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Solvothermal preparation of an Al/CuO nanothermite – study of practical considerations
Solwotermalna preparatyka nanotermitu Al/CuO – badanie uwarunkowań praktycznych

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Abstract: *Nanothermites are promising energetic materials (EMs) which can replace current primary EMs, due to their high linear combustion velocities, short ignition times and high energy density. In this work, Al/CuO compositions were prepared and tested in terms of sensitivity to friction, impact and electromagnetic radiation, as well as in terms of its selected properties, such as specific impulse, combustion velocity and bulk density. The results of these investigations show the necessity of refining the method of preparing nanothermites, thereby provide a foundation for further research.*

Streszczenie: *Nanotermity to obiecująca grupa materiałów wysokoenergetycznych (MW), która może zastąpić MW inicjujące, gdyż cechuje się wysoką liniową prędkością spalania, krótkimi czasami zapłonu i wysoką gęstością energii. W niniejszej pracy przygotowano i zbadano parametry bezpieczeństwa kompozycji Al/CuO, tzn. wrażliwość na tarcie, uderzenie i promieniowanie laserowe, a także jej wybrane właściwości, tzn. impuls właściwy, prędkość spalania i gęstość. Wyniki przeprowadzonych badań wskazują na konieczność dopracowania metody wytwarzania nanotermitu, lecz dostarczają niezbędnych podstaw do dalszych prac badawczych.*

Keywords: *nanothermite, MIC, nanomaterial, energetic material, CuO, Al*
Słowa kluczowe: *nanotermit, MIC, nanomateriały, materiał wysokoenergetyczny, CuO, Al*

Abbreviations

CL-20	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexazatetracyclo[5.5.0.03,11.05,9]dodecane
EDS	Energy Dispersive Spectroscopy
EM	Energetic Material
F	Trust force [N]
F2311	2-[(3-Chlorophenyl)diazenyl]-1-phenylbutane-1,3-dione
g	Gravitational acceleration (9.8067 m/s^2)
HPMC	Hydroxy propyl methyl cellulose
I_{sp}	Specific impulse s
m	Mass [g]
MIC	Metastable Interstitial Composition
PS	Polystyrene
PVDF	Poly-1,1-difluoroethene
SEM	Scanning Electron Microscopy
t	Time [s]
TMD	Theoretical Maximum Density [g/cm^3]

1. Introduction

Nanothermites, also referred to as MICs or superthermites, are a relatively new group of EMs, composed of at least one fuel and one oxidising agent. They function on the same basis as classical thermites, i.e. via a reduction-oxidation reaction between a fuel and an oxidising agent [1].

Nanothermites differ from classical thermites in terms of grain dimensions – where for classical thermites component grain dimensions are typically in the order of micrometres, whereas for nanothermites they are in the order of nanometres. In terms of definitions, it is sufficient for grains of one of the nanothermite constituents to have one characteristic dimension lower than 100 nm. This decrease in grain dimension translates to a vastly higher active surface area for nanothermites than for classical thermites. The lower grain dimensions facilitate homogenization of their components, resulting in increased combustion velocity and heat of combustion. Despite such benefits, there are some drawbacks associated with grain size reduction, namely elevated sensitivity to initiation by stimuli, along with increased costs and complexity of production, compared to classical thermites [2].

The interactions between the constituents are the main factors determining the combustion mechanism and parameters, making their choice essential, particularly in terms of potential applications of the nanothermite [3]. Equivalence ratio is defined as the ratio of the actual number of moles of fuel in a given system to the number of moles of oxidising agent, divided by the analogous ratio which, for a composition in stoichiometric ratio, is an extremely important parameter [4]. The equivalence ratio allows the degree of excess fuel in the pyrotechnic system to be assessed, which is associated with the manifestation in reality of higher performance by systems richer in fuel in relation to the stoichiometric ratio [5].

1.1. Protocols for producing nanothermites

Nanothermites can be produced via a variety of methods. The most important methods include:

– **Dry mixing**: Dry mixing is primarily used to prepare classical thermites, as their insensitivity to mechanical stimuli allows this [6]. In the case of MICs, sensitivity to friction of most compositions prohibits employing this method. That said, there are specific instances of this approach, i.e. compositions with significant resistance to mechanical stimuli, for which other preparation methods are problematic, as in the case of nanothermites composed of aluminium and sulfates [7].

