

Metastable Nanosized Aluminum Powder as a Reactant in Energetic Formulations

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ABSTRACT

Aluminum powder is an important ingredient in many propellant, explosives and pyrotechnic applications. The production of nanosized aluminum powder by the electroexplosion of metal wire has been practiced in the former USSR since the mid 1970's. Differential scanning calorimetry, differential thermal analysis and x-ray phase analysis was performed on aluminum powder both before and after air passivation, as well as aluminum that was protected under kerosene, pentane, toluene and hexane. Earlier Soviet reports of unexplained thermal releases and metastable behavior have been investigated. Anomalous behavior previously reported included phase transformations at temperatures far below melting with the release of heat and chemoluminescence and self sintering of particles with a heat release large enough to melt the powders.

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INTRODUCTION

Nanosized aluminum powders have shown great promise for use as reactive fill in advanced projectiles, ammunition primers, super thermites and as additives to rocket propellants and explosive formulations. Nanosized aluminum powders can be readily and economically manufactured using the exploding wire process.

Most of the competing approaches for the manufacture of nanosized aluminum powders utilize equilibrium gas condensation techniques to produce very fine powders as small 0.02 μm in diameter. Current production rates for gas condensation are 20 g/hour. By comparison current production rates for the exploding wire technique are 125 g/hr. Low production rates are a serious impediment to the evaluation of nanosized aluminum powders in conventional weapons applications and in fact have prevented the evaluation of other types of nanosized aluminum powders in strand burn tests and in applications requiring more than a few grams of powder.

Preliminary samples of exploded aluminum powder have been tested by Sigman et al.¹. These workers observed a ten fold increase in the burning rate for ammonium perchlorate with the addition of nanosized aluminum powders made by the exploding wire process (ALEX). Normally the addition of aluminum to ammonium perchlorate provides at best only a slight increase in the burn rate.

EXPERIMENTAL

In the exploding wire process a capacitor is discharged into a fine metal wire which is, for the most part, vaporized into plasma. The explosion is contained in a reaction chamber which contains an inert gas, normally argon. A typical wire is less than a millimeter in diameter. The plasma condenses into a fine black

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metal powder of approximately 5 to 100 nm (0.005 to 0.05 μm) in size depending on the experimental parameters. An electrical schematic of the exploding wire process is shown in Fig. 1. The capacitor (1) is discharged by closing the switch (2) into the wire (3).

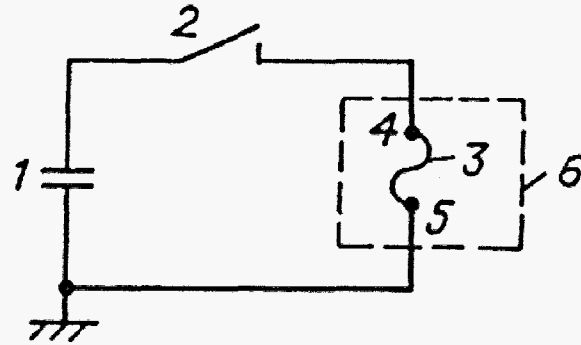


Figure 1. Electrical Schematic of the Exploding Wire Process. The components identified are, the capacitor 1, switch 2, wire 3, contacts 4 and 5 and chamber 6.

