Nanoenergetic composite based on I_2O_5/Al for biological agent defeat

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ABSTRACT

The risk of bioterrorism events involving the intentional airborne release of contagious agents has led to development of new approaches for bio agent defeat technologies both indoors and outdoors. The spore-forming bacteria, in particular Bacillus anthracis is one of the biologic agents most likely to be used as a bio-weapon. Novel approaches to defeat harmful biological agents have generated a strong demand for new active materials, including nanostructured high density energetic composites. This report describes nanoenergetic gas generators (NGG) system that exhibit long term stability and superior release of biocidal substances for destruction of spore forming bacteria. By using nano-thermite reactions, with energy release up to 25 kJ/cc, based on I_2O_5/Al nanoparticles we intend to generate high quantity of vaporized iodine for spatial deposition onto harmful bacteria for their destruction. The study has shown that I_2O_5/Al nanosystem is extremely effective to sterilize potentially harmful biological agents in seconds.

Keywords: Nanostructured thermite, biocide, E-coli, Iodine, I_2O_5/Al

1 INTRODUCTION

Iodine-based substances have been an effective, simple and cost-effective for disinfection for hundreds of years. Iodine has been used in France during World War I to disinfect water; US Army used Globalin (tetraglycine hydroperiodide) tablets during World War II. More recently, iodine based disinfection has been used by NASA in space flights [1]. Since early 50s numerous reports have been published about disinfection efficiencies of various forms of iodine [2-4].

Iodine is rapidly bactericidal, fungicidal, tuberculocidal, virucidal, and sporicidal [3]. Although aqueous or alcoholic (tincture) solutions of iodine have been used from the 19th century, they are usually unstable [4]. In solution, at least seven iodine species are present in a complex equilibrium, and only molecular iodine is primarily responsible for antimicrobial effectiveness. This ultimately has led to development of iodophors (“iodine releasing agents”), the most widely used of which are povidone-iodine and poloxamer-iodinein both antiseptics and disinfectants. Iodophors are complexes of iodine and a solubilizing agent or carrier, which acts as a reservoir of the active "free" iodine [3]. Although germicidal activity is maintained, iodophors are considered less active against certain fungi and spores than are tinctures [5]. Iodine is a quick antimicrobial agent even at low concentrations; it rapidly penetrates into microorganisms, and attacks key groups of proteins, nucleotides and fatty acids, which culminate the cell death. Iodine is also effective against viruses; however nonlipid viruses and parvoviruses are less sensitive than lipid enveloped viruses [6]. However, in case of iodine solution applications to have disinfecting abilities it is required to treat infected areas for at least 20 minutes with iodine concentration not less than 0.5-1 mg/l. The development of innovative methods for effective destruction of aerosolized biological agents remains an integral part of defense research programs in the US [7].

In this work we use nanostructured thermite systems [8, 9] to realease atomic iodine, which are extremely active compared to iodine solutions. The nanothermites are mainly mixtures of two nanoparticles components, one of which is defined as a fuel and the second as oxidizer. The use of nanoscale particles instead of micro particles increases the intimate contact between the fuel and oxidizer. This decreases mass transport limitations which increases the reaction rate and reactivity of the mixtures. The nanothermite systems can have higher energy densities than conventional explosives and can generate shock wave with velocities of up to 2500 m/s [10-11]. Nanostructured thermite reaction based on I_2O_5+Al may produce intensive iodine gas phase, which can be used as biocidal agents to destroy harmful bacteria and microorganisms. The other significant advantage to use nanothermites is the time efficiency. If the iodine solutions are effective after 20 minutes, the nano-structured thermite mixture is effective in seconds-after explosion and deposition of iodine on infected surface. The controlling experiments show that vaporising of iodine in quantities of milligrams it is possible to disinfect areas of hundreds of meters.

