Processing of Aluminum-Based Nanothermites in a Circulating Mixer

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Energetic nanothermite research supports an effort to replace heavy metals (lead) in current military applications,

for example:

- **percussion primers (small and medium caliber),**
- **electric primers (electric matches, pyrotechnics),**
- **low energy initiators (LEI).**

Several metastable energetic nanocomposites, also known as metastable interstitial composites (MIC) or nanothermites (superthermites) were identified as the potential substitutes for currently used lead styphnate or lead thiocyanate.

Aluminum-based nanothermites (aluminum-metal oxide systems) are of particular interest in terms of their energetic characteristics.

Examples: $Al\text{-}MoO_3$, $Al\text{-}WO_3$, $Al\text{-}CuO$ and $Al\text{-}Bi_2O_3$,

Thermodynamic properties of selected thermite reactions

Thermite reaction	Q [cal/g]	Q [cal/cm^3]	Gas generation 1 atm, [g gas /g mixture]	T_{ad} [K]
$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$	945.4	3947	0.0784	3135
$2Al + Bi_2O_3 \rightarrow 2Bi + Al_2O_3$	505.1	3638	0.894	3319
$2Al + MoO_3 \rightarrow Mo + Al_2O_3$	1124	4279	0.2473	3688
$2Al + WO_3 \rightarrow W + Al_2O_3$	696.4	3801	0.1463	3253
$2Al + 3CuO \rightarrow 3Cu + Al_2O_3$	974.1	4976	0.3431	2843

J.A. Puszynski, C.J. Bulian, J.J. Swiatkiewicz, J. of Propulsion and Power, Vol. 23, No. 4, 698-706, (2007).

Distinct characteristics of nanothermites:

1. **Nanothermites consist of at least two reacting component (fuel and oxidizer);**

2. **Combustion reaction rate of the nanothermite mixtures strongly depends on reactant's particle size and particle intermixing;**

3. **Energy release can be tuned by choice of the reactive components.**

Characteristics 2 and 3 are relevant specifically to the percussion primer and other types of initiators.

Metastable energetic nanocomposites (nanothermites) are difficult to process safely due to their sensitivity to friction and electrostatic discharge (ESD).

A typical small scale preparation of such powders involves mixing of nano-size reactant powders in an inert solvent (wet mixing).
After sufficient mixing of a slurry, the solvent is evaporated and solid mixture is dried, resulting in a loose powder of the nanothermite.

Any handling of nanothermite powder must be carried out with extreme caution; for example, an ESD discharge at energy level of a fraction of μJ can ignite loose powder of Al-Bi_2O_3.

Nanothermite System	ESD ignition energy (mJ)
Al-Fe_2O_3, powder	0.113
Al-MoO_3, powder	0.050
Al-Bi_2O_3, powder	0.0001
Al-Bi_2O_3, granule	1.5