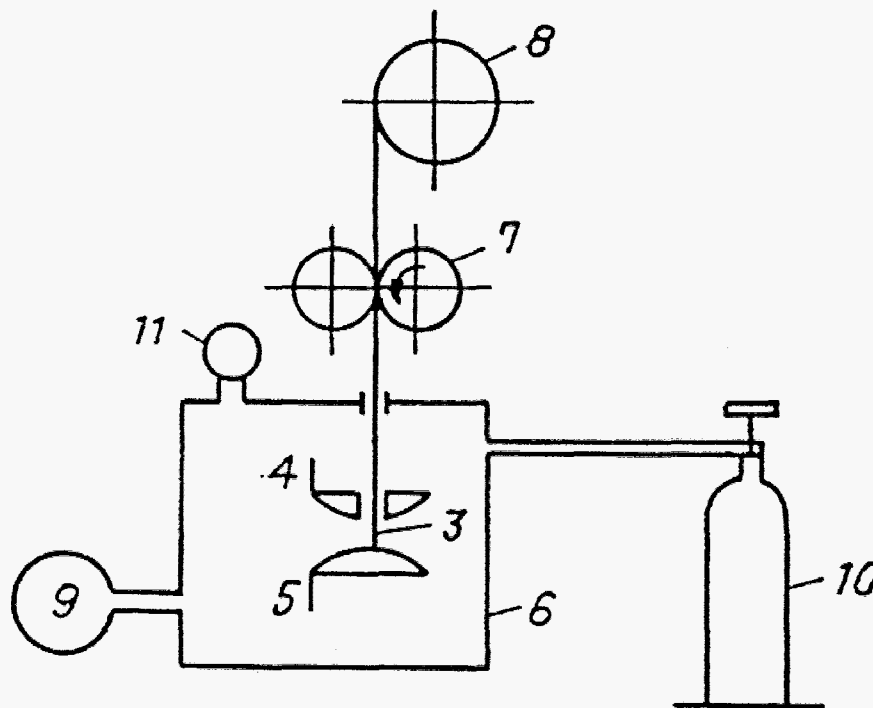


Figure 2. Diagram of Exploding Wire Apparatus. The components identified are, the wire 3, upper electrical contact 4, lower electrical contact 5, experimental chamber 6, wire rollers 7, wire spool 8, collection chamber 9, inert gas bottle 10 and pressure gauge 11.

Figure 2 is a schematic diagram of a typical exploding wire apparatus. The process is completely automated and operates continuously. The wire (3) is feed from a spool (8) through rollers (7) into the chamber (6). The wire passes through the upper contact (4) and explodes upon touching the lower contact (5). The powder is collected in (9) by partially evacuating the experimental chamber (6). A typical production rate for this type of apparatus is 1 kg/ 8 hour shift (125 g/hour). Upon collection the respective powders were placed in storage containers containing the atmospheres shown in Table I.

Thermal analysis was performed using either a Shimadzu DSC-50Q or a Shimadzu DTA-50¹. Beginning with the "D" series of samples as listed in Table I, thermal analysis was performed in high purity argon which was further purified using an in-line Oxiclear[#] gas purifier model number DGP-250-R1 which lowers the oxygen and water content of the gas to below 50 ppb. X-ray analysis was performed using a Scintag[~] PAD V diffractometer.

RESULTS AND DISCUSSION

Figure 3 is a typical differential scanning calorimeter plot for ALEX powder. The bottom curve with the large exothermic peak is for heat-up. The other curve with the two small exothermic peaks is for cool-down. The central features of this curve is an exothermic event at an average temperature of 585^o C and an endothermic event at an average temperature of 653^o C. The cool-down curve shows an exothermic event corresponding to solidification and another exothermic event with a peak at the same place as the exothermic event during the heat-up cycle.

The data for ten DSC and DTA runs are tabulated in Table 1. The temperature at which the endothermic event occurs is well defined with very little scatter in the experimental data. The variance within the ten runs is from a low of 652.2 to a high of 654.85^oC. The Janaf Thermochemical Tables² lists the melting point of aluminum at 660.3^oC (933.45 K). Aluminum calibration standard run in conjunction with these experiments shows a melting point of 659.63^o C. The ALEX powders examined in this study appear to have a melting point depression of about 7^oC. This melting point depression is small and of a magnitude normally associated with micron rather than nanometer sized particles. It is likely that the individual ALEX particles may have sintered together or otherwise agglomerated prior to melting.

The origin of the exothermic event which occurs between 579 and 594^o C is somewhat more difficult to explain. The exotherm occurs during both the heat-up and cool-down cycles. The magnitude of the cool-down exotherm is smaller than the heat-up exotherm. Some of the more speculative explanations have attributed previously observed exotherms to metastability, high defect density and spontaneous sintering. Since the exothermic between 579 and 594^o C occurs during both heat-up and cool-down possible causes such as metastability, high defect density and spontaneous sintering can be ruled out. Simpsons et al.³ observed a similar peak during the characterization of similar ALEX powders manufactured by the U.S. Army at MICOM. These workers were able to suppress the exotherm by flushing high-purity helium through the DSC cell for seven hours. These workers attributed the observed exotherm to hydride formation.

* Shimadzu Corp., Kyoto, Japan

Oxiclear, Oakland, CA.

