High-temperature and pressure aluminum reactions in carbon dioxide rich post-detonation environments

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Abstract. Powdered aluminum is a common additive to energetic materials, but little is understood regarding its reaction rate at very high temperatures and pressures in specific oxidizing gases such as carbon dioxide. Aluminum reaction kinetics in carbon dioxide have been studied in various reaction conditions, but difficulties arise in the more specific study of Al oxidation at the high pressures and temperatures in detonation reactions. To study these reactions, small particle size Al or the inert surrogate, LiF, was added to the energetic material benzotri fluoroxan (BTF). BTF is a hydrogen-free material that selectively forms CO2 as the major oxidizing species for post-detonation Al oxidation. High-fidelity PDV measurements were utilized for early wall velocity expansion measurements in 12.7 mm copper cylinders. The JWL equation of state was solved to determine temperature, pressure and energies at specific time periods. A genetic algorithm was used in conjunction with a numerical simulation hydrocode, ALE3D, which enables the elucidation of aluminum reaction extent. By comparison of the Al oxidation with LiF, data indicate that Al oxidation occurs on an extremely fast time scale, beginning and completing between 1 and 25 microseconds. Unconfined, 6.4 mm diameter rate-sticks were also utilized to determine the effect of Al compared to LiF on detonation velocity.

1. Introduction
Various studies exist regarding Al combustion in oxidizing environments such as air, oxygen, steam or carbon dioxide, typically with low initial temperatures near ambient pressure or those obtainable from a shock tube. While these conditions may replicate many of the environments that Al will be exposed to in real-world applications, it falls short of the temperatures and pressures in a detonation or post-detonation environment. The time scale of aluminum reactions in explosive environments is difficult to determine, and the conditions to promote prompt reactions are not well understood or universally accepted.

In a post-detonation environment with most explosives, H2O and CO2 are prevalent as product gases. When metals or semi-metals are formulated with an explosive, these post-detonation products become the predominate oxidizing species for the slower reacting metals. While in practice metals such as Al have been utilized in explosive formulations for nearly 100 years, little is understood of the reaction kinetics of Al at the temperatures and pressures of a detonation reaction zone, or the post-detonation expansion zone. This lack of understanding is due to a number of reasons; detailed experiments such as these are costly and difficult to set-up, and most experiments are performed with explosives that form a complex mixture of oxidizing gases, so only a global understanding of Al reactions in a mixture of gases is achieved. In order to limit the variables of different reactive gases in...
the post-detonation environment, we have prepared explosives that are free of either hydrogen or carbon, so that the predominate oxidizing species formed would be either CO₂ or H₂O, respectively. These materials have been formulated with Al in order to better understand the post-detonation reaction chemistry between Al and CO₂ vs H₂O. Lithium fluoride (LiF) was prepared in identical formulations as an inert surrogate for Al, given its similarities in density, 2.64 gcm⁻³ (Al = 2.70 gcm⁻³), melting point 875 °C (Al = 660 °C), molecular weight, 25.9 gmol⁻¹ (Al = 27 gmol⁻¹) and shock Hugoniot, Uₜ/Uₚ = 7.509/1.696 mmµs⁻¹ (Al = Uₜ/Uₚ = 7.489/1.606 mmµs⁻¹) [1].

The explosive benzotrifuroxane (BTF; figure 1) was chosen for this experimental series because it is free of hydrogen, therefore CO₂ is the primary post-detonation oxidizer formed. Aluminum reactions in a carbon-free, H₂O-forming explosive will be evaluated in a separate study.

2. Materials and Method

BTF was prepared following literature procedures [2]. Additional material was provided by Phil Pagoria at Lawrence Livermore National Laboratory. Aluminum flake (2 µm) was obtained from Firefox FX Enterprises, and LiF (< 5 µm powder, was purchased from Aldrich. Pellets were pressed containing a formulation of BTF with 15% Al or LiF for each rate stick and cylinder test.

The cylinders were 127 mm (5 in) in length, with 12.7 mm (½-in) ID and 15.2 mm OD, scaled down proportionally from the standard 1-in cylinder test configuration (figure 2a). For wall velocity measurements, PDV (Photonic Doppler Velocimetry) probe rail mounts were prepared with probe holes at 5.5 degrees to angle the probe tips toward the detonator. In each Cu cylinder/test stand, a total of four PDV probes/fiber optic cables were connected to the probe rails. The probe head and laser spot locations were measured to an accuracy of ± 0.5 mm. The probe fibers were connected to a 4-channel PDV interferometry system which comprised the interferometer, one laser and two 8-GHz, 20 Gsamples/s digitizers (Tektronix 6804B).

For the detonation velocity data, 44 gauge (0.05 mm diameter) formvar-coated Cu magnet wire was attached at 8 points along the tube, and measured with an optical height gauge (Mitutoyo) to ± 0.01 mm accuracy. The wires were held at a potential of -100 V using a Dynasen pin mixer and monitored with digitizing oscilloscopes (Tektronix TDS 540B) for the transient response of an RC circuit by shorting at the detonation front. The detonation velocity was obtained from a linear regression between the position of the magnet wire and the time of arrival of the detonation front, where initial times were normalized to zero. Charges were initiated with an SE-1-31 detonator and a 12.7 mm diameter × 12.7 mm long cylindrical pellet of PBX-9407. Plate dent profiles were determined using Solarius Development Inc., Viking 150 profilometer.