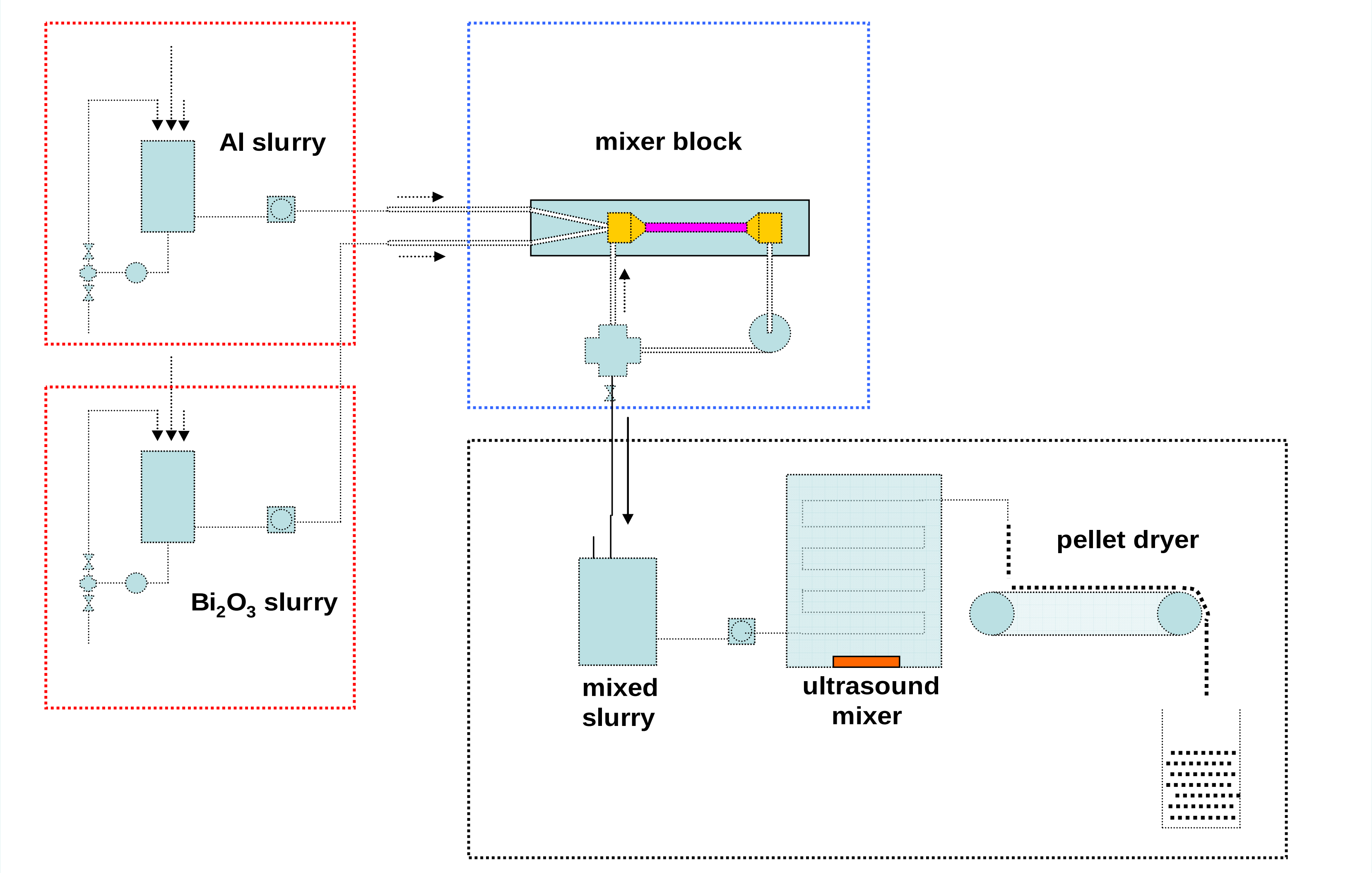
Wet mixing in organic solvents and loading operations are limited to small quantities performed in a batch mode (a few grams). These processes are difficult to scale-up due to possible stratification of slurry and the VOC concerns.

Need for design of a process of nanothermite wet mixing and loading which would support:

- **flexibility of mixing various components,**
- **choice of the solvent (including specifically water),**
- **yield larger quantities of product (hundred grams/day or more).**

A new mixing process of the nanothermite components in a water slurry was developed and tested in the Innovative Materials and Processes LLC. The developed process uses a circulating mixer that continuously operates during the mixing and dispensing cycles.

The proposed scheme of continuous mixing in a in-line mixer with recirculation of a slurry combined with ultrasonic agitation.



1. Water-based mixing process is inherently safe.
2. Formation of compact granules has ESD safety advantages.
3. Dense slurry can be dosed directly to the application (primer cup).

Mixer implementation:

Tubing pumps: variable flow rate, minimal dead volume in tubing, easy disposal and deactivation of residual slurry.

Tubing: broad range of sizes, various materials (Silicone, Tygon, PFTE, Norprene).

In-Line Static Mixer: 3/16” OD stainless steel tube and various number of helical elements of the mixing insert.

Pressure drop on tested mixer was less than 10 psi at maximum flow rate of 400 ml/min for the most dense slurry of Al-Bi_2O_3 in water.