~ Scientific Computer and Instruments, USA.

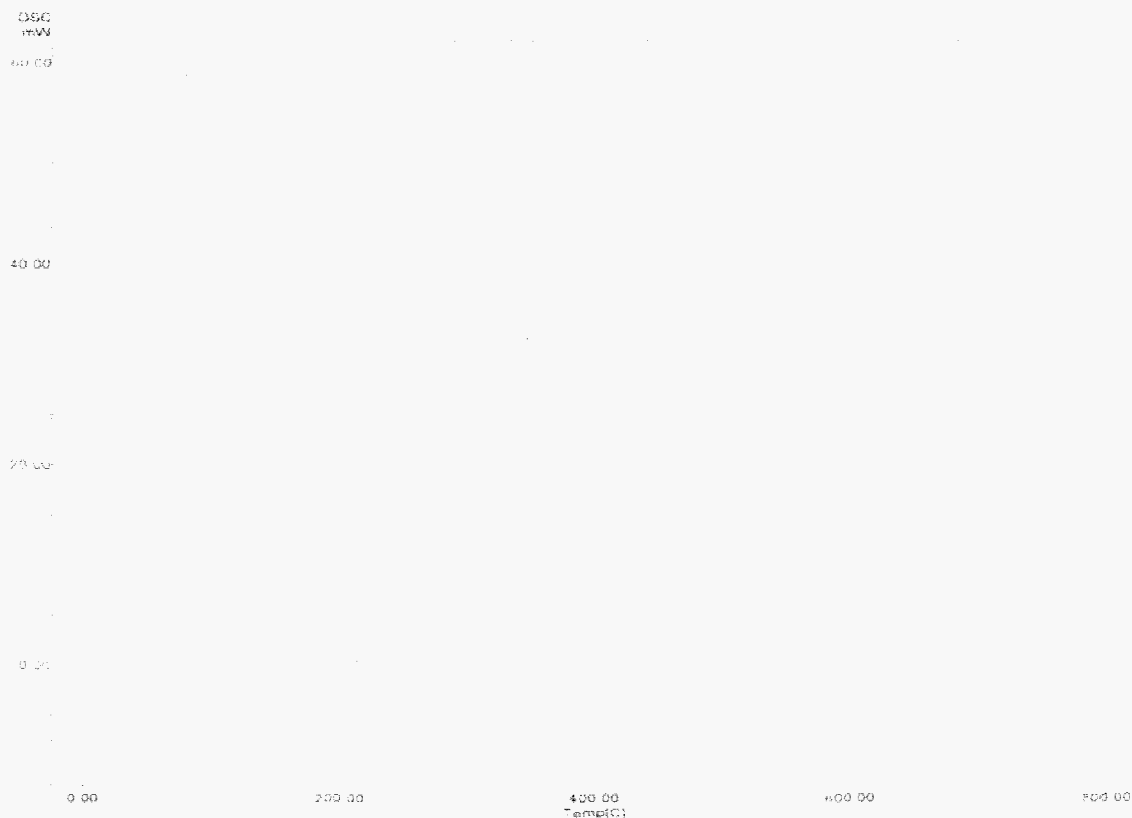


Figure 3. DSC plot of exploded aluminum powder sample. The bottom curve with the large exothermic peak is for heat-up. The other curve with the two small exothermic peaks is for cool-down.

TABLE 1. Thermal Analysis Data for Exploded Aluminum Powder

Sample	Storage	Technique	Atmosphere	Exothermic Peak Temperature	Endothermic Peak Temperature
C166	air	DSC	N ₂	584.63	653.39
C166	air	DTA	Ar	585.04	654.53
C167	kerosene	DSC	N ₂	593.48	654.04
C197	N ₂	DTA	N ₂	593.97	654.85
C197	N ₂	DSC	N ₂	586.47	652.8
C197	N ₂	DSC	Ar	587.56	652.2
D022	pentane	DSC	Ar	578.59	652.4
D023	kerosene	DSC	Ar	581.62	653.34
D024	toluene	DSC	Ar	578.94	652.44
D025	hexane	DSC	Ar	587.14	652.72

