Effect of Aluminum Nanopowder Characteristics on Preparation and Performance of Al-Metal Oxide Nanoenergetic Mixtures

Christopher J Bulian, Tyler T Kerr, Jacek J Swiatkiewicz, and Jan A Puszynski
Department of Chemistry and Chemical Engineering,
South Dakota School of Mines and Technology.
501 E Saint Joseph, Rapid City, SD 57701

Abstract
Recent study of aluminum-copper(II) oxide metastable intermolecular composites (MIC) revealed that surface and bulk characteristics of aluminum nanopowder used in preparation of this nanoenergetic mixture has enormous influence on its ignition properties and combustion propagation velocity. Performance of aluminum containing MICs, in general, is affected by particle size, morphology, coating and reactive metal content of the aluminum nanopowder. This research study focuses on ignition, propagation and energetic effects of Al/Fe_2O_3, Al/CuO, Al/Bi_2O_3, and Al/MoO_3 MIC systems under unconfined and confined conditions. Experiments, including ignition by electric discharge, pulse laser, and thermal stimulus as well as propagation velocity measurements are correlated with preparation conditions of the MICs. Specifically, the effect of aluminum surface coating on performance characteristics will be discussed.

Introduction
MIC, in a general sense, is a thermite mixture containing both fuel and oxidizer components. When ignited by some sort of stimulus, the mixture reacts, releasing large amounts of energy. MIC is unlike conventional thermite mixtures in that it releases all its energy in much less time. This increase in reaction rate is due to the use of nanosized particles to comprise the thermite mixture. The smaller particles result in a much higher surface area for reaction as well as shorter distances between fuel and oxidizer particles[1]. The rapid release of energy allows for the use of MIC in several practical applications. It has already been incorporated as an additive in explosive mixtures, a pyrotechnic mixture in lead-free electric matches[2] and as an environmental safe replacement for lead based gun primers.

Although smaller particle size and larger surface area are the main factors contributing to increase rate of energy release, many other factors can influence the reactive behavior of MIC systems. These factors include oxide layer thickness of the aluminum particles, reactive metal content of the aluminum particles, fuel and oxidizer particle size, oxidizer behavior and the use of protective organic coatings on the surface of the aluminum particles.[3]

Experimental

Reaction Propagation Rate

Propagation velocity measurements under unconfined conditions were performed in an open burn tray apparatus. The burn test equipment consists of an open tray 43 mm long, 18 mm wide, and 8 mm deep, in which the reactant mixture is placed. Two 1 mm holes are bored in the tray 2 cm apart running the length of the tray and centered in the width. A set of baffles was place into the reactant mixture to minimize the displacement of the reactant during propagation and to prevent premature recording of the light signal.

Upon ignition by piezoelectric spark the reaction front propagates down the tray emitting light. The emitted light is collected by the fiber optics and sent to an optical to electrical signal converter. The oscilloscope readout displays two curves each with a peak in voltage signal. The average propagation velocity is then calculated by dividing the distance between the holes (2 cm) by the difference between the peaks (time).

Ignition Delay Time

Ignition delay time measurements were performed in a constant volume pressure vessel. A piezoelectric igniter is used to initiate reaction of powders held in a sample cup inside the vessel. As the reaction takes place, pressure inside the vessel increases due to the vaporization of the reaction products and gas expansion due to heat generated by the reaction. A pressure transducer measures pressure responses. The pressure transducer sends a signal to the signal conditioner, which amplifies the input signal. An oscilloscope then collects the output from the conditioner.

The oscilloscope also records the voltage of the piezoelectric igniter as well. The voltage generated by the igniter is used as the trigger for the oscilloscope. Ignition delay is defined as the time from the trigger of the reaction (generation of the piezo electric spark) to the time the reaction begins to propagate as signaled by an increase in system pressure.

Coating and Aging of Aluminum Powder

Aluminum powder, coated and uncoated was subjected to elevated temperature and humidity levels for extended periods of time to determine the effect of organic coating on the aging of aluminum as well as the affect of aging on propagation velocity and ignition delay. The aging procedure consisted of subjecting the aluminum powder to a constant humidity level of 97% RH at 40 ^{o}C. At various time intervals, samples of the powder were removed and tested for reactive aluminum content and reactivity when mixed with copper oxide.