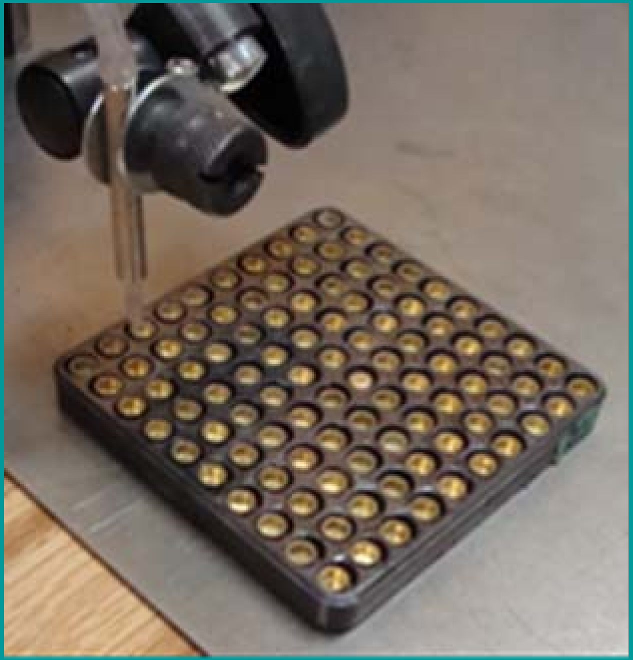
Assembled mixer and metering modules used for preparation of $Al\text{-}Bi_2O_3$ nanothermite mixture.

The system is capable to produce 600 small caliber percussion primers during a 30 min cycle.

Total amount of dry nanothremite is ~23 g, about tenfold increase over the laboratory batch scale.

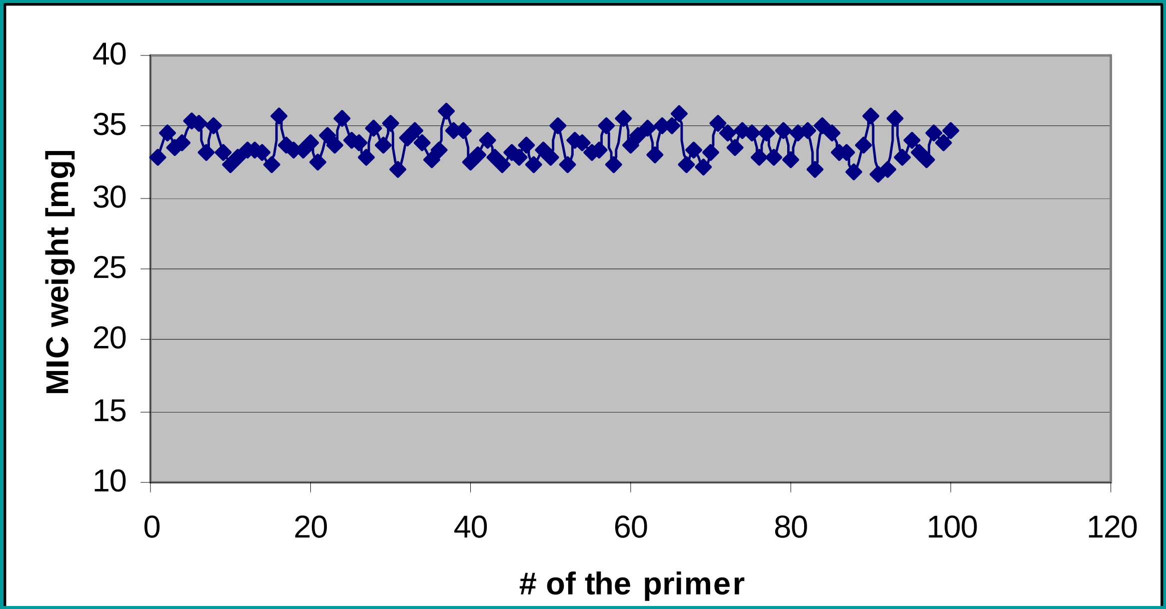
Further increase of the throughput can be achieved by the increase of the mixer reservoir volume (from 30 ml to up to 300 ml in this implementation).

After 30 minute of mixing and ultrasound agitation the slurry is ready for metering.



A tray of 100 cups before filling with the nanothermite slurry.

Weight of Al-Bi_2O_3 primer mixture after dosing slurry into small caliber primer cups



Average weight is 33.7 mg with the STD of 1.3 mg.

Impact sensitivity test of the assembled primers:

50% probability to fire: height 5.15 ± 0.51 inch

using ball drop test (1.94 oz)

Mixing of Al-(Fe_2O_3, Bi_2O_3) nanothermite system in water.

A slurry containing Al-Fe_2O_3 nanothermite in water was mixed using circulating mixer. This slurry was then combined with a Al-Bi_2O_3 suspension mixed earlier, while the mixer was continuously running.

