

Article

Novel NSTEX System Based on Ti/CuO/NC Nanothermite Doped with NTO

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Abstract: Modern energetic materials (EMs), e.g., nanothermite and NSTEX (Nanostructured Thermites and Explosive) compositions are attracting increasing research interest. In this work, we present the results of our investigation on the properties of a novel Ti/CuO nanothermite system doped with cellulose nitrate (NC) and 5-Nitro-1,2-dihydro-3H-1,2,4-triazin-3-one (NTO). In terms of safety parameters, the friction (40→360 N), impact (40→50 J) and laser irradiation sensitivity were determined for tested systems, which indicated tunable properties. The combustion velocity (up to 735 m/s), pressure parameters for combustion in closed vessel, thrust parameters and open-air combustion behaviour were measured. Moreover, in order to deeply study the impact of NTO on the combustion mechanism, SEM, DSC/TG and XRD analyses were conducted. The obtained results indicate that the Ti/CuO/NC/NTO system is extremely promising for future applications.

Keywords: NSTEX; nanothermite; energetic material



Citation: Polis, M.; Stolarczyk, A.; Szydło, K.; Lisiecka, B.; Procek, M.; Sławski, S.; Gołofit, T.; Hawelek, Ł.; Jarosz, T. Novel NSTEX System Based on Ti/CuO/NC Nanothermite Doped with NTO. *Energies* **2024**, *17*, 3675. <https://doi.org/10.3390/en17153675>

Academic Editor: Tapas Mallick

Received: 2 July 2024

Revised: 15 July 2024

Accepted: 18 July 2024

Published: 25 July 2024



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1. Introduction

The last two decades have seen a stable and continuous development of new energetic materials (EMs), which are used in many civilian and military areas [1–3]. Groundbreaking development occurred in the field of nanotechnology and it has been utilised just as thoroughly in medicine, environmental protection and ceramic materials, as in defence applications [4–7]. Novel nanoenergetic materials, containing nanosize particles or bearing nanoscale structural features have aroused significant research interest. The application of material nanoengineering principles to the preparation of EMs enables detailed control over the composition and density of the EMs, as well as their morphology and particle size distributions at the nanometer scale. Nanothermites, also referred to as metastable interstitial composites (MICs) are good examples of the above trend [8–12].

Nanothermites are highly reactive and solid-phase EMs composed of nanometric metallic fuels and oxidising agents that are intimately mixed with each other [13–16]. Compared to micrometric thermites, nanothermites are characterised by high surface area-to-volume ratios, high energy density, rapid release of energy and high sensitivity to stimuli. These features increase the reaction rate, heat release, pressure and thrust output of nanothermites [17–19]. On the other hand, the existing limitations in the applications of

nanothermites result from the agglomeration of nano-reactants before ignition, incomplete combustion and relatively long ignition delays [2,20,21].

The electronegativity of metals used as fuels is one of the key parameters considered in the design of nanothermites, with metals, which have electronegativity in the range of 1.5–2.5 on the Pauling scale, being a favourable choice [11,22]. This stems from the fact that a viable fuel for nanothermite compositions must exhibit significant reducing properties, high density, high heat of combustion, a moderate amount of gases released, low melting point, stability, compatibility with other components and low toxicity. Consequently, aluminium (Al), magnesium (Mg), silicon (Si), titanium (Ti), tantalum (Ta) and even boron (B) are commonly used as fuels [23], though the latter two less so, due to their significant toxicity.

Taking into account the thermochemical properties of the fuels, nanometric titanium (Ti) is a promising fuel for producing nanothermites, as it exhibits high reactivity and the presence of a protective oxide layer, which is responsible for the passivation of its surface. The temperature, at which oxidation of nanometric Ti begins, is 100–200 °C, while complete oxidation occurs only at 1000 °C. Ti is also known to readily react with copper(II) oxide, lead oxides and permanganates, providing a clue as to potential oxidising agents to be used in tandem with it [23,24]. The most frequently used oxidising agents are copper(II) oxide (CuO), iron(III) oxide (Fe₂O₃), molybdenum(VI) oxide (MoO₃), bismuth(III) oxide (Bi₂O₃), tungsten(VI) oxide (WO₃), sulfates, iodates and periodates [25,26].

