Effect of nitrocellulose and 1-methyl-3-nitro-1,2,4-triazole on properties of CuO/Al and Bi\textsubscript{2}O\textsubscript{3}/Al nanothermites

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Abstract. Here we examined how the addition of high-energy materials such as nitrocellulose and 1-methyl-3-nitro-1,2,4-triazole (1Me-3N) would influence the properties of Bi\textsubscript{2}O\textsubscript{3}/Al and CuO/Al nanothermite composites. The additives allowed the improvement in explosion force (F) and burning rate (u) of the composites, achieving the maxima at concentrations of 5 % NC and 9 % 1Me-3N for the Bi\textsubscript{2}O\textsubscript{3}/Al/1Me-3N mixture, and of 15 % 1Me-3N for CuO/Al/1Me-3N. A further increase in concentrations of the additives decreased the combustion performance of the composites. The effect of the said additives on the properties of nanothermite composites has been considered herein from the standpoint of a simplified model of convective burning in a single pore.

1. Introduction

Nanothermites are commonly known as mixed nanosized powders of a metal and a less reactive metal oxide, which exhibit a high burning rate (up to 2600 m/s) and are capable of burning in thin layers in milligram quantities [1–4]. Nanothermites are viewed as a promising energetic scaffold for microscale pyrotechnic devices (micromotors, microignitors and the like) [5–9]. The difficulties using nanothermite composites in practice are due to their high friction and electric spark sensitivities [10–13].

The feasibility of desensitizing nanothermites through incorporation of various additives (carbon nanotubes, graphite, molybdenum disulfide, isoprene rubber, etc.) was studied [10,14-16]. The additives can reduce sensitivity, yet deteriorating the combustion performance of composites through to the loss of their ability to burn in the thin layer. Investigated nanothermites doped with high-energy materials (NC, RDX, AP) that improved the combustion performance; in some cases, for instance, when NC was added, the sensitivity reduction was achieved simultaneously [6,17-20]. However, such additives have rarely been used to date because their effect on the properties of nanothermites is little studied. In this regard, studies on properties of nanothermite composites doped with high-energy materials remain a live issue today.

The present paper explored the combustion performance of Bi\textsubscript{2}O\textsubscript{3}/Al and CuO/Al nanothermites doped with NC and 1-methyl-3-nitro-1,2,4-triazole (1Me-3N). NC and 1Me-3N exhibit almost the same energy potential (~5000 J/g) but have different reactivities. NC decomposes exothermally at about 170 °C and is capable of burning in microgram quantities, whereas 1Me-3N melts at about 65 °C and decomposes exothermally at above 220 °C. NC is a polymer material, whereas 1Me-3N is a low-molecular crystalline solid. These differences stir up an interest in comparative studies of these energetic additives in formulations of nanothermite composites.
2. Materials and method

2.1. Materials
The following materials were used as constituents of nanothermite mixtures:
- Bismuth oxide, Bi\(_2\)O\(_3\) (Sigma Aldrich, USA), a mean particle size of 90÷210 nm, main component contain 99.8 \%;
- Copper oxide, CuO (Plasmotherm, Russia), a mean particle size of 60÷110 nm, main component contain 99.9 \%;
- Aluminum, Al (Advanced Powder Technologies LLC, Russia), a mean particle size of 90÷110 nm with 85 \% active aluminum;
- NC (Aleksinskiy Khimicheskiy Kombinat, Russia), a polymer material with a nitrogen content of 12 \%;
- 1-Methyl-3-nitro-1,2,4-triazole (1Me-3N) was synthesized at the IPCET SB RAS [21]. This is an insensitive high-energy compound with empirical formula C\(_3\)H\(_4\)N\(_4\)O\(_2\), enthalpy of formation \(\Delta H = 1.42\) kJ/g, melting temperature \(T_m \approx 65^\circ\)C, and decomposition temperature \(T_d \approx 240÷250^\circ\)C.

2.2. Preparation of nanothermite composites and test method
The thermodynamic parameters of combustion of nanothermite composites (heat \(Q\), combustion products pressure \(P\)) were calculated using the REAL software package [22]. Conditions of adiabatic combustion of a nanothermite charge were simulated in a confined space; the charge density was taken constant and equal to 1.365 g/cm\(^3\).