– **Mixing in liquids:** Mixing in liquids is the most common method, due to its simplicity and low cost. Components of the nanothermite are mixed in a liquid, using a magnetic stirrer or ultrasound to ensure

uniform dispersion of the constituents. The liquid is then removed using a drying oven. Because a liquid is used, surface forces are reduced, resulting in a lower tendency for particles to agglomerate, resulting in overall better homogeneity of the finished product [8]. Liquids for mixing are mainly organic with a high dipolar moment, such as acetonitrile, acetone, hexane and cyclohexane. To be suitable, they need to meet certain characteristics, namely:
(i) low boiling point to speed up the evaporation,
(ii) good dispersive properties for the best homogeneity,
(iii) possibly high chemical stability,
(iv) lowest possible toxicity for safety in production,
(v) lowest possible price,
(vi) high market availability.

– **Sol-Gel method:** The Sol-Gel method (Figure 1) works on the basis of initial formation of "sol", meaning nanoparticles suspended and dispersed in solvent. Furthermore, the suspension is transformed into a 3D solid network, with liquid occupying empty pores, known as "gel". This transition can be achieved in a number of ways, including manipulation of temperature and pH, use of gelling agents or ionic strengthened solutions. The last step of the process is removal of the solvent through slow evaporation or by supercritical extraction with CO_2 [9].

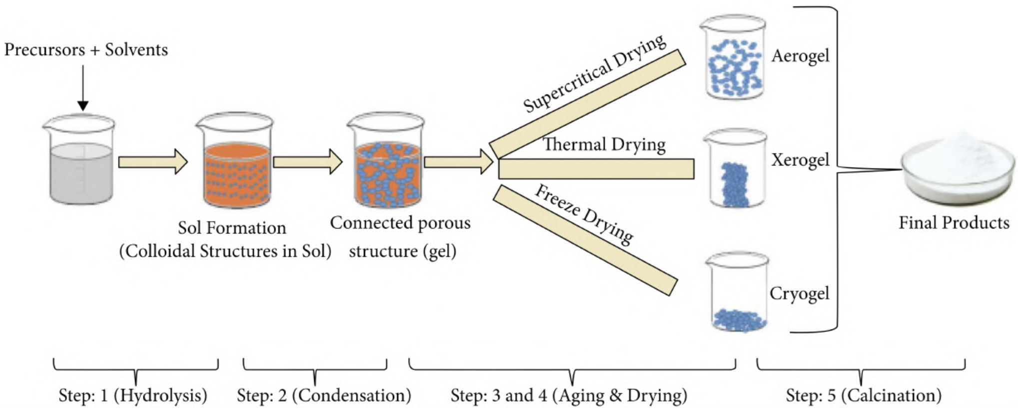

Figure 1. Sol-Gel method diagram [10]

Nanothermites prepared by the Sol-Gel principle tend to form micron-sized spheres made up of nanoparticles of their constituents. In a study concerning the production of Al/CuO composite, it was determined that MICs produced in this way release up to 1.5 more heat during combustion than those prepared by simple mechanical mixing [11].

– **Electrospray method:** Electrospray method, also called deposition via electrohydrodynamic atomization, works on the principle of charged drops of solution or suspension. Droplets are deposited on a flat, conductive surface, like a steel plate, from a syringe with a steel needle. Both plate and needle are connected to a high voltage, where one acts as the anode and the other as the cathode, to form a Taylor cone. Additionally, there should be enough space between electrodes, to let the solvent evaporate and to achieve the most uniform and controlled conditions [12, 13].

