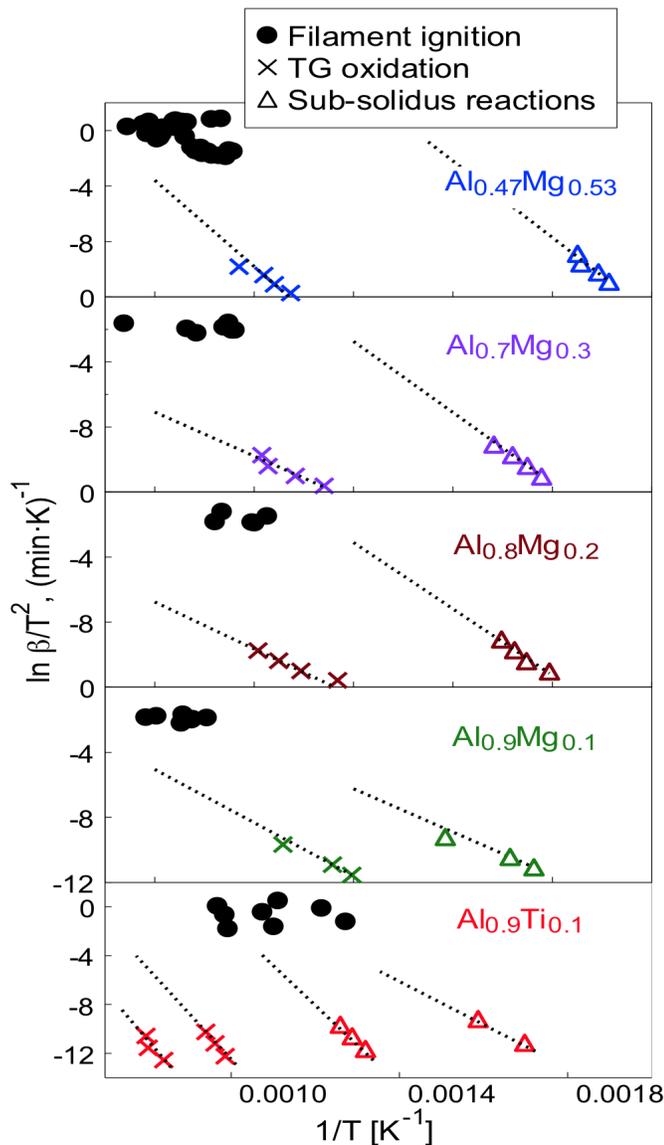


Figure 5: Kissinger plots showing correlations between exothermic events observed in DSC and TGA with wire ignition for the mechanically-alloyed Al-Mg and Al-Ti composites.

DISCUSSION

Experiments showed that iodine is an effective PCA for mechanical alloying of Al-Mg powders. The initial nominal amount of I_2 added to the powder is retained in the prepared materials (as detected by TGA, cf. Fig. 3). Ignition temperatures of Al-Mg powders are much lower than the ~ 1850 K reported for ignition of pure Al at similar heating rates, and seem to be close to the ignition temperatures of pure Mg [4].

Correlating thermo-analytical experiments with ignition experiments shows that for Al-Mg, the crystallization and growth of intermetallic Al_3Mg_2 phase at ~ 250 °C is probably the cause of ignition. For Al-Ti, ignition is likely caused by the exothermic formation of transition phases of $L1_2$ and DO_{23} between 600-800 K prior to the formation of the equilibrium Al_3Ti phase [8].

CONCLUSION

Thermo-analytical experiments were used to characterize prepared Al-Mg and Al-Ti powders. Ignition temperatures for the Al-Mg powders vary from approximately 860 to 1060 K for the range of heating rates covered in the present ignition experiments. Kinetic correlations using Kissinger analysis were made to identify the reactions that may cause or contribute to ignition. Ignition for both Al-Mg and Al-Ti powders is associated with low-temperature, sub-solidus reactions.

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By Yasmine Aly, Mirko Schoenitz, and Edward L. Dreizin

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