To prevent aging, two different organic coatings were used. These were oleic acid and Dow Corning Z6124 Silane or phenyltrimethoxy silane. To coat the powders, a certain amount of the organic coating was dissolved in ethanol. The aluminum powder was then added to the solution and mixed using and ultrasonic bath for 10 minutes. The solvent was subsequently allowed to evaporate, leaving the aluminum powder and organic coating behind.

Results

Aging Effect on Propagation Velocity

As aluminum powder is aged, the amount of reactive metal content decreases and the thickness of the oxide layer increases. Both of these phenomena have an adverse affect of the propagation velocity of MIC containing the aged aluminum. Figure 1 shows the effect that reactive aluminum content has on propagation velocity.

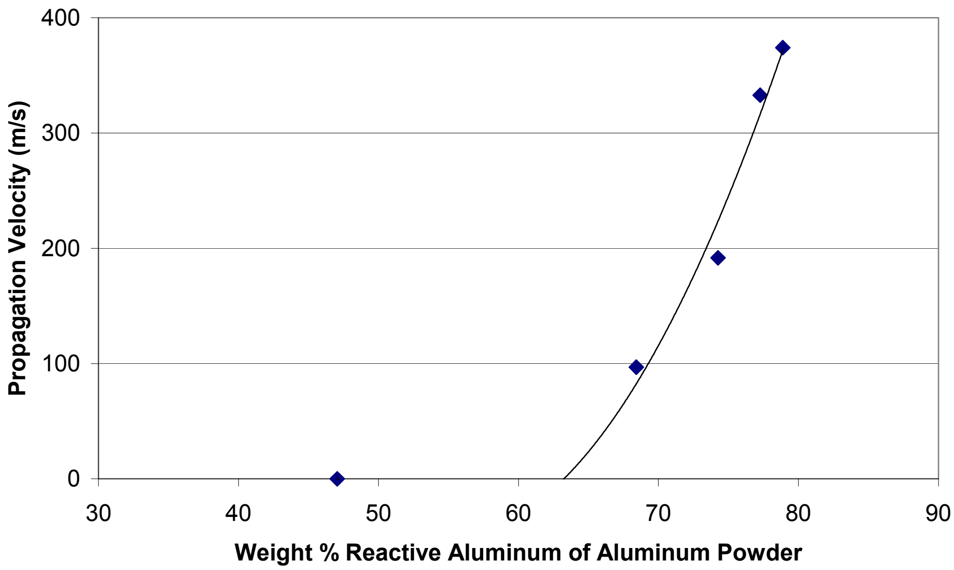

Figure 1: Propagation velocity vs. reactive aluminum content in Al/CuO system. Aluminum nanopowder aged in 97% RH in air.

As the amount of reactive aluminum content is decreased even slighty, there is a noticeable drastic effect on the propagation velocity. To prove that the decrease in propagation velocity is due to oxide layer thickness and not to the amount of active aluminum in the mixture, a second set of experiments was completed. In this second set, an additional amount of aluminum was added to the MIC mixtures to account for the amount that was lost due to the aging reaction. This assures that the same stoichiometric ratio of active aluminum content to oxidizer was maintained. The results are shown in Table 1.

Table 1: Propagation velocities in the Al/CuO system using 50 and 100 nm Nanotechnologies aluminum. Aluminum samples aged in 97% RH in air. Constant reactive aluminum content.

Sample	Weight % Reactive Al	Propagation Velocity
50 nm	77	528
	67	357
100 nm	84	405
	80	104

Effect of Organic Coating on Aging

To determine the effect of coating, two samples of Nanotechnologies 80 nm aluminum powder had coating applied to them. One sample had 5 wt% oleic acid coating and the other had 5% silane coating. For comparison, another sample of aluminum with no coating was used. The samples were all placed in the same aging chamber and tested for active aluminum content and various hourly intervals. The results of these tests can be seen in Figure 2 below.