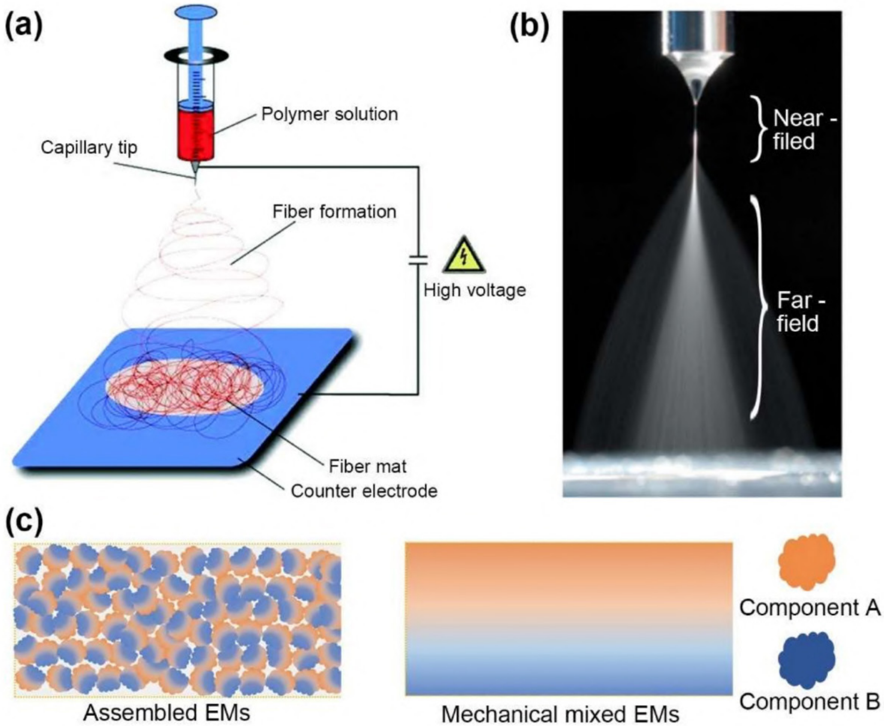

Figure 2. Schematic diagram of electrospinning (a), electrospray process with Taylor cone, emitted jet and broken-up droplets (b) and comparison of dispersion of particles assembled by electrospray method and mechanically mixed (c) [14]

In this technique, a precursor has to be prepared beforehand. In the case of nanothermites, this is done by the creation of a suspension of fuel and oxidising agent particles in a fluid medium, with earlier ultrasonication to break particle agglomerates. This way, other compounds like nitrocellulose, ammonium perchlorate or CL-20 [15-17] can be sprayed together with the MIC, to adjust its parameters. A different approach within this topic is electrospinning, where drops don't fom into a Taylor cone, but electrostatic force is used instead to stretch the solution during its solidification. The transition between electrospinning and electrospraying is dependent on liquid viscosity, conductivity and volatility, as well as nozzle geometry and the voltage difference between the electrodes [18].

– **3D printing:** 3D printing is a relatively new method in the manufacture of nanothermites, allowing the creation of complex structures using prepared inks or filaments, depending on the technique employed, e.g. direct ink writing (DIW), fused-deposition modelling (FDM), stereolithography (SLA), digital light processing (DLP) [19, 20], with additives in the form of various polymers, to decrease sensitivity and agglomerate formation [21]. Some examples of binders include: polyvinylidene fluoride (PVDF) [22] free-standing energetic composites with loading of up to 90 wt% Al-CuO were fabricated by 3D printing. A polymer hybrid of 3 wt% hydroxy propyl methyl cellulose (HPMC, hydroxy propyl methyl cellulose (HPMC) [22]free-standing energetic composites with loading of up to 90 wt% Al-CuO were fabricated by 3D printing. A polymer hybrid of 3 wt% hydroxy propyl methyl cellulose (HPMC, polystyrene (PS) [22]free-standing energetic composites with loading of up to 90 wt% Al-CuO were fabricated by 3D printing. A polymer hybrid of 3 wt% hydroxy propyl methyl cellulose (HPMC and fluorinated rubbers (e.g. F2311) [21].

In this work, we have investigated the validity of a recently reported protocol [23] for the preparation of core-shell structured nanothermites, as well as the claim of high particle size and composition homogeneity of the product using this protocol.

2. Experimental section

2.1. Utilised materials

Aluminium powder (in the form of flakes) 99.7% purity grade, aerodynamic particle size 11 μm was obtained from Alfa Aesar. Ethyl alcohol 96 wt.% aqueous solution and ammonia 25 wt.% aqueous solution were obtained from Chempur. Copper(II) nitrate hemi(pentahydrate), 98% purity grade was obtained from Sigma-Aldrich.