2 THERMODYNAMIC ANALYSIS

Thermodynamic analysis was used to predict the combustion behavior of nanoenergetic system and to narrow down the choice of raw materials and to predict optimal concentration of components that will generate maximum vaporization of biocidal substances and adiabatic temperature. The thermodynamic prediction of the equilibrium composition of multicomponent multiphase systems requires minimization of the thermodynamic free energy (G) subject to material and energy balances [11, 12]. The system under study is commonly assumed to be chemically and thermally uniform so according the following equation:

$$G = \sum_{i=1}^{N_{ph}} \sum_{j=1}^{N_i} n_{ij} \left(\{n_{ij}\}\right), T \qquad (1)$$

then

$$\sum_{i=1}^{N_{ph}} \sum_{j=1}^{N_i} a_{ij}\, n_{ij} = n_k \qquad k = 1, 2, 3 \ldots, Ne \qquad (2)$$

where a_{ij} is stoichiometric coefficient of the chemical element, k in the j^{th} component of phase i; n_k = moles of element k in the system; N_e is number of chemical elements in the system.

For gaseous components (ideal mixture) $\mu_{gj} = \mu_j(T) + \ln(P_j)$ where P_j is the partial pressure of the j^{th} gas. For ideal liquid or solid solutions of arbitrary composition, $\mu_{ij} = \mu_{ij}(T) + \ln(X_{ij})$, where x_{ij} is the mole fraction of component j in phase i. For a solid uniform composition, $\mu_{ij} = \mu_{ij}(\mathrm{T})$. The adiabatic temperature satisfies the enthalpy balance:

$$\sum_{k=1}^{N_k} n_k\, I_k(T_0) = \sum_{i=1}^{N_p} \sum_{j=1}^{N_i} n_{ij}\, I_{ij}(T_{ad}), \qquad (3)$$

where N_k is the number of reagents, n_k is the number of moles of reagent k, $I_k(T_o)$ is the enthalpy of species k at T_o and $I_{ij}(T_{ad})$ is the enthalpy of component j of phase i.

Where N_{ph} is number of phases; N_i is number of components which form the i^{th} phase; n_{ij} = moles of component j in the i^{th} phase; μ_{ij} = chemical potential of component j in the i^{th} phase; T = temperature (K).

Thermodynamic calculations of the I_2O_5–Al system were made by using HSC-7 Software. The stoichiometric reaction to release iodine gas occurs by following scheme:

$$3I_2O_5 + 10Al = 5Al_2O_3 + 6I \qquad (2)$$

Figure 1 represents thermodynamic calculations, which have shown that I_2O_5-Al nano thermite system is highly exothermic ~25 kJ/cc with maximum adiabatic temperature of T_{ad} = 3830 K. The boiling point of iodine is 184.3^o C, so in the reaction temperatures iodine is completely vaporized and present always in atomical state.

Adding 0.5-1 mol amount of Al increases adiabatic temperature up to 2500 K, during which I_2O_5 reduces completely yielding at first I_2 which almost immediately vaporises to an atomic iodine and at n=0.8 the temperature T_{ad}>2300K . Increasing the amount of Al from n=2 to n=6 keeps temperature in highest level (about 3800 K), during which some gaseous of AlO is observed. At n > 6 leads to decrease combustion temperature due to some decomposition of Al_2O_3 and evaporation of gaseous Al with yielding also some gaseous to form AlI (aluminium iodine). Increasing n value from 6 to 12 decreases adiabatic temperature more than 1000 K.

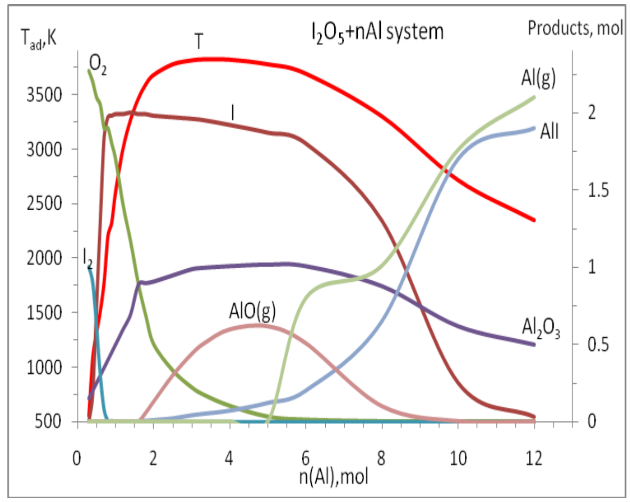

Figure 1: Thermodynamic calculations for I_2O_5-Al system.