Nanothermites, as modern, interdisciplinary materials, play a significant role, both academic (e.g., in materials engineering) and technological, increasing the effectiveness in many industry sectors (both civil and military) [18]. Nanothermites can be used in micro- and nano-welding, materials synthesis, ejection seats and safety airbags. Propellants and pyrotechnics based on nanothermites increase energy density and lower sensitivity to external stimuli of propulsion systems used in the aerospace industry [8,27]. In the military industry, nanothermites are used as energetic materials for advanced munitions and demolition systems. They are used in microigniters, microthrusters, primers, correction engines, delay systems and gas generators [28]. The NSTEX-type (NanoStructured Thermites and Explosives) composition can also be used as a “green” substitute for lead salts in the design of initiating agents [29]. Moreover, nanothermites are increasingly used in materials science and materials engineering, through the development of modern composites, coatings and even energy storage devices [30–32].

The aim of this work was to develop an NSTEX composition that would exhibit high safety parameters, while having high performance parameters. A secondary aim was to elucidate the effect of changes in the EM content, in our case, the EM being NTO, on the parameters and mechanism of combustion of this group of NSTEX formulations.

2. Materials and Methods

2.1. Materials and Preparation

Copper(II) oxide (>99.99%, d ≈ 40 nm, Iolitec GmbH, Heilbronn, Germany), titanium (>99.99%, d ≈ 50 nm, Iolitec GmbH, Heilbronn, Germany), propan-2-ol (>99.9%, Electro Chem, Gliwice, Poland) and NTO (>99.5%, d ≈ 200 μm, Nitrochem S.A., Bydgoszcz, Poland) were used as received. Nitrocellulose was obtained through the drying of 4 wt.% solution (Sigma-Aldrich, Darmstadt, Germany).

The equivalence ratio of basic nanothermite was calculated according to Equation (1), without taking into account the presence of titanium oxides:

$$\phi = \frac{n_{\text{fuel}} / n_{\text{oxidising agent}}}{n_{\text{stoichiometric fuel}} / n_{\text{stoichiometric oxidising agent}}} \quad (1)$$

where

ϕ —equivalence ratio of the nanothermite;

$n_{\text{fuel}} / n_{\text{oxidising agent}}$ —the molar ratio between actual fuel (i.e., Ti)/oxidising agent (i.e., CuO) dispersed in the electrolyte;

$n_{\text{stoichiometric fuel}}/n_{\text{stoichiometric oxidising agent}}$ —the fuel/oxidising agent molar ratio in a stoichiometric reaction.

The stoichiometric molar ratio of fuel to the oxidising agent was 1:2.

The NSTEX composition samples were prepared for 4 different NTO contents, on the base of the Ti/CuO composition with an equivalence ratio of 1.4, as presented in Table 1. All compositions contained 1 wt.% of NC additive.

Table 1. Content of tested compositions.

Composition Name	NTO wt.%	Ti wt.%	CuO wt.%	NC wt.%
1NTO	1	29	69	1
3NTO	3	28	68	1
5NTO	5	28	66	1
10NTO	10	26	63	1

In order to prepare compositions, the wet-mixing method was employed, followed by electrospaying.

All components were weighed and dried for 12 h at 60 °C in air. In the next step, components were transferred into glass vessels, which were filled with propan-2-ol to achieve a solid loading equal to 125 mg/mL. The suspensions were stirred for 30 min and sonicated for 30 min (0.7/0.3 sonication/break cycle), followed by stirring for 48 h. After this process, the compositions were electrospayed in 1 cm³ batches through stainless steel nozzles (0.5 mm internal diameter, 10 mm length) at a 19 kV voltage difference between the nozzle and collector. The flow rate was equal to 3 cm³/h, and the distance between collector and nozzle was fixed at 10 cm. After the deposition process, the collector plates were dried for 6 h at 60 °C in air. In the final step, the NSTEX compositions were gently removed from the collector plates and stored in sealed containers.

2.2. Friction and Impact Measurement

All tests were performed in accordance with international standards [33,34], using a Peters apparatus and a BAM Fallhammer apparatus.

2.3. Laser Sensitivity Tests

Laser irradiation sensitivity ($\lambda = 520$ nm) tests were carried out for optical power values in the range of 100–300 mW (Laser Green 520-1000-SMA pulse generator, SpectraLaser, Opole, Poland), which were validated using a MIER-4W-USB thermal radiation power detector (SpectraLaser, Opole, Poland). Ignition time was calculated as a time between the UV-VIS (350–850 nm) photodetector reaction and signal from the pulse generator. Both the photodetector and pulse generator were connected with a Rigol MS05104 digital (produced by Rigol Technologies, Beijing, China) oscilloscope, with 10 MSa/s sampling. Tests were performed for 15 mg samples with the set-up presented in Figure 1.