2.2. Methods

2.2.1. Preparation of core-shell structured nanothermite

It was decided to prepare a composition with an equivalence ratio of 1.0, i.e. equivalent to the stoichiometric ratio of fuel to oxidant. Preparation was carried out in small portions, following literature, in order to achieve the core-shell structure required [24]although they are commonly fabricated as powders, films, multi-layers and other heterostructures which desire an effective interface between reactive components but are not colloids and typically immobile. Little information is available in the literature on fabrication and characterization of standing-alone and mobile core-shell MIC micro-particles. In this paper, we report on a wet-chemistry method to synthesize micron-sized spherical colloids of Al/CuO with a core-shell structure. Scanning electron microscopy (SEM:

1. From the ammonia 25% solution, a 15% solution was prepared by adding distilled water.
2. To a beaker (25 cm^3 volume) 1 g of $Cu(NO_3)_2 \cdot 2.5H_2O$, 10 ml of 96% ethyl alcohol solution and 2 cm^3 of 15% ammonia solution were added.
3. To a beaker (250 cm^3) 0.5 g of flaked aluminium and 100 cm^3 of 96% ethyl alcohol solution were added, forming a suspension, which was then mixed using a magnetic stirrer with a rotational speed of 450 revolutions/min for 15 min.
4. The mixture from point 2 was added to the suspension of aluminium powder.
5. The sample was covered with paraffin film and left mixing at a rotational speed of 450 revolutions/min for 24 h.
6. The sample was gravity filtered and placed on a ceramic plate, which was then put into a laboratory dryer for 144 h at 150 °C.

2.2.2. Sensitivity to electromagnetic radiation

Tests concerning sensitivity to laser radiation were conducted using a wavelength of 520 nm and power in the range 25-320 mW. 15 mg samples of the composition were placed in copper shells of outer diameter 4.85 mm, wall thickness 0.2 mm and depth 4.3 mm, which were then placed inside a carrier so that laser radiation could fall on the material. The area of the laser spot was equal to 2 mm^2. The power of the radiation was tested with a radiation power meter before each power change. The laser impulse time of 60 s, was constant for all tries. Reaction of the samples was recorded with a digital oscilloscope Rigol MS05104, connected with photodetectors for wavelengths of 380-800 and 900-1600 nm.

2.2.3. Sensitivity to impact and friction

Impact sensitivity of the composition was tested in accordance with standard PN:EN-13631-4:2004, via the BAM Impact Test. Friction sensitivity of the composition was tested in accordance with standard PN:EN-13631-3:2006, via the BAM Friction Test.

2.2.4. Bulk density measurements

Bulk density measurements were conducted as follows: a copper shell of known volume (153.3 mm^3) was weighed. The nanothermite sample was funnelled into the shell until a small build-up of material over the edges became visible. Excess material was removed using a smooth spatula and the filled shell was weighed. For each determination, the procedure was repeated 15 times, with each repetition using a new portion of sample.

2.2.5. Thrust measurements

Tests and calculations of thrust parameters of the composition were based on literature [25]relatively low peak pressure, smaller thrust output, and incomplete combustion represent some of the potential problems associated with nanothermites. In this study to improve the combustion performance of nanothermites, varying quantities of nitrocellulose (NC. The test system consisted of a heavy, steel base for stability, connected to a force sensor, further connected to the carrier holding a copper shell of outer diameter 4.85 mm, wall thickness of 0.2 mm and depth of 4.3 mm. The carrier was closed with a nozzle (cylindrical or convergent-divergent) integrated into a nut. The top edge of the shell was touching the bottom edge of the nozzle to achieve a configuration similar to a microthruster (Figure 3).
Tests were carried out using a Rigol MS05104 digital oscilloscope, signal conditioner PCB Piezotronics 480E09, force sensor PCB Piezotronics 208C02. Each test was carried out using 30 mg portions, which were put in the copper shell, which was then placed inside the carrier and closed with the nut. Samples were initiated with chromonickel resistance wire of 40 μm diameter and resistance of 309 Ω/m, powered with a 5A laboratory power supply.

