Effect of additives on CuO/Al nanothermite properties

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Abstract: The effect of additives on CuO/Al nanothermite properties is reported. The incorporation of additives resulted in the decreased sensitivity. It had an adverse impact on gas dynamic characteristics of CuO/Al nanothermite, up to the loss of the unique capability of burning in narrow channels.

1. Introduction
A metal fuel mixed with a less reactive metal oxide as the oxidizer at the nanoscale is commonly called nanothermite. Such a system is characterized by a high reaction temperature and a small amount of exhaust products. In contrast to micron-sized thermite systems, nanothermites exhibit a high burning rate and are capable of burning in microchannels of 0.1 mm and less [1-4].

A lot of reports have shown the promising outlook of using nanothermites in pyrotechnics (incendiary and priming formulations, etc.), microelectromechanical systems (MEMS), dedicated fastening and connection of materials (nanoscale welding), etc. [1,5-6]. The practical application is hindered by extremely high sensitivities to friction and electrostatic discharge comparable to some priming explosives [6-9]. The incorporation of additives into nanothermite composites is considered to be one of the options to solve this challenge. For instance, introducing fluoropolymers contributes to decreasing the electric spark sensitivity [10], in contrast to additives such as soot or graphite [11]. The incorporation of carbon nanotubes or molybdenum disulfide can decrease the mechanical susceptibility [11-12]. Along with that, reports focused on reducing the sensitivity of nanothermites often do not provide information on how formulation variations influence explosion performance of systems studied.

The present work aimed at investigating the effect of additives on explosion performance and sensitivity of CuO/Al nanothermite composites.

2. Materials and Method

2.1. Materials
A CuO/Al nanothermite system and a formulation based thereon were examined herein. The characteristics of the formulation components are summarized in Table 1.

The following additives were studied: SKI-NL M isoprene rubber (Technical Specifications TU No. 38.03.1.031, hereinafter “SKI”), PMS-20 polymethylsiloxane (Russian State Standard GOST No.13032-77, hereinafter “PMS”), F-42L fluoropolymer (Russian State Standard GOST No. 25428-82, hereinafter “FL-42”), SKF-26 fluororubber (Russian State Standard GOST No. 18376-79, hereinafter “SKF-26”); TAUNIT-M multilayer carbon nanotubes (made by Nanotekhtsentr, 8-15 nm outer diameter, 4-8 nm inner diameter, 2 µm average length) and single-layer carbon nanotubes...
OSUNT-75 powder with a specific surface of 440 m$^2$/g, containing 75% single-layer tubes 1.4-1.6 nm in diameter, up to 1 µm long, manufactured by Uglerod ChG company, hereinafter “OSUNT”.

Table 1. Basic characteristics of nanosize components.

| Component                        | Mean particle size, nm | Content, % | Manufacturer                                      |
|----------------------------------|------------------------|------------|---------------------------------------------------|
| ALEX Aluminum powder, Al         | 50-70                  | 85.0       | Peredovyye Poroshkovyye Tekhnologii, Tomsk         |
| Copper oxide powder (II), CuO    | 30-110                 | 99.5       | Plazmoterm, Moscow                                |

2.2. Fabrication of composites and test specimens

A general procedure for the fabrication of composites involved the following steps:

- Prearrangement of the components: nanopowders were preliminary deagglomerated; a low-viscosity solution or suspension of the additive in organic solvent was prepared;
- Ultrasonic mixing of the powders in the solution/suspension of the additive;
- The solvent was evaporation to a residual content of about 50% relative to the weight of the solid components;
- The pyrotechnic mixture was ground under the layer of the volatile liquid being not a binder solvent or plasticizer;
- The suspension was vacuum dried to give a composite that represents a powder of agglomerated particles of the target composition.

To determine the burning rate at bulk density, the powders were loaded into polymer tubes of 2.4 mm i.d. with a wall thickness of 0.2 mm.

To measure the burning rate in the thin layer, the powders examined at bulk density were placed between two steel plates with dimensions of 10x20 mm, the layer thickness being adjusted by special assemblies whose schematic diagrams for the burning rate measurement are illustrated in Figure 1.

Figure 1. Schematic diagrams of assemblies for the burning rate measurement: a) in polymer tube at bulk density; b) in thin layer (1 – pyrotechnic igniter, 2 – ionization detectors, 3 – test specimen, 4 – polymeric shell, 5 – punch, 6 – steel support, 7 – steel plates).
2.3. Test methods
The calculated characteristics (heat of combustion \(Q\), adiabatic flame temperature \(T_a\)) of the studied compositions were obtained using the REAL software package [13]. On the basis of the calculations made, basic composites were formulated.

The friction sensitivity in shock shear was determined on a K-44-II friction tester pursuant to GOST No. 50835-95 (lower limit, LL\(_{\text{friction}}\), kgf/cm\(^2\)) and impact sensitivity on a K-44-III impact tester pursuant to GOST No. 4545-88 (lower limit, LL\(_{\text{impact}}\), mm).

The burning rate was recorded by ionization detectors according to the diagrams shown in Figure 1. The detectors were at a distance of 20 mm when the burning rate was measured in the tube, and were at a distance of 20 mm when the burning rate was measured in the thin layer. All the test specimens were thermally initiated from one of the end faces of the explosive charge.

To determine the minimum energy of electrostatic spark \((W_{\text{min}})\), the test specimen at bulk density was placed into a polymer tube about 4.5 mm in height. Afterwards, spark discharge of the specified energy was transmitted from the live capacitor through the specimen layer located between the electrodes. The response or its absence was recorded. The experimental results were recorded as follows: \(W_1<W_{\text{min}}<W_2\), where \(W_1\) – is the spark energy at which no ignition occurs in any of the twenty experiments; \(W_2\) – is the spark energy at which ignition takes place in each of the twenty tests. The lower measurement limit of this method was 0.022 mJ.