2.4. SEM-EDS Tests

The morphology of the compositions and post-combustion residues was investigated with an FEI Inspect S50 (FEI, Hillsboro, OR, USA) scanning electron microscope (SEM). The chemical compositions of the post-combustion residues were researched with a X-ray energy dispersive spectrometer with a Detector EDS Octane Elect Plus and Analyzer EDAX Z2-i7 (Bruker, Billerica, MA, USA), enabling the simultaneous acquisition of micrographs and Energy Dispersive X-ray (EDS) maps of the investigated samples. The measurement parameters were as follows: working distance of 10 mm, acceleration voltage of incident electrons in a range from 5 kV to 30 kV, current intensity of about 95 μ A and spot size of the electronic beam size equal to 5 nm².

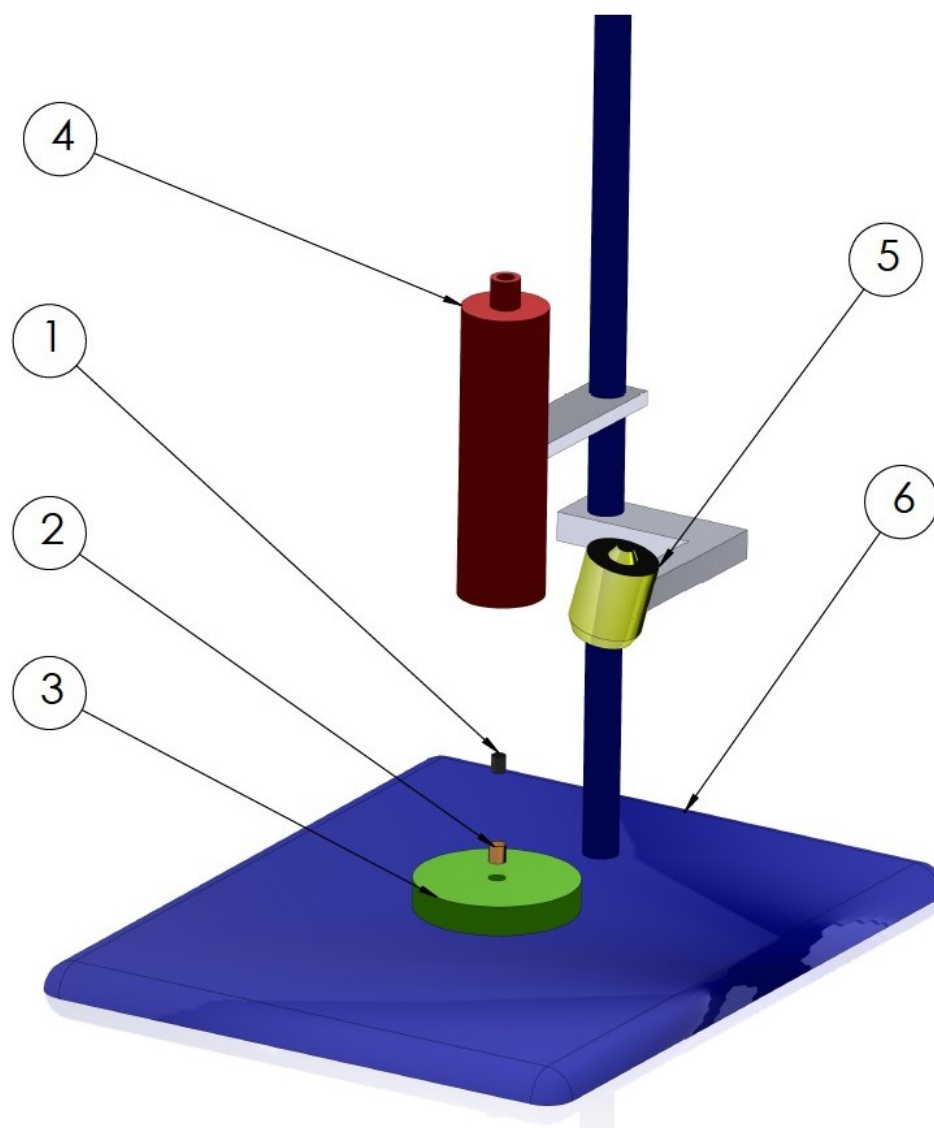


Figure 1. Conceptual scheme of the set-up for radiation/irradiation sensitivity experiments 1—tested composition; 2—copper shell; 3 —alumina positioning ring; 4—collimator; 5—UV-VIS sensor; 6—mounting elements.