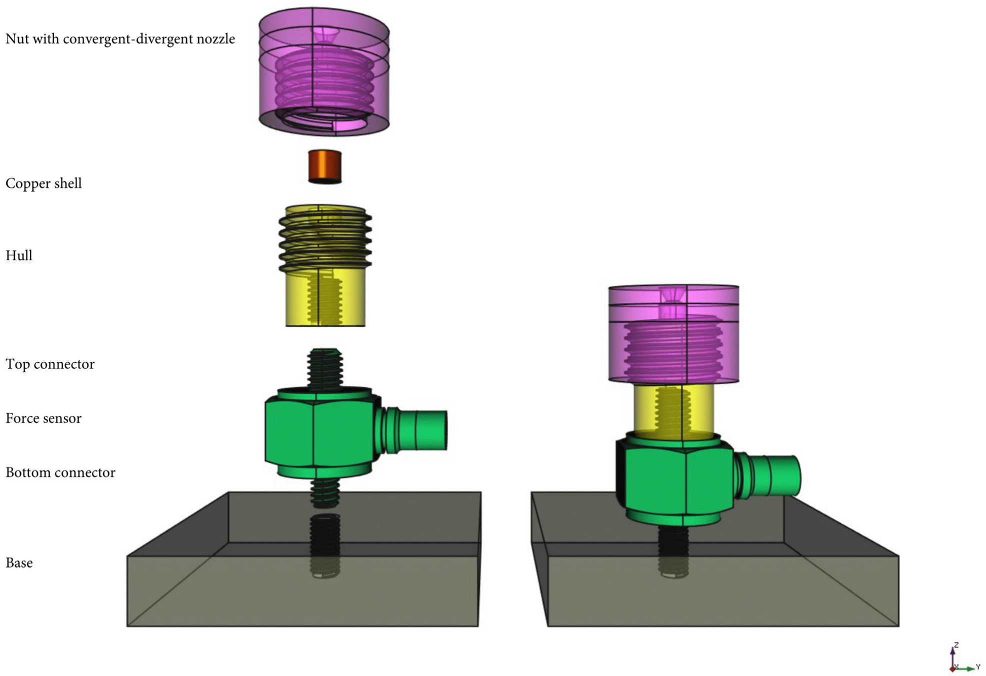

Figure 3. Schematic depiction of the experimental system used for thrust measurements

Data was analysed with an emphasis on the calculation of maximum thrust force (F), specific impulse (I_{sp}) and working time, following the equation:

$$I_{sp} = \int_{t_0}^{t_1} F dt \quad (1)$$

where: t_1 – end burning time (in s), t_0 – initial burning time (in s) and F – generated thrust (in N).

3. Results and discussion

3.1. Sensitivity to electromagnetic radiation

The results of sensitivity to electromagnetic radiation measurements (Table 1) reveal that the produced nanothermite samples are insensitive to irradiation with λ = 520 nm, for optical power values below 320 mW. This suggests that the system has a relatively high ignition temperature, as the absorption spectrum of CuO extends through most of the visible light range [26].

Table 1. Sensitivity of Al/CuO composition to electromagnetic radiation

Nominal power [mW]	Measured power [mW]	Result („initiation" to „no initiation" ratio)
1000	320	0/5
944	300	
782	250	
620	200	
457	150	
295	100	
133	50	
52	25	

3.2. Sensitivity to impact and friction

The Al/CuO samples tested exhibited slightly higher sensitivity to impact (Table 2) than other nanothermites, including other Al/CuO nanothermites [27]. This is probably caused by our use of flaked aluminium rather than the more commonly used atomised aluminium.

Table 2. Sensitivity of Al/CuO composition to impact (Bruceton analysis)

Energy[J]	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
10	N*)	–	–	–	–	–
15	N	–	–	–	–	–
20	N	–	–	–	–	–
25	N	–	–	–	–	–
30	N	–	–	–	–	–
35	N	–	–	–	–	–
40	N	N	I**)	–	–	–
35	N	N	I	–	–	–
30	N	N	N	N	N	I
25	N	N	N	N	N	N

*) N – no initiation; **) I – initiation

Composition shows much higher sensitivity to friction (Table 3), with upper insensitivity limit of 18 N, than other Al/CuO MICs and can be classified as sensitive [27].

Table 3. Sensitivity of Al/CuO composition to friction (Bruceton analysis)

Force [N]	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
42	I*)	–	–	–	–	–
36	I	–	–	–	–	–
32	I	–	–	–	–	–
24	I	–	–	–	–	–
20	N**)	N	I	–	–	–
18	N	N	N	N	N	N

*) I – initiation; **) N – no initiation

3.3. Bulk density

The test compositions were produced to exhibit an equivalence ratio of 1.0, which translates to a theoretical maximum density (TMD) of 5.61 g/cm^3. The measured bulk density of the samples (Table 4) is in the order of 3.33% TMD. Interestingly, the spread of bulk density across the tested samples is relatively high (approx. 18% of the average), indicating limited homogeneity, possibly related to deviations in grain shape, which is the main parameter affecting particle loading and, hence, bulk density.

