Pressure waves generated by metastable intermolecular composites in an aqueous environment

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Abstract. In the present study, pressure waves generated by a metastable intermolecular composite (MIC) have been measured experimentally in an aqueous environment and correlated with flame speed measurements. Underwater experiments were performed in a 1.0 L high-pressure chamber mounted with high-resolution pressure transducers and designed with optical access. Samples consisting of a stoichiometric mixture of aluminium and copper(II)-oxide particles were evaluated. Two types of samples were synthesized; a mixture of micron-sized raw powders, and ball-milled powders with a fine-scale nano-structure. A planetary mill was used to refine reactant powders from micron- to nano-scale dimensions. The dynamics of the pressure wave and high-pressure gas bubble were monitored via pressure histories and high-speed Schlieren visualization. The effect of reactant particle size has been evaluated quantitatively. The dynamics of the pressure wave were correlated with the rate of expansion of the high-pressure gas bubble.

1. Introduction
Past research has shown that by controlling the microstructure of thermite materials, one can control their burning rate, and thus, the rate at which high-pressure gases are released. In particular, a reduction in the mean particle size of the material has been found to yield faster burning rates and increased pressurization rates [1, 2]. One method that has shown the ability to fine-tune the microstructure of these materials is mechanical alloying. In this process, fully-dense powders with reactive components uniformly mixed on the nano-scale can be synthesized [3].

Recently it has been shown that thermite reactions underwater give rise to more moderate pressure pulses than conventional explosives [4]. These unique and tunable pressure profiles were found to be more conducive to applications such as cellular transfection and drug delivery [5]. In their investigation, microchips formed by the consolidation of nano-scale Al₂Bi₃O₇ and Al-CuO were used to generate pressure pulses in order to transfect fluorescent plasmids into primary cells. Compared with previous technologies, an improvement in both the transfection rate and cell survivability was observed.

In the present study, a thermite mixture of aluminium and copper(II)-oxide prepared via mechanical alloying was investigated experimentally. Burning characteristics of both micron-scale and mechanically alloyed mixtures were compared via open-channel flame-speed experiments. Pressure pulses emit in an underwater environment were measured and visualized.
in a closed vessel. Results were compared with analytical calculations based on measurements of gas bubble growth.

2. Experiment

2.1. Material preparation
Aluminium (Al, Atlantic Equipment Engineers, 99.9% pure, -325 mesh sifted to less than 25 μm) and copper(II)-oxide (CuO, Atlantic Equipment Engineers, 99.9% pure, 1-5 μm) were blended and mechanically alloyed using a planetary ball mill (Fritsch Pulverisette 7). A procedure similar to Umbrajkar [6] was utilized for the refinement process. The mixture was blended in stoichiometric proportions (2Al-3CuO by mole, 18.4% Al-81.6% CuO by mass). To produce ball-milled samples, blended powders were placed inside 80 mL tempered steel vials containing fifteen hardened steel milling balls (9.25 mm diameter). Vials were loaded in an argon environment with 1 g of the blended mixture and 4 mL of Hexane (C₆H₁₄). Hexane was used as a process control agent (PCA) to inhibit reactions during the milling procedure. The mill operated at a rotational speed of 450 rpm with a cycle duration of 2 min. The direction of rotation was set to reverse at the end of each cycle. The number of cycles was varied to evaluate the mixture at numerous stages of milling. Five samples were considered in this study: unmilled powders, and milled powders resulting from 16, 30, 46 and 60 minutes of refinement.

2.2. Material characterization
Evaluation of the sample mixtures was conducted via scanning electron microscopy (SEM) and X-ray diffraction (XRD). Figure 1 shows the XRD pattern of the blended (unmilled) and mechanically alloyed (milled) samples. The molecules corresponding to relevant peaks are shown in the legend. Unmilled powders are found to have peaks corresponding to Al, CuO and a small quantity of Cu₂O.

![Figure 1. X-ray diffraction (XRD) pattern of unmilled and milled powders.](image)

After 16 minutes of milling, the composition of the mixture was found to be nearly identical to that of the unmilled powder. Minor broadening of the reactant peaks was found, indicating that some of the mixture reacted locally to form intermediate and product species. These reactions were very limited as no other significant peaks were found. By 30 minutes of milling,
peaks corresponding to Al$_2$Cu, Al$_2$CuO$_4$, AlCu, and elemental Cu were observed. Broadening of the peaks further increased due to the formation of these new species. After 46 minutes of refinement, the concentration of intermediates and products was found to further increase. The presence of Cu$_2$O re-appeared due to increasing concentrations. Finally, after 60 minutes of refinement, the concentration of intermediates and reaction products was approximately uniform with that of the original constituents.