3 EXPERIMENTAL

3. 1 Preparation and characterization of biological samples

To obtain quantitative results with statistical data we use the technique called the pGLO transformation of bacteria with a gene that codes for Green Fluorescent Protein (GFP). We use the Escherichia coli bacteria HB101 K-12 strain which is not a pathogenic organism like the E. coli strain O157 H7 that has sometimes been implicated in food poisoning. HB101 K-12 has been genetically modified to prevent its growth unless grown on an enriched medium. Following the transformation procedure, the bacteria express their newly acquired jellyfish gene and produce the fluorescent protein which causes them to glow a brilliant green color under ultraviolet light, which allows us to use UV microscope technique. We threat the surface of growing culture plates with either iodine-iodic acid solution (obtained with solving of nano-thermite reaction products in water) or exposing them to nano-thermite explosion of I_2O_5/Al mixture after 1 hours of incubation of bacteria. A hermetically closed plexiglass chamber with dimentions of 20x20x70 was used to make micro explosion inside, using electro-detonator technique to ignite the micro charge. To avoid effects of temperature and explosive pressure wave we placed biological samples in at least 0.5 m away from explosion center. Due to the high energetic nature of the reactions they were conducted with a small sample, i.e., not exceeding 0.5 g reactant mixture. We investigated the effect depending on mixture weight, as well as exposure time and sample distance from explosive.

3.2 Preparation of exothermic micro samples

Aluminum and iodine pentoxide powders were purchased from Sigma-Aldrich Co. and stored under nitrogen (99.9 vol. % N_2 with 50 ppm O_2) in a glove box to prevent contamination by impurities present in the air. Stoichiometric mixtures of the reactants according reaction (2) were mixed in a closed cylinder containing hexane and nitrogen for up to 9 hrs by a rotary mixing machine. This environment avoids the partial oxidation of the fine Al particles. The hexane prevents electrostatic charge build up that may lead to ignition and/or explosion of the powders during the mixing and handling.

4 RESULTS AND DISCUSSION

4.1 Treatment with explosion products

In the first stage of research we investigated the effect of solution obtained from solving explosion products in water in order to receive 880 mg/L solution. The traditional technique (treatment of plates after 1 hr of incubation with 25 µl iodine-iodic acid solution) is ineffective because Iodine kills bacteria only in presence of water when it remains on bacteria infected surface for more than 20 minutes and if the concentration of Iodine is 0.5-1 mg/L. Although in our solution the concentration of Iodine is 880 mg/L, it quickly evaporates from even 70 µl solution of Iodine: pH of non-diluted and diluted iodine-iodic acid solutions was recorded as:

Non-diluted (880mg/L)-4
Diluted 10 times (88mg/l)-5.12
Diluted 50 times (18mg/L)-5.45
Diluted 100 times (8.8mg/L)-5.55.

In order to have statistical data for disinfection properties of iodine solution, we performed experiments with control sample and three different concentrations of diluted iodine treated samples. We prepared samples in order to have about 350 colonies of E-coli if no Iodine solution is mixed in final stage of dilution. In addition it was prepared three other samples where in final stage we used the iodine solution diluted in water 50, 100 and 200 times, respectively. As far as the colonies were very distinctive under UV radiation, we could count them with a help of image processing and have quantitative, statistical data presented in Figure 2. Solution with concentration of iodine 4.4mg/L, kills only 14% of bacteria.

Figure 3 illustrated the sample of control image of E-coli bacteria colony under UV light, which didn't treate with iodine.

Figure 4a illustrated E-coli bacteria colony under UV light. In Fig.4b is shown the sample treated with iodine solution diluted 100 times (concentration of iodine in solution diluted 100 times is 8.8mg/L), number of colonies-245 (killed 25%).

Finally, Figure 4c illustrates sample treated with solution diluted 50 times (corresponding concentration of Iodine is 18mg/L), there is no colony of bacteria here, so apparently iodine killed all of them in 10 minute during the final stage.