2.5. XRD Tests

X-ray diffraction (XRD) with Cu $K\alpha$ radiation ($\lambda = 1.54183 \text{ \AA}$) was performed to identify the crystalline phases using Rigaku MiniFlex 600 (Rigaku Co., Tokyo, Japan) at RT using a one-dimensional detector (Rigaku D/teX Ultra 250) and zero-background sample holder (monocrystalline Si). The X-ray tube was operated at 40 kV and 15 mA. Additional measurement parameters were 2θ range of 22.5° – 62.5° , IHS slit = 5 mm, Soller slits = 2.5° , DS slit = 1.25° , scanning step size 0.01° and exposure time at each point of 1.67 s without sample rotation.

2.6. DSC/TG Tests

DSC/TG tests were conducted using a TA Instruments SDT Q600 apparatus, employing a heating rate of $20^\circ\text{C}/\text{min}$ and purging with argon gas (5.0. purity grade, $200 \text{ cm}^3/\text{min}$). The tested samples were poured into ceramic crucibles and closed with a gold disc, with a 0.3 mm hole in its central part. The design of the closing discs allows the escape of gases, while maintaining limited contact of the samples with the environment.

2.7. Closed Vessel Combustion

All tests were performed for 50 mg samples of compositions. Pre-weighed samples were poured into a closed vessel (volume of 15 cm³), equipped with a pressure sensor (PCB Piezotronics 102B, PCB Piezotronics, New York, NY, USA). The sensor was connected with a signal conditioner (PCB Piezotronics 480E09, PCB Piezotronics, New York, NY, USA) and digital oscilloscope (Tektronix TBS2401B, Tektronix, Beaverton, OR, USA), with a 25 MSa/s sampling rate. In each case, the samples were ignited with a laser pulse (700 mW, 100 ms).

2.8. Thrust Force Measurements

A custom experimental set-up (Figure 2) was utilised to conduct measurements, as described in detail in the Supplementary Information.

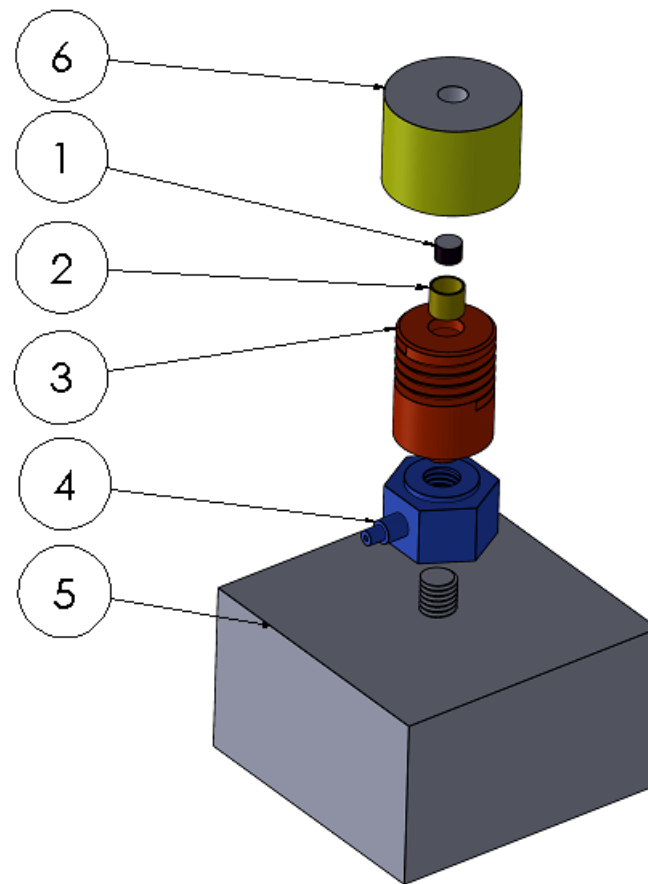


Figure 2. Scheme of thrust measurement set-up, where 1—tested composition; 2—copper shell; 3—cylindrical connector; 4—force sensor; 5—base plate; 6—nozzle.

The specific impulse was calculated according to Equation (2):

$$I_{sp} = \frac{F\Delta t}{g\Delta m} \quad (2)$$

where

I_{sp} —specific impulse [s];

F —thrust force [N];

Δt —combustion time [s];

g —gravitational constant = 9.81 [m/s²];

Δm —mass of the composition that was burned [kg].