The TMD for each mixture as a weighted average of the pure solid densities of the all reactants. The bulk densities for these experiments ranged from 12% to 24% TMD.

3. Results and Discussions
The first phase of the research was to investigate the effect of different polymer additives on the CuO/Al nanothermite properties. The results are summarized in Table 2.

| No | Composition, wt.-% | Calcd data \(^a\) | Experimental data | Sensitivity |
|----|-------------------|----------------|------------------|-------------|
|    |                   | \(Q\), \(kJ/g\) | \(T_a\), K | TMD, | \(U\), m/s | friction, kgf/cm\(^2\) | impact, mm | \(W_{\text{min}}\), mJ |
| 1  | CuO/Al 76/24      | 3.84 | 3930 | 21 | 570-650 | 30-70 | 400 | >500 | <0.022 |
| 2  | CuO/Al/SKI 73/21/6| 3.82 | 3190 | 23 | 0.5-0.7 | 0 | 1600 | >500 | <0.022 |
| 3  | CuO/Al/PMS 76/21/3| 3.82 | 3560 | 22 | 150-250 | 0 | 800 | >500 | <0.022 |
| 4  | CuO/Al/F-42 76/21/3| 4.10 | 3980 | 24 | 250-350 | 10-50 | 450 | >500 | <0.022 |
| 5  | CuO/Al/SKF-26 76/21/3| 4.11 | 4075 | 23 | 300-350 | 10-50 | 450 | >500 | <0.022 |

\(^a\) Aluminum nanopowder was considered in the calculations as mixed 85/15% Al/Al\(_2\)O\(_3\)

The broad spread of the experimental values of the burning rate is due to the convective mechanism of the reaction front propagation and is, as practice shows, typical of nanothermite composites at low bulk factors [14-15].

The incorporation of the polymer additives resulted naturally in the decreased burning rate. However, this decrease is by no means significant: the rate remains quite high, except for specimen No.2 having higher polymer content. A decrement in the explosive charge thickness led naturally to
the decreased burning rate for all of the composites. The fluoropolymer additives (specimens No. 4 and 5) inserted into the basic nanothermite diminished the burning rate in the thin layer negligibly, whereas the introduction of hydrocarbon (SKI) and silicon (PMS) rubbers (specimens No. 2 and 3), which are inert with respect to the nanothermite components, led to the burning interruption.

The friction sensitivity of the thermites was decreased to an acceptable processability level by introducing the inert SKI and PMS, whereas fluoropolymers did not almost decrease the sensitivity. Together with that, the minimum energy to ignite the nanothermite composites by electrostatic discharge was extremely high, and the incorporated polymer additives did not alter this parameter.

The conventional way of reducing the electrostatic stimulus sensitivity is to insert electrically conductive powders into high-energy composites. We examined a series of nanothermite systems with carbon nanotubes (CNT) added. The study results are given in Table 3.

**Table 3. Characteristics of CuO/Al/CNT nanothermite composites.**

| No. | Composition, wt.-% | Q, kJ/g | Experimental data |  
|-----|--------------------|---------|--------------------|
| 1   | CuO/Al 76/24       | 3.84    | TMD, % | Burning rate, m/s | Sensitivity |
|     |                    |         | in tube | in layer | friction, kgf/cm² | W_{min}, mJ |
| 2   | CuO/Al/MUNT 69/22/9| 3.54    | 24      | –       | 20–60       | 400         | <0.022 |
| 3   | CuO/Al/OSUNT 69/22/9| 3.54    | 24      | –       | 20–60       | 400         | <0.022 |
| 4   | CuO/Al/MUNT/ SKF 68/19/10/3 | 3.71 | 12      | 50–100   | 0 a                   | 2000 | 0.032 < W_{min}  |
|     |                    |         |         |         |            |             | **W_{min} < 7.36** |

a At a layer thickness of 0.5 mm

It follows from the data obtained that incorporating carbon nanotubes did not bring about the desired outcome: the spark sensitivity remained that of the basic nanothermite composite. The application of that type of additives did not help decrease the friction sensitivity as well. The burning rate in the thin layer diminished marginally compared to that of the basic composite even at a relatively high CNT content of up to 9 wt.%.

The incorporation of the fluoropolymer (specimen No.4, Table 3) into the CuO/Al/CNT system appreciably lowered the sensitivity values, but such a composite was unable to burn even at a layer thickness of 0.5 mm.

It can be said on a whole that embedding the polymers and carbon nanotubes into the nanothermite system assists in decreasing the sensitivity parameters, but in this case, the resultant composites lose their unique detonation properties right up to the lost capability of burning in the narrow channels.

**4. Conclusions**

Incorporating the inert polymers (PMS, SKI) into the CuO/Al nanothermite system discernibly diminishes the friction sensitivity, but with that, the critical combustion thickness rises. The use of the fluoropolymer additives (F-42, SKF) has an influence on the latter parameter to the lowest extent, but the friction sensitivity cannot measurably be achieved as well. None of the additives examined enables the acceptable electrostatic discharge sensitivity to be attained. The appropriate sensitivities to friction and electric spark are achieved by simultaneously introducing carbon nanotubes and fluoropolymer (MUNT and SKF) into the nanothermite system; however the resultant composite drastically loses the burning rate and is unable to propagate the flame front even at a layer thickness of 0.5 mm.
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