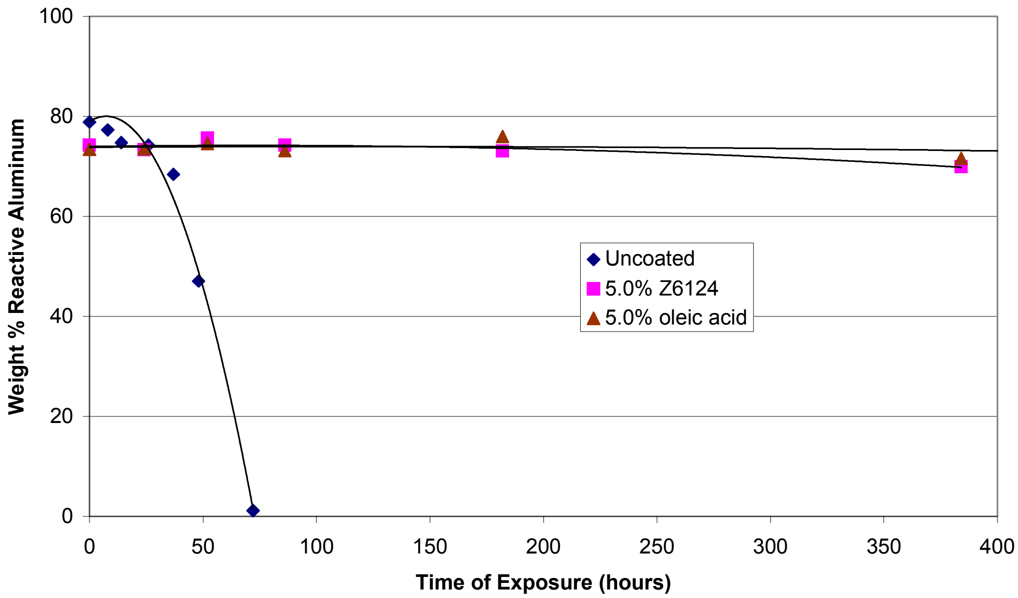

Figure 2: Aging of 80 nm Nanotechnologies aluminum with 5 wt% coatings of Z6124 silane and oleic acid. Aging results for an uncoated sample are provided for comparison. Aging was done in 97% RH in air.

The graph of aging data shows that uncoated aluminum has aged completely in a 72 hour period while the coated material maintains its active aluminum content for close to 400 hours without any significant loss in active aluminum.

Coating Effect on Propagation Velocity

Although effective at preventing the aging of aluminum, it was not known what effect coating would have on the reactivity of MIC reactant mixtures (specifically aluminum/copper oxide) containing coated aluminum. Samples of aluminum containing 0, 1, 3, 5, 10, and 15 wt% coating (silane or oleic acid) were mixed with CuO and tested in the open burn tray. The results can be seen in Table 2. There does appear to be a slight trend of increase in propagation velocity for the mixture containing the Z6124 silane but all of the values fall within the standard deviation. The oleic acid, however, tends to increase the propagation velocity as the weight percent of coating is increased. This is most likely due to the behavior of the coating as a gas generate contributing to the convective transport of heat during propagation. In both cases though, there is an upper limit where too much coating creates a diffusion barrier that does not allow ignition of the MIC.

Table 2: Results for the measurement of propagation velocity in Al/CuO system as a function of weight percent coating on the aluminum nanopowder. The coatings used were Z6124 and oleic acid.

	Z6124 Silane		oleic acid	
Weight % Coating	Propagation Velocity (m/s)	Std dev	Propagation Velocity (m/s)	Std dev
0	528	27	528	27
1	538	30	589	49
3	500	46	673	67
5	576	47	747	56
10	580	70	780	14
15	no ignition	------------	no ignition	------------

Ignition Delay Time

The effects of two different factors on ignition delay time were measured for this study. These factors include percent active aluminum content and average particle size. As the aluminum is aged, the oxide layer thickness grows and the amount of active aluminum in powder decreases. This was expected to correlate to a longer ignition delay time. Results from this experiment are shown in Figure 3.