2.9. Open-Air Combustion

In order to study the combustion of NSTEX compositions, an experimental set-up (Figure 3), analogous to ones used in literature [35–37], was utilised. The tested NSTEX samples (15 mg) were poured onto a ceramic plate and ignited with a laser pulse (700 mW, 100 ms).

The combustion process was recorded with a Phantom 9.1. high-speed camera, placed at a distance of 500 mm from the sample and recording at 6400 frames/second. Between the camera and the sample, 2 mm thick PMMA screens were placed in order to protect the optical elements. The ignition time and time of combustion were calculated based on image analysis.

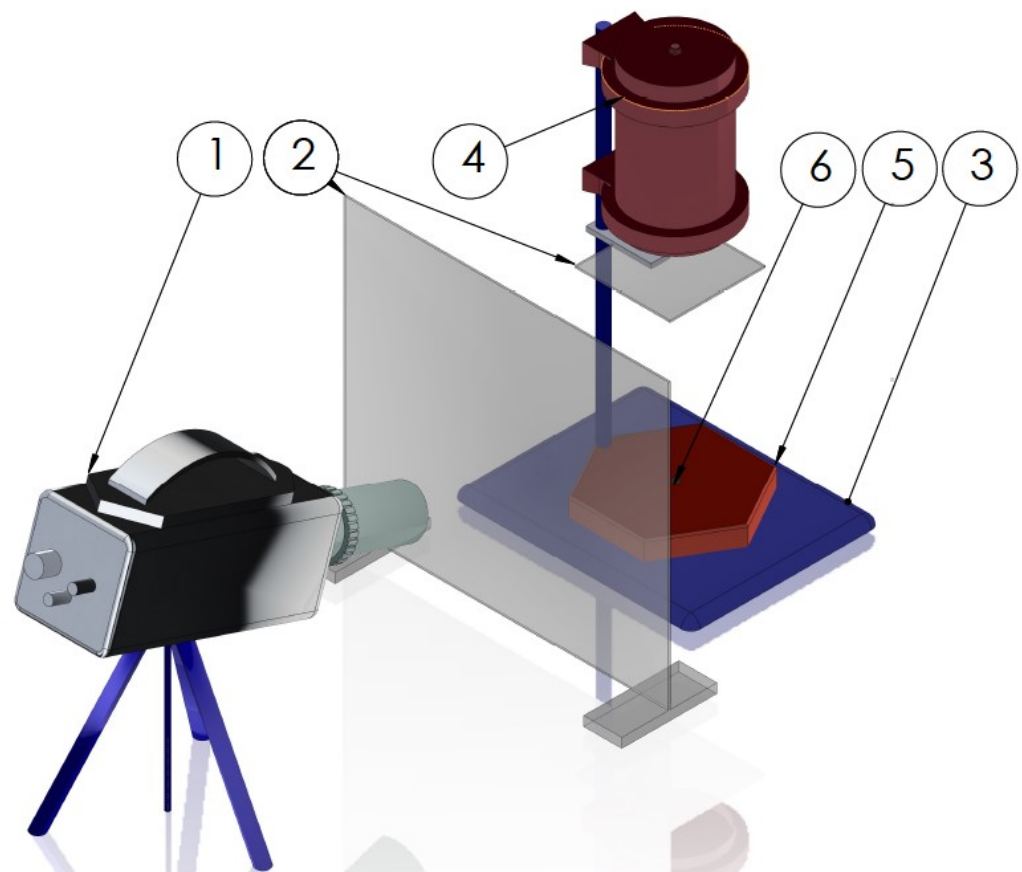


Figure 3. Set-up used in open-air combustion test, where 1—high-speed camera; 2—PMMA plates; 3—steel support; 4—collimator; 5—ceramic basic plate; 6—tested composition.

2.10. Combustion Velocity Measurements

The tested charges made from PMMA tubes (70 mm long, 4×2 mm in diameter) were closed at one end with a PMMA plate (2 mm thick) and elaborated with tested NSTEX samples (Figure 4) in order to achieve a density of 9 % TMD for each composition.

Tests for the 3NTO composition also included the measurement of combustion velocity for charges with densities of 10.5 % TMD and 12 % TMD.

After elaboration, the charges were closed with 3D-printed plugs (PETG, printed with Prusa Mk3, Prusa Research, Holesovice, Czech Republic). Prepared charges were placed on a testing stand, between two steel jaws to ensure the reproducible mounting of samples. The Phantom 9.1 high-speed camera was placed 1.5 m away from the sample at 90 degrees to the charge axis. Each sample was ignited with a laser pulse (700 mW, 100 ms). The time of combustion was calculated based on image analysis. The average combustion velocities were calculated based on the integral mean value theorem [38].