For comparison thermal analysis was also performed on a commercial atomized aluminum powder* with a size distribution between 150 and 90 microns. Figure 4 is the DTA analysis for this powder sample along with one of the ALEX samples. We observed an exothermic event at a slightly higher temperature for this sample and of a somewhat different character. This event is much more broad and gradual as compared to the ALEX powder. Table 2 is a compilation of x-ray analysis results for various ALEX powder samples before and after thermal analysis. For some of the powders trace amounts of alumina or aluminum nitride was observed before thermal analysis. In all cases alumina, aluminum nitride or aluminum oxy-nitride are observed after thermal analysis. Aluminum oxy-nitride is only denoted as AION in Table II. Various aluminum oxy-nitride stoichiometric were observed but are not differentiated because the x-ray patterns for many of these compounds overlap. Hydrated aluminum oxide compounds such as diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) or gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) were not observed.

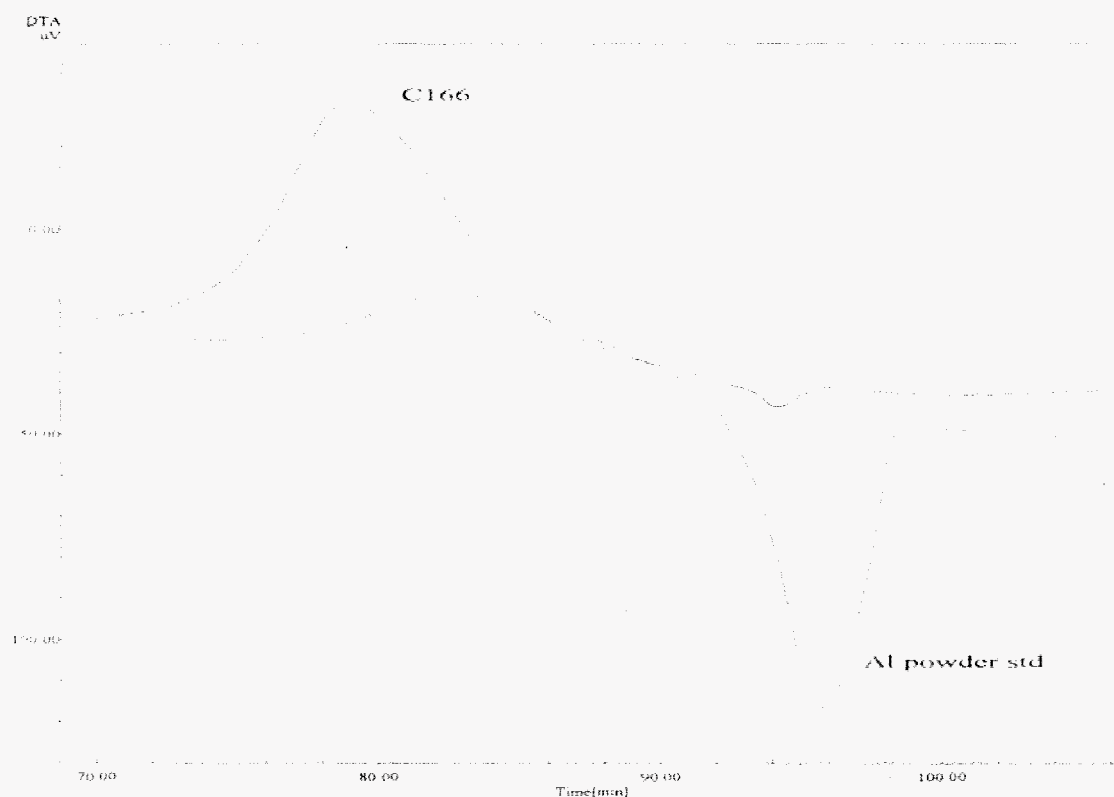


Figure 4. Comparative Differential Thermal Analysis plots for ALEX, sample C166, and commercial atomized aluminum powder sample.

Another possible explanation for the observed exothermic peak is the formation of amorphous aluminum hydroxide. To examine this possible a stability diagram was calculated at 27°C for the aluminum-alumina-aluminum hydroxide system. examination of this diagram which is Figure 5 shows that aluminum hydroxide has a very small stability field, only being stable at water partial pressures above 0.028 atmospheres. The field of stability shrinks rapidly and amorphous aluminum hydroxide is only stable above one atmosphere of water at 50°C.

* Valimet, Stockton, CA.

