Nanocomposites for underwater deflagration

A nanoparticle composite for explosive underwater reaction applications has been designed with a nanomatrix of polytetrafluoroethylene and aluminum.

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Nanometer aluminum fuel particles demonstrate orders of magnitude higher ignition sensitivity and reactivity than micrometer aluminum particles. This enhanced ignition sensitivity could enable a submerged reaction to propagate and react to completion without quenching. Energetic composites consisting of micrometer Al fuel particles cannot react submerged because too much energy from the reaction is lost to the surrounding water, causing the reactants to quench. However, Al nanoparticles can be synthesized with significantly higher surface-area-to-volume ratios that enable them to exhibit new and unique combustion properties that are much improved over their micron scale counterparts.

One such property is enhanced ignition sensitivity, which has the potential to open a new realm of underwater reaction applications. These could include fuses, propulsion, underwater ordnance, torch or metal cutting technologies, offshore oil drilling, blasting, and welding, as well as alternative power sources in oceanic environments.

Polytetrafluoroethylene (PTFE) (CnF2n+2) is an ideal oxidizer for underwater reactions because it is a fluorine compound and it is hydrophobic. An oxidizer is a reactant that either releases oxygen atoms or gains electrons in an oxidation-reduction (redox) reaction. Fluorine compounds are powerful oxidizers because fluorine is the most electronegative element and gains electrons more readily than oxygen. Also, because PTFE is hydrophobic, a mixture containing PTFE should reduce or eliminate permeation of water through the reactants, thus preventing loss of reaction energy to the water, permitting the reaction to go to completion.

Combustion reactions can be categorized by their speed. Reactions that take place at supersonic speeds via shock compression are called detonations; whereas reactions that take place at subsonic speeds are called deflagrations. Most flames observed in daily life are deflagrations, and they propagate via modes of thermal energy transport (conduction, convection, radiation, for example). The Al-PTFE reactions discussed here fall into the deflagration category of combustion reactions.

The submerged mixture is ignited by a heated Nichrome wire. As the PTFE is heated, the CnF2n+2 chain decomposes and releases fluorine gas, which is highly reactive with aluminum. No current studies are available in the literature that demonstrate a naturally hydrophobic solid energetic composite’s ability to burn or deflagrate while submerged underwater. However, this study proves that with nanometric particles, this reaction underwater is possible. Furthermore, we have characterized the submerged reaction dynamics. Understanding the reaction dynamics will help engineers design equipment for various underwater applications.

Particle size effects

Novacentrix provided mixtures of aluminum particles with an average diameter of 84 nanometers; and Atlantic Equipment Engineers provided mixtures of aluminum particles with an average diameter of 1 to 3 micrometers. Each mixture was combined with submicron PTFE particles 200 nm in diameter, supplied by DuPont (trade name: Zonyl MP1150).

The balanced reaction, shown as Eq. 1, was used to determine the stoichiometric fuel-to-oxidizer ratio for the Al-PTFE composites. A specified equivalence
ratio $\phi$, defined by Eq. 2; and the stoichiometric fuel-to-oxidizer ratio determined from the reaction in Eq. 1, were used to calculate the mass for each of the reactant samples. An $\phi=1.0$ corresponds to stoichiometric, while $\phi > 1$ is fuel rich.

$$4Al + 3C_2F_4 \rightarrow 4AlF_2 + 6C$$

(1)

$$\phi = \frac{(\text{Fuel mass} / \text{Oxidizer mass})}{(\text{Fuel mass} / \text{Oxidizer mass})_{\text{stoichiometric}}}$$

(2)

The powder mixtures were pressed into pellets that ranged from 20 to 40% of the theoretical maximum density (TMD) and submerged in water.

Figure 1 shows a scanning electron microscope (SEM) micrograph of 40% TMD pressed sample. It reveals that the submicron spherical morphology of Al and PTFE are maintained after the reactant powders are pressed into pellet form. A constant mass of 30 mg powder mixture was placed in a horizontal, cylindrical cavity at the bottom of an acrylic tank and ignited with a hot wire.

Figure 2 illustrates the aquarium apparatus for these tests. The reaction was recorded with a high speed digital camera at 5000 frames per second. A fiber optic light guide provided additional illumination to improve visualization. Along with the high speed video, pressure data was recorded with an underwater blast pressure sensor at 10 kHz. The aquarium setup allows the gas/water interface to be visualized (Fig. 1), and can be used as a method for estimating the gas generation from the reaction.

**Effects of size and shape**

The hydrophobic PTFE powder reduces wetting of the Al-PTFE sample such that the pellets stayed intact and would still ignite after two months submerged.

- **Micrometer Al-PTFE**: Micron Al-PTFE composites would burn only adjacent to the ignition source, then quench. The micrometer Al reaction requires a higher apparent activation energy than nanometric aluminum. Upon reaction, micrometer aluminum may not produce enough power to counter the heat lost to the environment, and thus does not propagate to the surrounding reactants.

- **Nanometer Al-PTFE**: The bulk density (quantified as TMD) and stoichiometry of the Al-PTFE samples were varied independently. Results characterize the reaction time, pressure, bubble radius, and shape.

**Bubble shape** depends on the bulk density of the sample. Figure 4 shows the variation in bubble formation from high- to low-density samples. High-density samples form a jet of small bubbles. Low-density samples form a single bubble that would grow, separate, and float toward the top of the tank. Mid-range density samples showed a transition during which the sample would either form a ball of small bubbles, or generate a few large bubbles. Dark clouds of black, solid products and gas from previous bubbles can be seen in the top of the images for the 40% and 35% TMD samples.

**Burn times** depend on the bulk density of the sample. Higher-density samples were observed to react for a longer duration. For 35 to 40% TMD, the reaction time ranged from 0.26 to 0.30 seconds (Fig.
3). In contrast, for 20% TMD, the reaction was more than five times faster at 0.05 seconds (Fig. 4). Based on repeatability, the uncertainty in these reaction times is on the order of ±0.01 second.

These results are consistent with previously published work studying nanometric Al composites reacting in air environments. Pressed nanometric Al mixed with MoO₃ react roughly two orders of magnitude slower than the same mass and composition reacting as a loose powder (i.e., 10% TMD). In the water environment, the implication from Fig. 3 is that faster reactions produce a single wave of gas and energy, apparent as a single bubble. Slower reactions can disperse energy and gas in a series of multiple bubbles.

Figure 4 shows a sequence of images from a 20% TMD sample with a fuel rich stoichiometry. The gas/water interface allows the radius of the bubble to be monitored, and if the bubble is assumed to be spherical, the gas volume can be calculated. As density increases, the bubble transitions from a single bubble to a pulsating jet of smaller bubbles.

Results also show more energy is available to displace water and do work for fuel rich compositions. These results show nanometric aluminum particles for underwater reactions can now be more fully exploited toward applications such as underwater ordnance and fuses, torch or metal cutting technologies, offshore oil drilling and blasting, and as alternative power sources in oceanic environments.

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