The component ratio of the composites for experiments was defined as follows: the additive content was set first, and then the contents of Al and the oxide (CuO or Bi\(_2\)O\(_3\)) were selected in such a manner that the \(Q\) value would be maximum at the specified additive content.

The compositing routine was described elsewhere [16]. The weighed portions of the constituents were put into an acetone-containing glass beaker. The beaker was then placed into a water-filled ultrasonic bath (PSB-1335-05, Ultrasonic Equipment Center PSB-Gals Limited, Russia) and sonicated for 30 min.

Relative explosion force \(F\) (%) was determined by measuring the amplitude of the signal recorded by an oscillograph when the sample weighing 20 mg was initiated in a T24AM single point load cell (Tenzo-M, Russia). The sample was ignited by a spark source made up of two 0.2-mm Ø twisted copper wires whose close ends contacted the surface of the test nanothermite composite. One hundred percent of magnitude \(F\) was equivalent to the ratios of 76/24 \% for the CuO/Al nanothermite mixture, and 87/13 \% for Bi\(_2\)O\(_3\)/Al.

The burning rate was measured by the test protocol, as reported [16]. The burning rate was determined by the ionization method using two configurations of charges:
- The charge in a polyethylene tube with an inner diameter of 2 mm, a wall thickness of 2 mm and a length of 60 mm. The distance between the ionization sensors was about 30 mm, the first sensor being about 10 mm away from the initiation point.
- The charge in a thin layer. The nanothermite composite layer 0.1 mm thick was made between steel plates 10 mm wide and 20 mm long in a steel assembly that prevented the combustion products from sideward scattering; the ionization sensors were located on the end-faces of the charge.

The nanothermite charges were initiated by electric matches.

The friction sensitivity was measured as per the Russian standard procedure (GOST RU 50835-95) in a K-44-III friction tester. The lower limit of sensitivity (LL\(_{\text{friction}}\), kgf/cm\(^2\)) is a minimum pressure of the sample between the two planes, at which no explosion occurs in 25 tests upon an 1.5-mm impact shear of one plane relative to the other.

The electric spark sensitivity was measured by determining the minimum ignition energy, \(W\) (mJ). The sample of a bulk density was housed into a polymeric shell 2.5 mm high and 4 mm wide, which
was placed between copper electrodes, and a spark discharge of a specified energy was sent through the sample layer from a live capacitor. The spark discharge energy, at which no ignition of the sample occurs in 25 sequential tests, is represented by \( W \). The lower measurement limit of this method is 0.023 mJ.

3. Results and discussion

The measurement results for relative explosion force \( F \) of the nanothermite composites are given in figure 1.

![Figure 1. Relative explosion force \( F \) at different contents of additives](image)

The incorporation of the explosive materials could increase the explosion force of the nanothermites, in which case the relationship between \( F \) and the additive content had an extreme nature: according to figure 1a, the maximum \( F \) value was observed when the 1Me-3N content was 15 % in mixed CuO/Al/1Me-3N (\( F \approx 177 \% \)) and 9 % in mixed Bi\(_2\)O\(_3\)/Al/1Me-3N (\( F \approx 120 \% \)); and as shown in figure 1b, the maximum \( F \) value was observed when the NC content was 5 % in mixed Bi\(_2\)O\(_3\)/Al/NC (\( F \approx 244 \% \)) and 5 % in mixed CuO/Al/NC (\( F \approx 170 \% \)). The nature of the variation in explosion force \( F \) when embedding the additives was different for the CuO/Al and Bi\(_2\)O\(_3\)/Al nanothermite matrices. Doping the CuO/Al system with 1Me-3N increased magnitude \( F \) by more than 1.5 times compared to the nanothermite matrices, whereas the increase in \( F \) for Bi\(_2\)O\(_3\)/Al turned out to be less significant, no more than 120 % of the nanothermite matrix level. The reverse is true for NC addition: the maximum \( F \) value was 2.5 times as great for the Bi\(_2\)O\(_3\)/Al/NC mixture as for the Bi\(_2\)O\(_3\)/Al matrix, whereas the insertion of NC into the CuO/Al system increased magnitude \( F \) by a factor of 1.7 only.