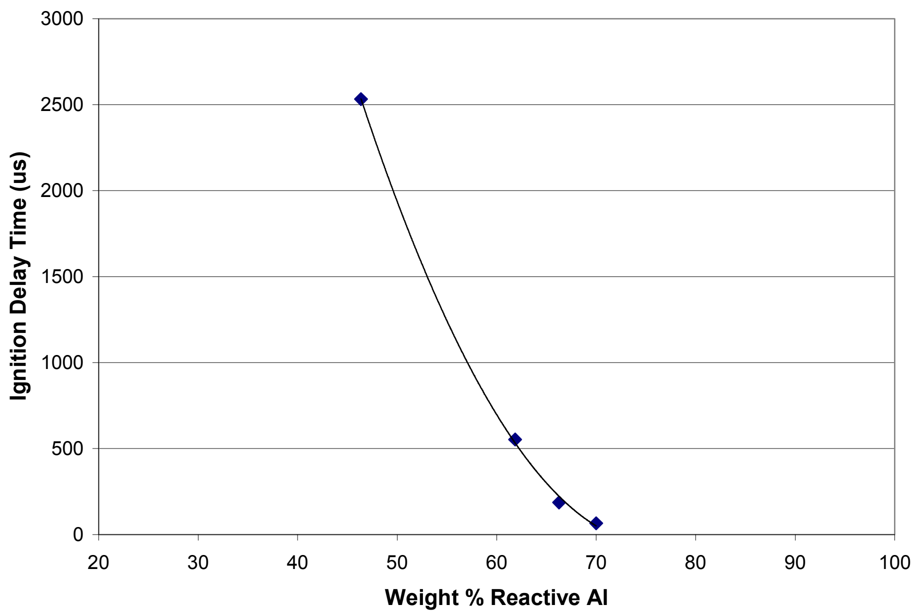

Figure 3: Ignition delay times as a function of weight % reactive aluminum in the Al/CuO system.

The decrease in active aluminum content has a considerable effect on ignition delay time. As the aluminum is aged from 70% active aluminum to 61%, the ignition delay time increases by over 5 times. This increase is likely due to the increase in oxide layer thickness as opposed to the actual amount of active aluminum. The next set of experiments proves this theory. Varying particle sizes of aluminum from 50 to 100 nm have different active aluminum contents but have the same oxide layer thickness. Results from the ignition delay tests presented in Table 3 show that delay time does not vary with active aluminum content but with oxide/hydroxide layer thickness.

Table 3: Ignition delay time in Al/CuO system as a function of average particle size of aluminum nanopowder.

Average Particle Size (nm)	Ignition Delay (ms)
50	89
80	84
100	88

Conclusions

The results of this study proved several things. Aging of aluminum under elevated temperature and pressure decreases the propagation velocity of MIC containing the aluminum. The use of organic coating on the aluminum at 5 wt% increased the shelf life of aluminum in the aging chamber from 72 hours to several hundred hours. The oleic acid coating in particular caused an increase in propagation velocity up to a critical amount near 15 wt% of the aluminum where ignition would not occur. Ignition delay time of the MIC is drastically increased as the aluminum is allowed to age. This is due to the increase in oxide layer thickness, however, as the average particle size does not affect ignition delay time.

Acknowledments

The authors gratefully acknowledge the financial support from the U.S. Army Research Office/DURINT Program (Grant # DAAD19-01-1-0503 and Grant # DAAD19-02-1-0456).

References

1. C.E. Aumann, G.L. Skofronick, and J.A. Martin, *Journal of Vacuum Science & Technology* B 13(2): 1178-1183 (1995).

2. Son, S. F., Hiskey, M. A., Naud, D. L., Busse, J. R., and Asay, B. W., “Lead-Free Electric Matches,” The International Pyrotechnics Society, The Twenty-Ninth International Pyrotechnics Seminar, Westminster, Colorado, USA, July 14-19, 2002.

3. C.J. Bulian, T.T. Kerr, and J.A. Puszynski, “Ignition Studies of Aluminum and Metal Oxide Nanopowders,” *Proceedings of the 31st International Pyrotechnics Symposium,* July 11-16, 2004.