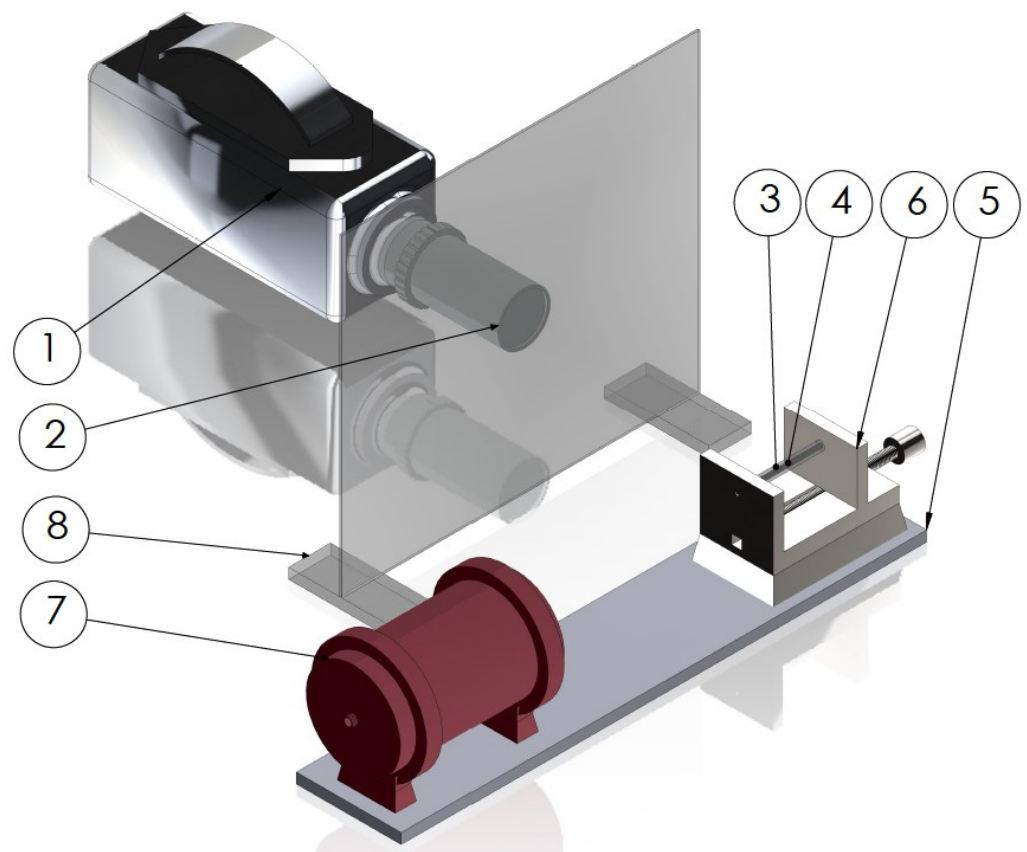


Figure 4. Scheme of set-up used in combustion velocity tests, where 1—high-speed camera; 2—lens; 3—PMMA tube; 4—tested composition; 5—massive steel support; 6—mounting jaws; 7—collimator; 8—PMMA plate.

3. Results and Discussion

3.1. Friction and Impact Sensitivity Measurements

The tested samples are insensitive to impact (Table 2), which is primarily related to the presence of the usually impact-insensitive nanothermite and secondary EM (NTO) in the tested formulation.

Table 2. Friction and impact sensitivity of tested samples.

Sample	Friction Sensitivity [N]	Impact Sensitivity [J]
1NTO	128	>50
3NTO	96	>50
5NTO	84	>50
10NTO	40	>50
NTO	>360	40

The friction sensitivity of the studied samples increases with increasing amount of NTO in the sample, contrary to what is reported in the literature for nanothermite/secondary EM systems [39]. Most likely, this is due to the texturising effect of NTO, as SEM analyses have shown the presence of larger grains for compositions containing higher NTO amounts.

3.2. Laser Sensitivity Tests

Regardless of the radiation energy, an increase in the ignition time as a function of the NTO content of the composition can be observed in almost every case studied (Figure 5).