Unconfined ¼ in rate sticks were prepared with time of arrival shorting wires (the same as described above for the cylinder shots) between pellets to determine detonation velocity (figure 2b). Front curvature measurements were made from streak images of the breakout of the detonation front.
recorded using a Hamamatsu C4742 digital streak camera. The streaks were tilt corrected, and an edge-finding algorithm was applied.

3. Results

Figure 3 shows front curvature measurements for the ¼-in (6.35 mm) rate stick tests composed of pressed pellets of BTF and 15% Al (BTF/Al) vs 15% LiF (BTF/LiF). Table 1 summarizes the detonation velocities obtained from the tests. Cheetah 7.0, a thermochemical code, was used to calculate the detonation velocity for each test, and the results are summarized in table 1. As predicted by Cheetah, the detonation velocity for BTF-LiF is 2% higher than that for BTF-Al. This is a significant increase, given the small uncertainty.

![Figure 3. Digitized front curvature measurements and Dn[κ] from the 6.35 mm rate stick tests of BTF-Al and BTF-LiF.](image)

Figure 4a shows wall velocity traces for BTF/Al and BTF/LiF in the ½-in (12.7 mm) copper cylinder test cases. The insert of figure 4a indicates that the wall velocity of BTF/Al becomes larger than that for BTF/LiF after ~1 µs. Table 1 summarizes the calculated and experimental detonation velocities. Unlike the rate sticks and the Cheetah 6.0 predictions, the detonation velocity for BTF/Al is only slightly lower (0.7%) than BTF/LiF, indicating a possible diameter effect related to Al effects in the detonation reaction zone. Plate dents were measured for each cylinder test and the data are summarized in table 1. The data show an increase of 27.4% in volume (9.845% increase in depth) between BTF/Al and BTF/LiF.

Table 1. Detonation velocities for BTF-Al and BTF-LiF tests in 6.35 mm rate sticks and 12.7 mm cylinders.

| BTF + Additive (Size) | Density (g cm$^{-3}$) | Detonation velocity (mm/µs) | Calculated detonation velocity (mm/µs)$^a$ | Plate dent depth (mm) / volume (mm$^3$) |
|-----------------------|------------------------|----------------------------|------------------------------------------|------------------------------------------|
| Al (6.35 mm)          | 1.918 (96.44%)         | 7.7067 ± 0.0004            | 7.725                                    |                                          |
| LiF (6.35 mm)         | 1.918 (96.68%)         | 7.8883 ± 0.0002            | 7.975                                    |                                          |
| Al (12.7 mm)          | 1.903 (95.67%)         | 7.829 ± 0.021              | 7.669                                    | 9.3142 / 2784.1                         |
| LiF (12.7 mm)         | 1.898 (95.67%)         | 7.890 ± 0.017              | 7.883 (8.228$^b$)                       | 8.3979 / 2021.3                         |

$^a$ Calculated from Cheetah 7.0.

$^b$ Calculated using completely inert Al in Cheetah.
4. Discussion

The explosive BTF is uniquely suited for the study of early Al reactions in CO$_2$. Its density is $\rho = 1.901$ g cm$^{-3}$, detonation velocity is 8.50 mm $\mu$s$^{-1}$ and CJ pressure is 33.1 GPa [3]. Thermoequilibrium calculations predict that the oxidizing CO$_2$ only exists for brief period in detonation reaction zone, and the equilibrium products calculated to form moments later predominately contain the reducing species CO (table 2). These calculations are verified experimentally with remarkable similarity by Ornellas via Detonation Calorimetry [4].

As shown in table 1, mixtures of BTF with Al had slower detonation velocities than the LiF formulations, as the oxidation of Al with CO$_2$ results in formation of solid/liquid products and thus a net reduction of gas before the sonic surface. The corresponding experiment with LiF as an inert surrogate for Al therefore resulted in a faster detonation velocity.

| Product (mol/mol BTF) | Detonation Calorimetry$^2$ (confined) | Calculated CJ State | Detonation Calorimetry$^2$ (unconfined) | Calculated Equilibrium State |
|-----------------------|----------------------------------------|---------------------|-----------------------------------------|-----------------------------|
| N$_2$                | 2.93                                   | 2.998               | 2.98                                    | 3.000                        |
| CO$_2$               | 1.56                                   | 1.901               | 0.006                                   | 0.889                        |
| CO                   | 2.87                                   | 2.195               | 6.03                                    | 4.223                        |
| C                    | 1.57                                   | 1.203               | Not detected                            | 0.889                        |
| H$_2$                | 0.010                                  | --                  | 0.039                                   | --                           |
| H$_2$O               | 0.09                                   | --                  | 0.030                                   | --                           |