TABLE 2. X-Ray Analysis of Exploded Aluminum Powder

Sample	Storage	Technique	Atmosphere	Pre X-ray	Post X-ray
C166	air	DSC	N ₂	Al, AlN	
C166	air	DTA	Ar	Al, AlN	Al, ALN
C167	kerosene	DSC	N ₂		
C197	N ₂	DTA	N ₂	Al, AlN	Al, AlN, AlON
C197	N ₂	DSC	N ₂	Al, AlN	Al, Al ₂ O ₃ , AlON
C197	N ₂	DSC	Ar	Al, AlN	Al, ALON, AlN
D022	pentane	DSC	Ar	Al only	Al, Al ₂ O ₃
D023	kerosene	DSC	Ar	Al only	Al, Al ₂ O ₃ , AlON
D024	toluene	DSC	Ar	Al, Al ₂ O ₃	
D025	hexane	DSC	Ar	Al only	Al, Al ₂ O ₃

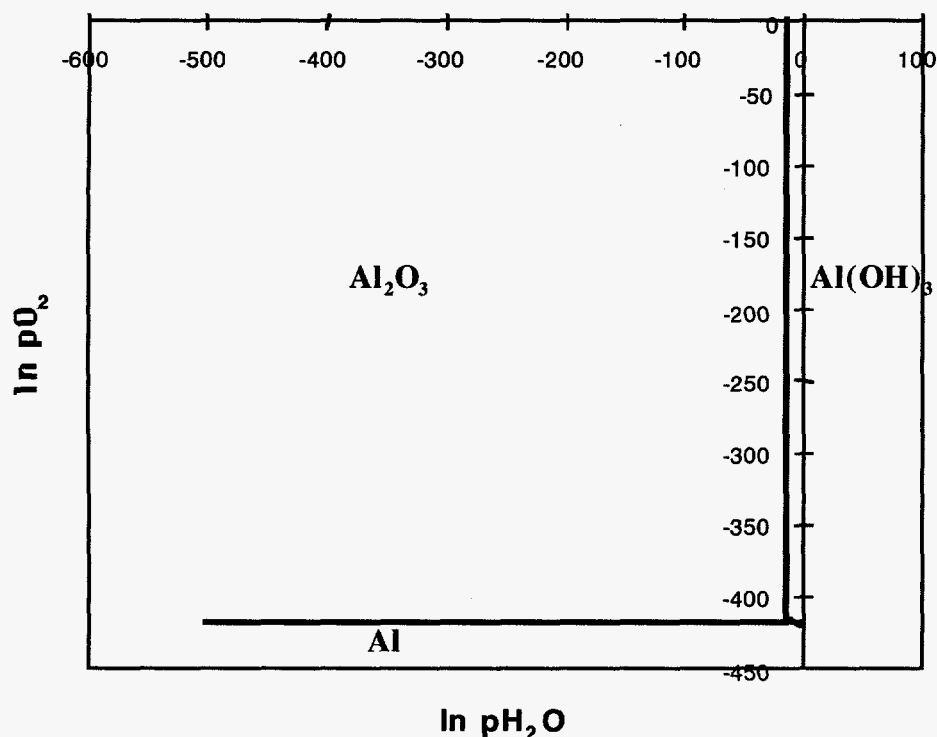


Figure 5. Aluminum-Alumina-Aluminum Hydroxide stability diagram calculated at 300 K. Calculated from data in reference 4.

SUMMARY AND CONCLUSIONS

Thermal analysis data of ALEX powders shows a sharp exotherm between 579 and 594 °C on both heat-up and cool-down. Similar analysis of a courser, commercially available micron sized powder reveals a much broader exotherm near the same temperature range. Critical examination of x-ray data of ALEX powder reveals that aluminum oxides, nitrides and oxy-nitrides have formed during thermal analysis in spite of efforts to eliminate trace impurities from the environment during the analysis. Unfortunately, lack of thermochemical data for aluminum oxy-nitrides prevented the calculation of a stability diagram for the aluminum-oxygen-nitrogen system which would be undoubtedly be of value in explaining this exotherm. No evidence of aluminum hydroxides was found and it is not thought to be responsible for the observed exotherm. Similarly, we did not observe any anomalous behavior due to metastable effects, high defect density or spontaneous sintering.

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