Scanning electron microscopy permit for monitoring the small-scale structure obtained at different milling times (figure 2). The unmilled mixture of Al (dark) and CuO (light) is shown in figure 2a in which the morphology and particle size of the raw materials are shown. Milling for a duration of 16 minutes was found to yield an alloyed mixture of the constituents as shown in figure 2b. Micron-sized particles consisting of nano-scale layers of Al and CuO were formed as a result of high-energy collisions between reactant particles and the surrounding surfaces. After 30 minutes of refinement, a reduction in the size of both the small- and large-scale structures was found and is shown in figure 2c. In figures 2d and 2e, corresponding to 46 and 60 minutes of refinement, a further reduction in the size of the small- and large-scale structures is apparent. These results indicate that increased milling durations yield more refined nano-structures and smaller macroscopic scales of the alloyed particles.

![Figure 2. Scanning electron microscope (SEM) images of prepared samples.](image)

2.3. Flame speed measurements
The reactivity of each mixture was characterized experimentally by measurement of the flame propagation speed in an open-channel. Experiments were conducted in a steel channel with dimensions $2.5 \times 2.5 \times 70$ mm. In each case, samples were loaded at approximately 30% of the theoretical maximum density (TMD). The reaction was initiated at one end sending a flame propagating the length of the channel. A Phantom V1210 high-speed camera was used to capture the location of the flame during the reaction event. Reconstruction of the video permit for measurement of the flame propagation speed. A typical experiment is shown in figure 3.

The average flame speed for each of these mixtures is presented in figure 4. In general, milled samples demonstrated higher flame speeds compared to the unmilled mixture; a result characteristic of a decrease in the mean particle size of the reactant mixture [7, 8]. For the milled samples, a decreasing trend in the flame speed occurred with increased milling time. This trend has been attributed to the increasing concentration of intermediates and reaction products associated with longer milling times which significantly reduces the energy density of the mixture.

As a result of these experiments, it was determined that the the mixture milled for 16 minutes exhibited the most significant improvement over the unmilled mixture. This mixture consisted of particles on the order of 1-10 $\mu$m with nano-scale layers of approximately 100-500 nm.
2.4. Underwater measurements

Experiments measuring the pressure pulses produced in water were conducted in a 1.0 L combustion vessel. The vessel has a rectangular internal cavity with dimensions $4.0 \times 4.0 \times 3.75$ inches. Acrylic windows permit for optical access while two wall-mounted pressure sensors (PCB 113B27) and one underwater free-field shock gauge (Neptune Sonar Tourmaline Model TII) are used to monitor the pressure. Ignition of the sample is achieved using resistive heating of a tungsten filament with a variable power supply. Schlieren visualization using a Phantom V1210 high-speed camera was used to capture the ignition event and subsequent phenomena.

Samples were prepared by loading powders into cylindrical glass vials embedded with a tungsten filament. Experiments using the unmilled and 16-minute milled mixtures were conducted with samples containing between 150 and 300 mg of the reactant mixture. The events of a typical experiment are shown in figure 5.

Within each experiment, distinct phenomena were found to occur over two time scales. In the early stages of the event a pressure wave is emitted from the sample, while at later times a high-pressure gas bubble expands radially from the ignition source. In figures 5a to 5d the
motion of the acoustic wave resulting from the ignition of the sample is shown. After \( t=20 \) \( \mu s \), the reaction within the capsule has initiated and a pressure wave transmits through the water. By \( t=40 \) \( \mu s \), the wave has reached the free-field sensor and by \( t=60 \) \( \mu s \) the wave has reached the end wall. Figures 5e to 5h show the motion of the high-pressure gas bubble. The bubble is shown expanding radially into the surrounding water, reaching its peak volume at approximately \( t=600 \) \( \mu s \). The bubble is then shown contracting at \( t=900 \) \( \mu s \), typical of a free-field underwater explosion [9].

![Figure 6. Pressure trace for the 16-minute milled and unmilled samples as a function of time.](image)

Free-field pressure histories for the two mixtures were obtained experimentally; typical waveforms are shown in figure 6. Milled samples were found to yield higher peak pressures over the same characteristic rise time when compared with unmilled samples. This result has been attributed to the increased flame speed and faster chemistry associated with the mechanically alloyed mixture. By increasing the rate at which high-pressure gas is generated, a larger compression of the surrounding medium results in higher pressures in the far-field. An increase in the peak pressure from approximately 300 kPa for the unmilled samples to over 700 kPa for the milled samples was observed. This result indicates that the pressure waveforms created by thermite reactions underwater can be adjusted by reducing the mean particle size of the reactant mixture via mechanical alloying.