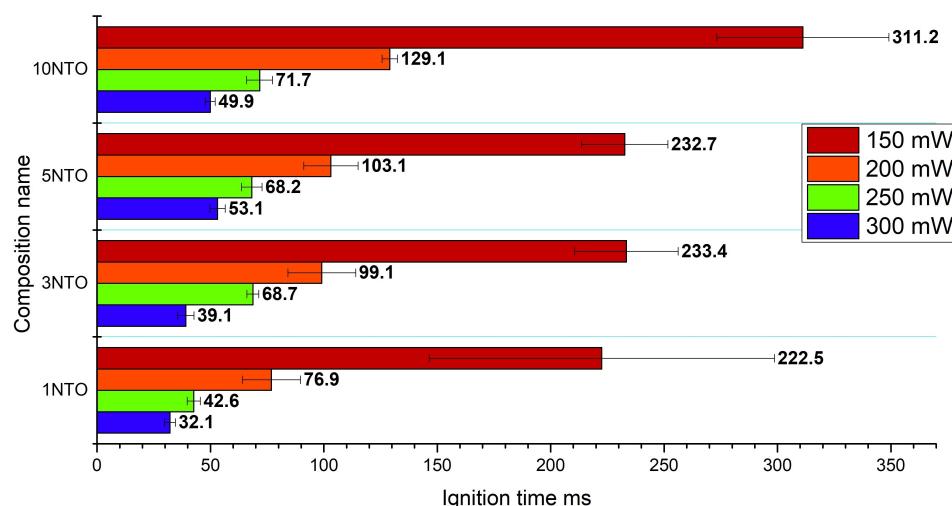


Figure 5. Ignition times of tested compositions for varied radiation powers.

The increase in ignition time can be attributed to one or more of several possible factors. The explanation could be a lengthening of the reaction time scale, where the addition of NTO slows down the ignition and full, stable combustion development of the composition. Moreover, it has been shown that the irradiation of porous surfaces of secondary EMs can result in the formation of cracks and free spaces, therefore, also faults in heat and mass diffusion, which could delay the ignition process [40]. Moreover, NTO has a significantly lower heat transfer coefficient ($0.14 \text{ W/K}\cdot\text{m}$ [41]), much lower than those of Ti and CuO ($21.9 \text{ W/K}\cdot\text{m}$ and $18 \text{ W/K}\cdot\text{m}$, respectively [42,43]), which limits heat transfer in a system where the ignition process of compositions of this type is dominated by heat transfer via conduction and convection. Changes in the morphology of the composition should be taken into account as the NTO content increases and as the grain size rises, there is a decrease in their sensitivity to thermal stimuli.

From the point of view of thermal explosion theory [44], the ignition is possible when the amount of heat generated during the reaction exceeds the heat losses to subsequent layers of the composition and to the environment. According to this, the increase in NTO content should facilitate easier combustion, due to lower effective heat exchange factors. Nevertheless, the observed increase in ignition times could be explained through the local overheating of NTO, causing it to either volatilize or undergo decomposition, producing gases, which promote heat loss from the sample.

3.3. SEM-EDS Tests

SEM-EDS analyses (Figures 6 and A1–A4) reveal that the tested samples have very well-developed surfaces, which significantly improves the bilateral adhesion of the particles. The direct adhesion of the oxidising agent to the fuel was confirmed, which is expected to improve the combustion properties of nanothermites.

Spherical titanium covered with well-developed copper oxide agglomerates was observed. Some of the particles have a smooth surface, others have a developed surface and a regular spherical shape. In each case, highly porous, multi-walled compositional agglomerates, formed from submicron particles are present. With increasing NTO content, it is possible to observe not only an increase in the size of these agglomerates but also the presence of more spherical and spindle-shaped structures of the submicron crystals that form part of the larger clusters. This apparent change in morphology is due to the fact that with increasing NTO content, crystallisation of solid particles occurs more rapidly during the electrospraying process.