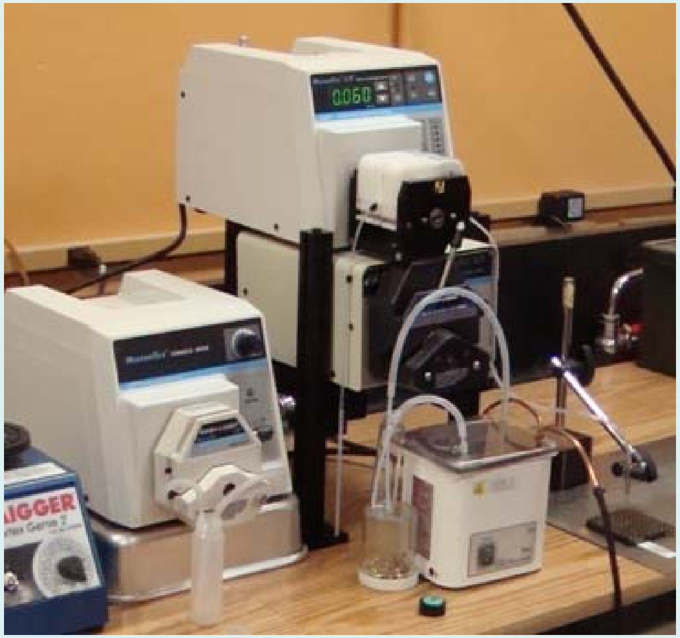
After 15 minutes of homogenizing in the in-line mixer and during ultrasound agitation the liquid suspension was dosed as 5μL droplets to form pellets on the PFTE surface (after drying).

This nanothermite mixture contains iron oxide and bismuth oxide in the weight ratio of 2.33.

By mixing various amounts of the premixed slurries any other oxide ratio can be obtained.

Mixing in Anhydrous Solvent

Composition containing Al, Fe_2O_3, and SiO_2 (as diatomaceous earth) is similar to one used as an ignition mix in pyrotechnic devices. This mixture does not contain nanosize powders but its preparation in the circulating mixer is a good example of the mixer application flexibility. Mixing was carried out in anhydrous isopropyl alcohol.



Advantages:

- **mixing is carried out in practically closed system; there is no loss of the solvent during mixing,**
- **tubing pump facilitates quick discharge of the slurry onto a drying pan, avoiding stratification of the components.**

Disadvantage:

- **expecting very viscous suspension to deal with, it was necessary to use additional tubing pump in order to premix the components before feeding slurry into the circulating mixer.**

Mixing in Anhydrous Solvent

Al-MoO_3 nanothermite components are typically mixed in an inert solvent like hexane. Hovever, for mixing Al-MoO_3 nanothermite components and nitrocellulose binder the preferable solvent is 1:1 by volume mixture of acetone and isopropyl alcohol.

Aluminum and molybdenum trioxide nanopowders were suspended in acetone/isopropyl alcohol containing dissolved nitrocellulose and mixed in the circulating mixer with ultrasound agitation for 30 minutes.

The resulting suspension was stable for long period of time (months) and could be used for making coating on surfaces. It is also suitable for preparation of electrical igniters.

Conclusions:

- Off-shelf tubing pumps (peristaltic pumps) were tested in several applications for mixing and metering of the nanothermite slurries in water as well as in anhydrous organic solvents.

- Combining simultaneous action of the in-line mixer and the ultrasound field allows very effective mixing of particles in the slurry for nanothermite systems based on aluminum – oxides (Bi_2O_3, Bi_2O_3/Fe_2O_3, and MoO_3) and micron size Al-Fe_2O_3/SiO_2 suspended in a solvent.

- Impact sensitivity tests conducted on the standard primer mixture (Al-Bi_2O_3) confirmed that new mixing method lead to the same primer performance as primers obtained from small size batch mixing.

- The method of circulating mixing of the nanothermite components in water can be easily scaled up from the current minimal volume of 30 mL to 300 mL, using the same pump system, by only increasing size of the mixing vessel and tubing diameter.

This work was supported by:

“Low Cost Production of Nanostructured Superthermites”
Contract No. N68936-08-C-0046
NAWCWD China Lake, CA

and
(in part) by

South Dakota School of Mines and Technology
Rapid City, South Dakota

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