The burning rates and sensitivities of the test nanothermite composites are summarized in table 1.

| No | Component ratio, wt.% | Density, % TMD | Burning rate \( u \), m/s | Sensitivity |
|----|------------------------|---------------|---------------------|-------------|
|    |                        |               | in tube \( \Theta 2 \) mm | in layer 0.1 mm | friction, kgf/cm\(^2\) | \( W_{min} \), mJ |
| 1  | CuO/Al 76/24           | 22            | 550÷650             | 30÷70       | \( \leq 400 \)       | <0.023 |
| 2  | CuO/Al/NC 71/24/5      | 22            | 600÷700             | 230÷290     | \( \leq 400 \)       | <0.023 |
| 3  | CuO/Al/NC 63/27/10     | 20            | 700÷800             | 130÷190     | \( \leq 400 \)       | <0.023 |
| 4  | CuO/Al/1Me-3N 55/30/15 | 22            | 750÷850             | 300÷350     | \( \leq 400 \)       | <0.023 |
| 5  | CuO/Al/1Me-3N 47/33/20 | 20            | 600÷700             | 100÷150     | 600                 | <0.023 |
| 6  | Bi\(_2\)O\(_3\)/Al 87/13 | 20          | 450÷550             | 410÷470     | \( \leq 400 \)       | <0.023 |
Table 1 shows that 5 % NC added to the CuO/Al nanothermite could increase the burning rate from ~50 m/s to ~260 m/s in the thin layer and from 600 m/s to ~800 m/s in the 2-mm ⌀ tubular charge (with 10 % NC). The insertion of 15 % 1Me-3H augmented the burning rate of the CuO/Al/1Me-3N composite up to 350 m/s in the thin layer and up to 850 m/s in the tube.

Doping the Bi₂O₃/Al nanothermite with 5 % NC and 9 % 1Me-3N raised the burning rates of the composites from ~500 m/s to ~640 m/s and to ~570 m/s, respectively, in the tube. However, when the Bi₂O₃/Al/NC and Bi₂O₃/Al/1Me-3N composites were tested in the thin layer, the burning rates decreased proportionally to the increased additive content.

On the whole, the obtained data suggest that the relationship between the combustion performance of the composites and the contents of 1Me-3N and NC additives have an extreme nature with pronounced maxima:

- For CuO/Al-based composites: ~15 % 1Me-3H and ~5 % NC;
- For Bi₂O₃/Al-based composites: ~9 % 1Me-3H and ~5 % NC.

The NC and 1Me-3N additives had almost no effect on the electric spark sensitivity: a slight decrement in the sensitivity was noticed only for Bi₂O₃/Al/NC. The insertion of the additives failed to reduce the friction sensitivity as well: a noticeable effect was observed only for the CuO/Al/1Me-3N composite doped with 20 % 1Me-3N.

Table 2 lists calculated heats of combustion (Q) and pressures (P) of the test composites. As per the calculations, the Q and P values increased proportionally to the increased contents of NC and 1Me-3N. The obtained experimental data are only in partial agreement with the predictions, that is, the increase in the combustion performance of the nanothermite composites with embedded additives was observed until certain additive content limits. These differences between the calculated and experimental data can be attributed to the combustion peculiarities of nanothermite mixtures which cannot be predicted by thermodynamic calculations.

**Table 2. Calculated thermodynamics of combustion of nanothermite composites**

| Composite            | Q, kJ/g | P, MPa | Composite            | Q, kJ/g | P, MPa |
|----------------------|---------|--------|----------------------|---------|--------|
| CuO/Al               | 3.84    | 36     | Bi₂O₃/Al/1Me-3H/NC   | 4.47    | 131    |
| 76/24                |         |        |                      |         |        |
| CuO/Al/NC            | 4.58    | 126    | Bi₂O₃/Al/1Me-3H/NC   | 4.95    | 194    |
| 71/24/5              |         |        |                      |         |        |
| CuO/Al/NC            | 5.21    | 195    | Bi₂O₃/Al/1Me-3H/NC   | 5.43    | 251    |
| 63/27/10             |         |        |                      |         |        |
| CuO/Al/1Me-3H        | 4.47    | 131    | Bi₂O₃/Al/1Me-3H/NC   | 5.43    | 251    |
| 71/24/5              |         |        |                      |         |        |
| CuO/Al/1Me-3H        | 4.95    | 194    | Bi₂O₃/Al/1Me-3H/NC   | 5.91    | 302    |
| 63/27/10             |         |        |                      |         |        |
| CuO/Al/1Me-3H        | 5.43    | 251    | Bi₂O₃/Al/1Me-3H/NC   | 5.91    | 302    |
| 55/30/15             |         |        |                      |         |        |
| CuO/Al/1Me-3H        | 5.43    | 251    | Bi₂O₃/Al/1Me-3H/NC   | 5.91    | 302    |
| 47/33/20             |         |        |                      |         |        |
The combustion of undensified nanothermites was shown to take place in the convective regime [23–26]. Thus, the effect of high-energy additives on the combustion process of nanothermites can be viewed from the standpoint of the known model of convective burning in the single pore [27,28]. The “single pore” is understood to be a tube whose walls are lined with an energy-rich material. In our case, this is a combination of Al particles, metal oxide particles (CuO or Bi₂O₃), and an explosive additive (NC or 1Me-3N). The burning rate in this model is defined by the travel velocity of combustion products inside the tube. The combustion product stream conditionally divides the tube by length into the preheat zone, burning zone and afterburning zone. It was previously found that the burning rate is defined by the processes taking place in the burning zone and depends on gas release intensity in that zone [27].

