Metallized reactive materials – a road to clean and sustainable pyrotechnics

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Since the introduction of nitroglycerine as a blasting explosive by Nobel in 1867, enormous progress has been made in improving performance and reducing sensitivity of energetic materials. The introduction of nitrogen rich (N>60%) oxidizers such as 5,5′-hydrazinebistetrazole (HBT) was one very important step in increasing the detonation performance and thermal stability of high explosives.

Concurrently, the introduction of metal fuels which can react at high temperature attracted significant interest to improving combustion performance while also reducing the sensitivity of propellants and pyrotechnics. This is largely because metals such as aluminum, magnesium, titanium, zirconium and boron have very high volumetric (30 - 140 $kJ.cm^{-3}$) and gravimetric energy density (10 - 50 $kJ.g^{-1}$) compared with other chemical fuels. These fuels are also chemically stable solid simplifying storage and transport. Furthermore, they can be ignited and burned with oxidizers (air, metal nitrate, metal oxides) or water, to produce large amounts of heat, or hydrogen and heat.

The study of metal fuel combustion dates to the 1960s driven by the potential applications as additives in propellants, explosives, and pyrotechnics to increase energy density and burn rates. Since then, large research efforts have been devoted to thermites and nanothermites using different metal/metal oxide combinations and custom nanostructured architectures. Unlike explosives, these materials undergo a rapid deflagration driven by a carbon free oxidation–reduction reaction, which form stable reaction products (metal oxides or hydroxides) that can be recycled with zero-carbon reduction processes Moore; they possess stronger mechanical strength and heat resistance than explosives; they are versatile: different combustion effects can be obtained by manipulating the reactive system (metal and oxide powders) and their microscopic and mesoscopic morphology; they can be printed which enables unique geometries and control over their energetic behavior, e.g., ignitability and mechanical characteristic which is not readily possible with explosives manufactured by slurry loading, melt-casting, cast-curing, powder-pressing; finally, thermites and nanothermites can burn in high vacuum, underwater and in other harsh environments.

That is why from 2000s onwards metallized reactive materials and related processes have attracted considerable attention from industry as highly useful energetic substances and technologies for: i) initiation [1-2], ii) clean propulsion [3] and power generation (thermal batteries), iii) self-destructing microchips and infrastructure protections [4-6], iv) energy sources or supplies for outer space uses and, v) long ceramic-lined pipes welding in geothermal power plants, and vi) agent deactivation. Many other applications will likely be addressed in the future. [7]

Yet, the effective deployment of such promising energetic materials into the various applications face a major hurdle. The “Edisonian” approach based on trial-and-error processes used in most research laboratories is not suited to these complex energetic systems in which not only the chemistry but also the microscopic (particle scale) and mesoscopic properties (systems of 100s particles, binder) influence macroscopic energetic performance [8].

A requirement-driven design approach relying on both mechanistic and statistical models should be preferred to cost-effectively customize best metal/oxide configurations to each function, considering all application requirements such as cost, technological compatibility and other constraints. To achieve these ambitious objectives research is needed on several fronts, specifically: i) developing mechanistic models for metal combustion in various oxidizing environments; ii) quantifying the key condensed and gas phase mechanisms that govern metal oxidation at elevated temperatures, particularly above the critical point where oxide solubility could change significantly and improve reaction rates and yields; iii) enhanced understanding of the physics of turbulent and "discrete" flames. These requirements necessitate the use of advanced diagnostics (laser-based optical diagnostics, time-resolved mass spectrometry) and state-of-the-art experimental methods to enable determination of reaction rates, energies, and rate-limiting mechanisms of these complex reactive systems.

Collaboration with data science researchers is also urgently needed to develop not only surrogates for physical models but inverse models which will enable discover new metal fuel/oxidizer configurations that cannot be imagined by the user because of the quantity of variables impacting metal fuel combustion, e.g., shape and size of the grain of each powder, compaction, stoichiometry, environment, etc.

In conclusion, fusion of physics simulation and machine learning approaches will lead to fully realizing the benefits of metallized reactive materials and may consequently bring to a paradigm shift in pyrotechnics.

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