3. Acoustic Analysis

Owing to the slow nature of the gas-bubble expansion relative to the sound speed of the surrounding medium, acoustic theory may be used to estimate the wave dynamics of the emitted pressure pulse. Using the motion of the gas sphere observed experimentally in figure 5, an estimation of the pressure signature can be obtained. Experimentally measured gas sphere radii are plotted in figure 7 and are fit to an inverse exponential function of the form

\[
R(t) = A \left( 1 - e^{-\frac{t}{\tau}} \right)
\]  
(1)

where \( A \) and \( \tau \) are fit parameters. The fitted equation is shown by the dashed line in figure 7. For spherical one-dimensional geometry, the acoustic wave equation has solution for the velocity potential of outward facing waves \( \phi = \frac{f(r-c t)}{r} \) where the fluid velocity and pressure can be obtained as \( u = \frac{\partial \phi}{\partial r} \) and \( p = -\rho \frac{\partial^2 \phi}{\partial t^2} \). Following a similar procedure to the acoustic spherical piston model described by Taylor [10], the time-evolution of the bubble radius can be used to obtain an expression for the pressure field as a function of position and time, equation (2). In this equation \( p \) is the pressure, \( \rho \) and \( c \) are the density and sound speed of the surrounding medium.
medium taken as 1000 kg/m$^3$ and 1500 m/s, respectively, $\dot{Q}$ is the volumetric acceleration of the gas sphere obtained from equation (1), $r$ is the radial position, and $t$ is time.

$$p(r, t) = -\rho \frac{\partial \phi}{\partial t} = \frac{\rho}{4\pi r} \dot{Q} \left( t - \frac{r}{c} \right)$$  \hspace{1cm} (2)

The estimated pressure-time signature for an unmilled sample is shown and compared with actual measurements in figure 8.

![Figure 7. Evolution of the high pressure gas bubble radius as a function of time.](image)

**Figure 7.** Evolution of the high pressure gas bubble radius as a function of time.

![Figure 8. Calculated pressure signature of the acoustic wave compared with experiment.](image)

**Figure 8.** Calculated pressure signature of the acoustic wave compared with experiment.

Comparison of the data shows that the magnitude of the theoretical pressure pulse agrees well with the experimentally measured peak pressure, while the pressurization rate is not well represented. While acoustic approximations were found to be a suitable candidate in estimating the bulk energy release produced by thermite reactions in water, the rate of energy release was underpredicted. In order to accurately predict the rate of energy release, a model capturing the non-linearities of the flow-field may serve to be more suitable.

4. Conclusions

Refinement of aluminium-copper(II)-oxide thermites has been shown to yield increased flame propagation speeds owing to a reduction in the mean particle size of the reactant mixture. Longer milling times coincided with a decrease in the reaction velocity owing to increasing concentrations of reaction products in the mixture. Faster burning rates associated with milled samples resulted in higher peak pressures and pressurization rates in water. Acoustic approximation of the pressure signal yielded comparable peak pressures with actual measurements, however the rate of energy release was underpredicted.

References

[1] Dikici B, Pantoya M and Levitas V 2010 Combust. Flame **157** 1581-5.
[2] Bockman B, Pantoya M, Son S, Asay B and Mang J 2005 J. Appl. Phys. **98** 064903-1.
[3] Schoenitz M, Ward T, and Dreizin E L 2004 Mater. Res. Soc. Symp. Proc. **800** AA2.6.1-AA2.6.6.
[4] Apperson S, Shende R, Subramanian S, Tappmeyer D and Gangopadhyay S 2007 Appl. Phys. Lett. **91** 243109.
[5] Apperson S, Thiruvengadathan R, Bezmelnitsyn A, Gangopadhyay K, Gangopadhyay S and Polo-Parada L 2008 Proc. 26th Army Sci. Conf.
[6] Umbrajkar S, Schoenitz M and Dreizin E 2006 Thermochim. Acta **451** 34-43.
[7] Weismiller M, Malchi J, Lee J, Yetter R and Foley T 2011 P. Combust. Inst. **33** 1989-86.
[8] Watson K, Pantoya M and Levitas V 2008 Combust. Flame **155** 619-34.
[9] Cole R 1948 Underwater Explosions Princeton, Princeton University Press.
[10] Taylor G 1946 Proc. Royal Soc. A **186** 273-92.