Table 4. Bulk density of Al/CuO composition

Mass [mg]	Density [g/cm^3]	Mass [mg]	Density [g/cm^3]	Mass [mg]	Density [g/cm^3]	Average density [g/cm^3]
28.8	0.188	28.2	0.184	26.1	0.170	0.187 ±0.01
26.5	0.173	31.2	0.204	28.1	0.183	
31.1	0.203	28.8	0.188	29.7	0.194	
27.5	0.179	28.2	0.184	29.1	0.190	
30.2	0.197	27.8	0.181	30.5	0.199	
28.8	0.188	28.2	0.184	26.1	0.170	

3.4. Thrust

Some samples initiated only after several ignition attempts, coinciding with the earlier evidence towards the relatively high ignition temperature of this nanothermite. The observed high variation of the results (Table 5) probably stems from the limited homogeneity of the nanothermite, indicating that the core-shell structure of the nanothermite particles, postulated in literature for the utilised method, is not achieved to the extent that Ref. [24]although they are commonly fabricated as powders, films, multi-layers and other heterostructures which desire an effective interface between reactive components but are not colloids and typically immobile. Little information is available in the literature on fabrication and characterization of standing-alone and mobile core-shell MIC micro-particles. In this paper, we report on a wet-chemistry method to synthesize micron-sized spherical colloids of Al/CuO with a core-shell structure. Scanning electron microscopy (SEM implies.

Table 5. Thrust parameters of Al/CuO composition

Test No.	Mass [mg]	Maximum thrust force [mN]	I_{sp} [s]	Working time [ms]
1	0.03	543.4	4.4	30.3
2		1142.0	10.2	46.3
3		1193.9	9.1	55.2
4		253.0	2.8	45.2
5		403.4	4.8	43.5
6		3368.3	34.5	31.3
7		234.3	4.2	93.0
8		376.9	5.0	49.2
9		281.7	1.8	93.2
10		1930.4	15.2	37.4

3.5. SEM analysis of nanothermites

Figure 4 shows SEM-EDS images of the obtained nanothermite. In the images, there is no CuO core coating observed. Both components of nanothermite occur as practically separate nanometric agglomerates of particles. CuO constitutes a separate phase and the shape of the particles does not allow the assumption that, as a result of the work, a core-shell structure was created, which could separate from the core during drying or after preparation of the sample.

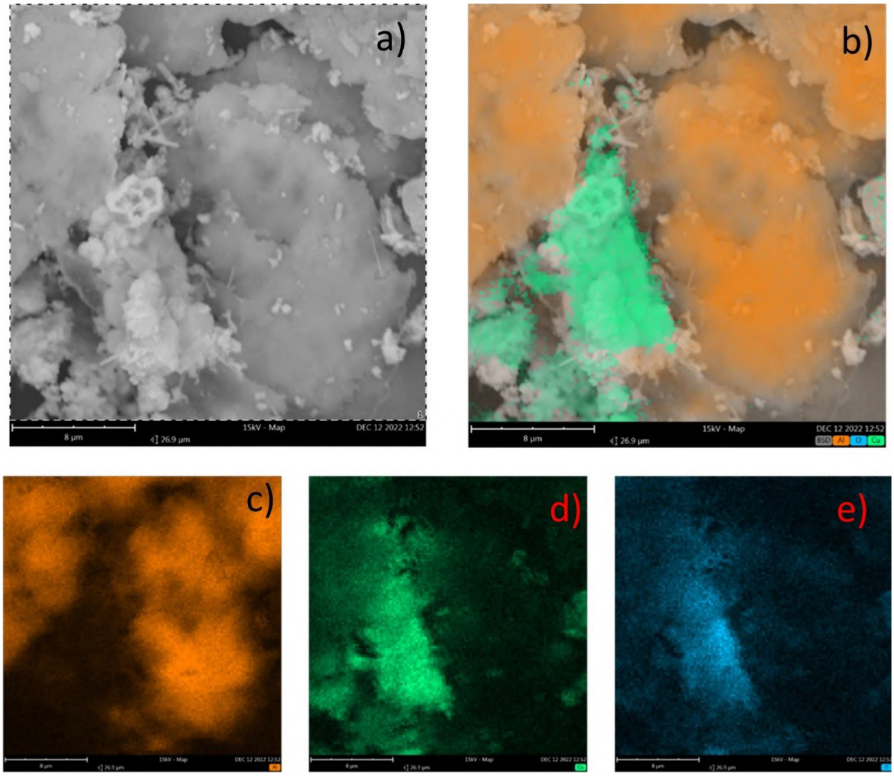

Figure 4. Result of SEM-EDS analysis for Al/CuO composition: SEM picture (a), EDS map (b), EDS map for Al (c), EDS map for Cu (d) and EDS map for O (e)

SEM-EDS analysis combustion products visible in Figure 5 together with their mapping show that the whole of the MIC reacted and produced dispersed Al_2O_3 particles together with copper spheres. Figure 5 shows products of combustion, as a result of complete combustion reaction, the formation of sinter-textured products occurred. Mapping displays higher agglomeration of CuO particles, compared to images from before reaction.