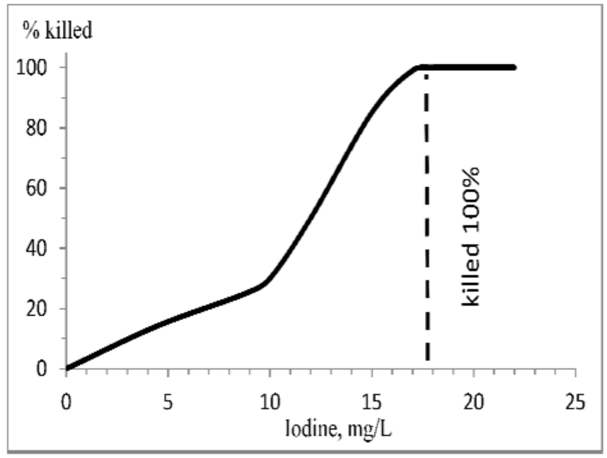

Figure 2. Statistical curve of killing abilities of active iodine generated by nanothermite reactions.

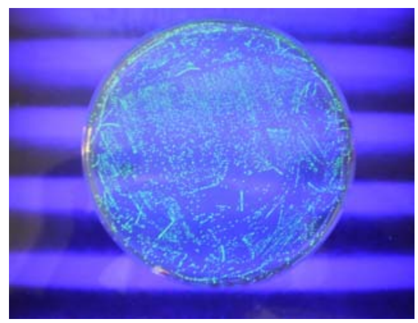

Figure 3: UV image of sample C (Control).

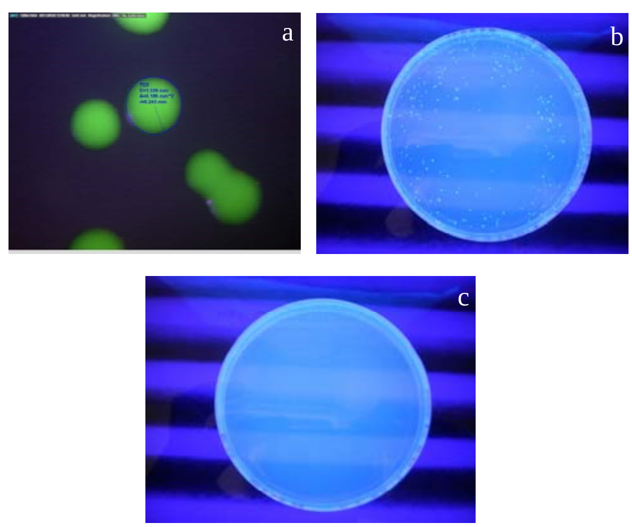

Figure 4: UV images of (a) separate colonies of GFP transformed E-coli; (b) Iodine treated (8.8mg/L of active iodine) colonies (75% reproduction); (c) Iodine treated (18mg/L of active Iodine) colonies (no reproduction, 100% effectiveness).

4.2 Disinfection with explosion

The next stage was exposition of bacteria colonies to nano-thermite explosion. Samples were attached inside hermetic container far from explosion center from 0.25 m to 0.7 meters. The effective explosion takes place if the charge mass is not less than 0.1g. We prepared the thermite mixture in ratio I_2O_5:Al=7:3. According to calculation, 0.1g mixture generates 0.53 g atomic iodine. In the case, when the internal surface area of reaction chamber was 24 m^2 the effective deposition concentration of iodine were 22 mg/m^2.

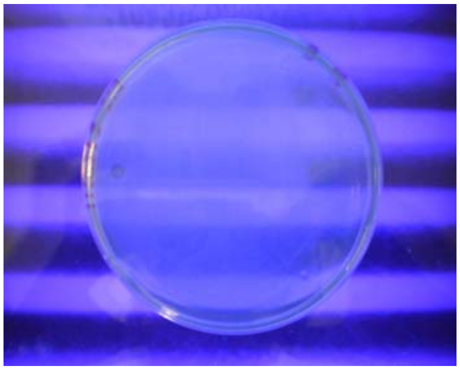

Figure 5: Sample exposed to nanothermite explosion.

All samples were completely disinfected (Figure 5, compare to Figure 3). Calculations show minimal effective content over infected area is 22 mg/m^2. Thermite mixtures less than 0.05g are not enough powerful to initiate explosive reaction to transfer atomic iodine to several meters. For real decontamination 0.1-0.3g capsules will be enough to disinfect several square meters each.

5 CONCLUSIONS

The complete thermodynamic estimation was made and the nanothermite mixture with optimal content of active biocidal agent was estimated. The effect of initial mixture composition, infected area, distance from source, as well as environment temperature and incubation/disinfection timing is investigated. The proof-of-concept of biocidal activity of I_2O_5-Al nanostructured thermite system is presented.

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