4.1 BTF+Al/LiF, detonation velocity-front curvature The digitized streak records shown in figure 3a and b indicate a clear difference in detonation front curvature between the BTF with Al or with LiF. Because of the similarities between the physical properties of Al and LiF (density, molecular weight, melting point and shock Hugoniot), it can be deduced that the aluminum reactive chemistry is responsible for the differences in detonation front curvature. Figure 3a and b shows the digitized streak images and 3c shows the Dn space for both the BTF-Al and BTF-LiF. These front curvature measurements suggest that differences exist in the reaction zone length ($\delta$), namely that $\delta_{\text{LiF}} < \delta_{\text{Al}}$ to the sonic surface. While detailed conclusions of Al reaction via front curvature would take more
experiments with higher resolution and variation in rate stick diameter, obvious and broad conclusions can be made here. At least some reaction of Al is occurring such that significant differences are observed in detonation front curvature, and thus within the ns timescale.

4.2 Solution of JWL equation of state parameters The JWL detonation product equation-of-state (EOS) was determined from PDV wall velocities by a refined version of a technique given in [5]. The JWL pressure isentrope is given by equation (1),

\[ P_s[V] = A \exp(-R_1 V) + B \exp(-R_2 V) + \frac{C}{V^{\gamma_{iso}}}, \]

(1)

where \( P \) is pressure, \( V = \rho/\rho_0 \) is the relative volume. The parameters \( A, B, R_1, R_2, \) and \( \omega \) are the coefficients to be fit. The JWL parameters for the two materials are listed in table 3.

Table 3. JWL parameters for BTF-Al and BTF-LiF.

| Material    | \( \rho_0 \) (g/cc) | \( D \) (mm/\( \mu \)s) | \( A \) (GPa) | \( B \) (GPa) | \( C \) (GPa) | \( R_1 \) | \( R_2 \) | \( \omega \) |
|-------------|-------------------|----------------|-------------|-------------|-------------|--------|--------|--------|
| BTF + 15% Al | 1.762             | 7.829          | 698.69      | 6.1889      | 0.93696     | 4.5796 | 0.92058 | 1/3    |
| BTF + 15% LiF | 1.757            | 7.890          | 645.06      | 4.8165      | 0.14541     | 4.3575 | 0.83878 | 1/3    |

Note that the five-figure precision of the \( A, B, R_1, \) and \( R_2 \) parameters is for the purpose of accurately enforcing the necessary constraints. They are not really known to the quoted level of accuracy. The Chapman-Jouguet and performance parameters are listed in table 4. As expected, the Al-loaded case releases much more energy than the LiF-loaded case. The JWL isentropes for the two cases are plotted in figure 5.

Table 4. CJ and performance parameters for BTF-Al and BTF-LiF.

| Material    | \( \rho_0 \) (g/cc) | \( D_{cj} \) (mm/\( \mu \)s) | \( V_{cj} \) | \( P_{cj} \) (GPa) | \( E_{cj} \) (kJ/cc) | \( \gamma_{cj} \) | \( E_0 \) (kJ/cc) |
|-------------|-------------------|----------------|-------------|-----------------|-----------------|--------|--------|
| BTF + 15% Al | 1.762             | 7.829          | 0.751       | 26.9            | 11.93           | 3.01   | 8.01   |
| BTF + 15% LiF | 1.757            | 7.890          | 0.750       | 27.3            | 9.74            | 3.01   | 5.76   |

Figure 5. JWL isentrope comparison for BTF-Al vs BTF-LiF.

The ratios of the energies of the BTF-Al and BTF-LiF were used as a measure of completeness of reaction of Al, and allowed for the direct comparison of measured and calculated values. We notice a remarkably similar value in the percentage increase in energy with the reacting Al explosive, which provides convincing evidence that all of the Al has reacted before cylinder break-up. The same
approach was taken using the $E_0$ calculated from Cheetah 6.0 and that of the JWL solution, and the results are given in table 5.

**Table 5.** Calculated (Cheetah $E_{100}$) and measured (Gurney) energies of BTF-Al and BTF-LiF. Calculated $E_0$ and $E_0$ from JWL solution of BTF-Al and BTF-LiF.

| Explosive     | $E_{100}$ Cheetah (kJ/g) | Measured Gurney (kJ/g) | $E_0$ Cheetah (kJ/cm³) | $E_0$ JWL solution (kJ/cm³) |
|---------------|--------------------------|------------------------|------------------------|----------------------------|
| BTF + 15% Al  | 5.586                    | 3.898                  | 13.07                  | 8.01                       |
| BTF + 15% LiF | 4.394                    | 3.038                  | 9.06                   | 5.76                       |
| % Increase    | +27.1                    | +28.3                  | +44.3                  | +39.1                      |

The results shown in table 5 confirm the results summarized in table 4, that all of the Al has reacted before cylinder break-up. Early PDV records indicate that the wall velocity of the mixture with reactive Al exceeds that of LiF, even as early as 1 µs. Taken with the observation obtained from the front curvature measurements, it is clear that Al reaction with CO₂ released from the detonation of BTF occurs on an extremely fast time scale. These conclusions are further supported by the data summarized in table 2, where the CO₂ available to oxidize Al exists only for a short period before CO is formed.

**References**

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