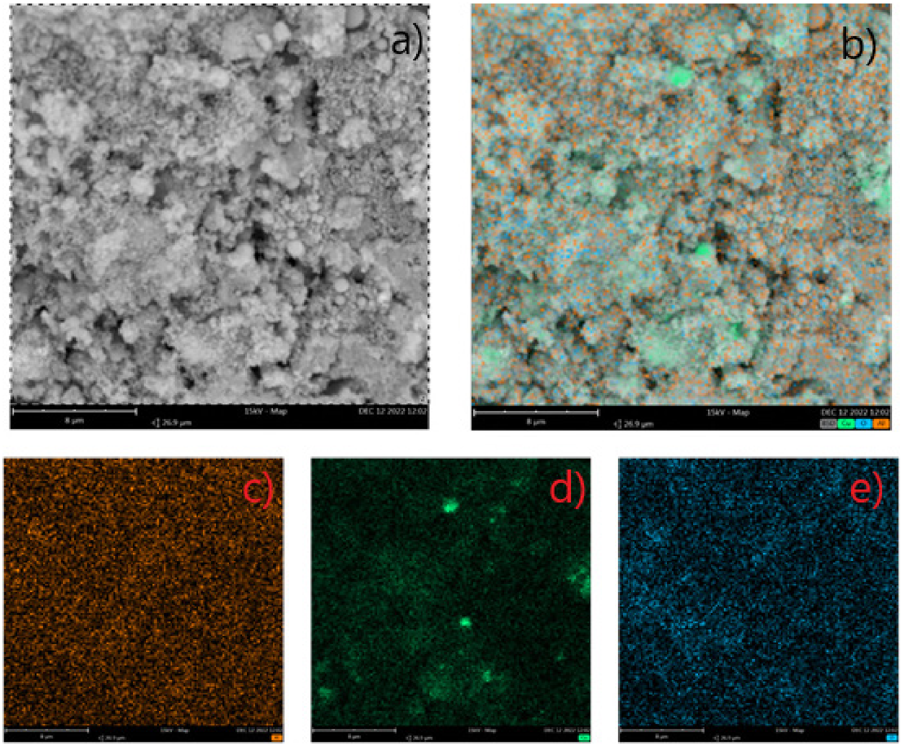

Figure 5. Result of SEM-EDS analysis for combustion products of Al/CuO composition: SEM picture (a), EDS map (b), EDS map for Al (c) EDS map for Cu (d) and EDS map for O (e)

4. Conclusions

- Preparation of an Al/CuO nanothermite was successful, as SEM images show nanometric cop- per(II) oxide particles. However, the obtained MIC does not resemble a core-shell structure, contrary to work described in the reference publication. It can be stated that these procedures require surface modification, e.g. in the direction of activating the core surface to improve CuO adsorption.
- Tests of sensitivity to electromagnetic radiation concluded that the composition is completely insensitive to radiation of wavelength 520 nm, below a power of 320 mW, which is associated with the maximum absorbance of constituents being in different wavelength ranges.
- Impact and friction tests results show higher sensitivity than values found in literature, which can be affected by the long drying time during preparation, as nanothermites tend to age quicker at high temperatures. Another factor concerning sensitivities can be the flaked aluminium powder used.
- Thrust measurements have shown, that the composition in its current state cannot be used in microthrusters, due to inconsistency in initiation and generated thrust, as in many instances samples were initiating only after 2-3 attempts and all parameters describing propelling abilities strongly differed with each run.

♦ The results indicate that the reaction follows a mechanism similar to a sintering reaction. However, it should be noted that in the incomplete reaction of the composition, both spherical and flat particles of unreacted fuel, spherical particles of metallic copper and spindle-shaped combustion products are visible. At the same time, the figure 5 shows complete combustion of the composition and a more even distribution of components. This most likely indicates the insufficient homogenization of the composition and discrepancies between the synthesized batches.

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