Addressing the burning of a nanothermite composite through the lens of this model, we suppose that the processes occurring within the single pore can be described as follows: the single pore walls are lined in a mosaic manner with particles of Al, metal oxide and additive. The estimated gas evolution upon decomposition of NC or 1Me-3N is greater than that upon interaction of the nanothermite pair of CuO/Al or Bi₂O₃/Al. However, under actual conditions, the hot product stream triggers the exothermic reaction of the nanothermite pair first, whereas the energetic effect of the NC or 1Me-3N additive manifests itself later on because the first stage of their decomposition is an endothermic nature.

Thus, the practical efficiency of the additive depends on how much of the additive will manage to have reacted during the reaction of a nanothermite pair. As the additive content increased, the endothermic processes in the first phase of its decomposition were able to cool down the reaction product stream and slow down its penetration velocity into the pore. Besides, the surface proportion of the pore walls populated with the particles of a nanothermite pair decreased whereby the initial heat release diminished, thereby decreasing even more the burning rate of the composite. This explains the extreme relationship between the combustion performance and the additive content.

The difference in extreme concentrations of the NC and 1Me-3H additives in the CuO/Al- and Bi₂O₃/Al-based composites can be explained by the different structures of the composites and by energetic factors:

- Structures of composites. The surface proportion of a single pore populated with the additive is defined not only by the additive quantity, but also by its distribution over the surface of the single pore. NC added to a nanothermite is known to generate films on the nanoparticles, whereas 1Me-3N distributes as compact crystals [17]. In the case of 1Me-3N, the surface contact of the particles of the nanothermite pair decreased to a less extent than in the case of NC. As a consequence, the combustion performance of the CuO/Al/1Me-3N and Bi₂O₃/Al/1Me-3N composites was observed to increase until the 1Me-3N content of ~15 % and ~9 % respectively, whereas the extreme content of NC in the CuO/Al/NC and Bi₂O₃/Al/NC systems was ~5%.

- Energetic factors. The completeness and decomposition rate of an additive depends on heat liberated by the reaction of a nanothermite pair. The reaction between the CuO and Al particles produced two times more heat than that between Bi₂O₃ and Al (~3.8 kJ/g and ~2.1 kJ/g, see table 2). It is logical to suppose that at the same content of the additives, their decomposition intensity will be greater in CuO/Al-based systems, as is corroborated experimentally. Alongside, the extreme content of NC in the CuO/Al- and Bi₂O₃/Al-based systems turned out to be the same. It is likely due to the structural differences of the composites, as was mentioned above.

4. Conclusion
The incorporation of NC and 1Me-3N into the CuO/Al and Bi₂O₃/Al nanothermites allowed the combustion performance of the composites to be improved to a large extent; the maximum explosion force and burning rate were observed when the additive contents in the mixtures were 9 % 1Me-3N for Bi₂O₃/Al, ~15 % 1Me-3N for CuO/Al, and 5 % NC for both systems. The further increase in the
additive content impaired the combustion performance. The insertion of the additives did not result in a considerable decrease in electric spark and friction sensitivities of the nanothermites. The effect of energetic materials on the burning process of nanothermite composites was examined from the standpoint of the ‘convective burning in the single pore’ model.

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