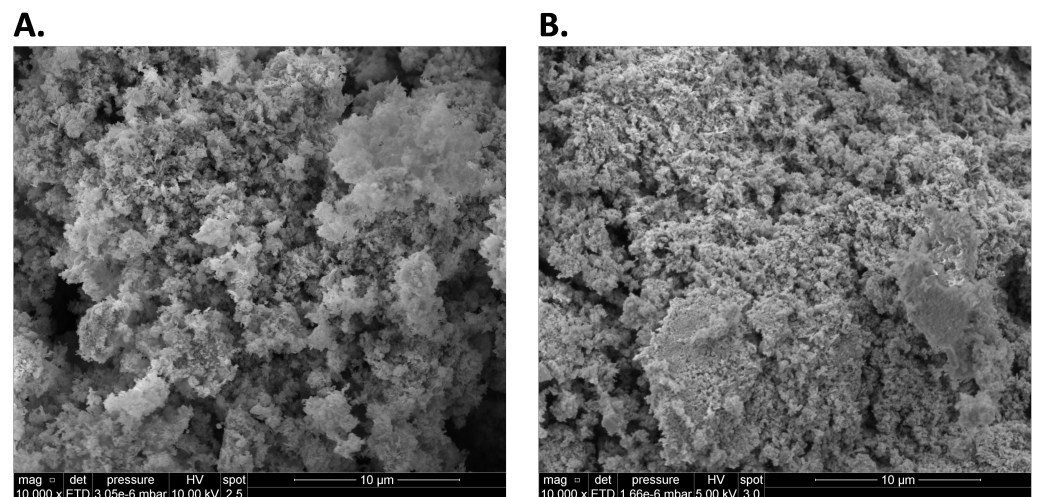


Figure 6. SEM images acquired for (A) 1NTO and (B) 10NTO compositions.

SEM-EDS analyses of the tested combustion products show quite good homogeneity of Cu, O, N and C in 1NTO combustion products (Figure A5). The Ti atoms are agglomerated in a few areas, visible as multi-walled, porous sinters or spherical particles. In both cases, these are most likely titanium oxides, trapped inside a remoulded copper and copper oxide matrix.

In the case of 3NTO combustion products (Figure A6), the morphology is quite different. Uneven distribution of Cu and Ti is observed, with the domains occurring in an alternating manner. Similar to the previous sample, the multi-walled agglomerates are composed mostly of Ti and O. The C, O and N atom distributions are equal across the sample surface.

The 5NTO sample (Figure A7) presents a morphology and atom distribution similar to those of the 1NTO sample, with titanium oxides trapped inside a Cu-based matrix. Nevertheless, few areas with lower Ti and Cu concentrations are visible.

The morphology of the 10NTO sample (Figure A8) is in line with that of the previous samples, following the trends observed for increasing NTO content. The Cu and Ti atoms are distributed unequally and the main part of the surface is made up of massive, multi-walled sintered structures composed of titanium oxides. The C, O and N atom distributions are uniform. The EDS tests suggest changes in the reaction mechanism with increasing NTO content (Figure 7), which leads to stronger disproportion of Cu and Ti in the compositions and an expansion of the presence of multi-walled structures.

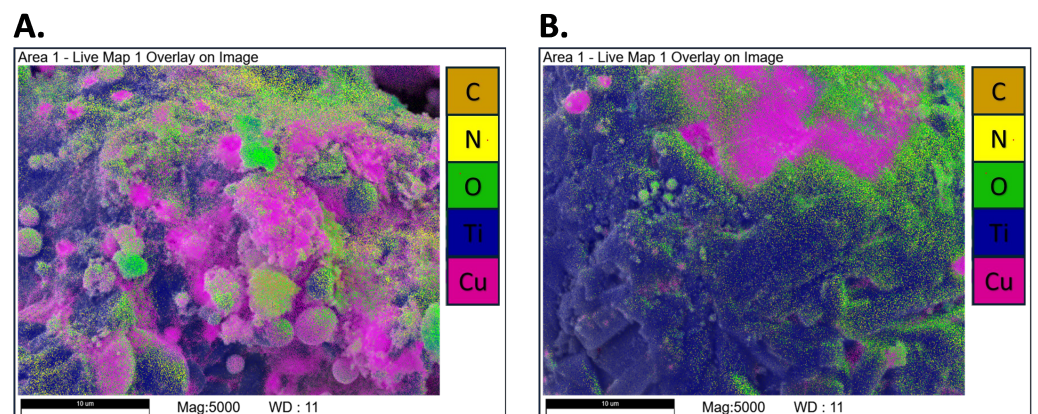


Figure 7. SEM-EDS images acquired for (A) 5NTO and (B) 10NTO compositions.

3.4. X-ray Diffractometry

The XRD patterns of four decomposition products are presented in Figure 8. Three main phases, Cu (PDF Card No. 00-004-0836), rutile TiO_2 (PDF Card No. 00-021-1276) and Cu_2O (PDF Card No. 01-071-3645), were identified in all four samples. The TiO_2 anatase phase (PDF Card No. 01-075-2547) was also found in the 10NTO sample. The occurrence of anatase may indicate that unreacted Ti was present in the combustion products, as anatase transforms into rutile in temperatures above 1267 K [45]. All the NTO intensity peaks were identified by the single-phase α -NTO crystal structure (triclinic symmetry) previously published in [46].

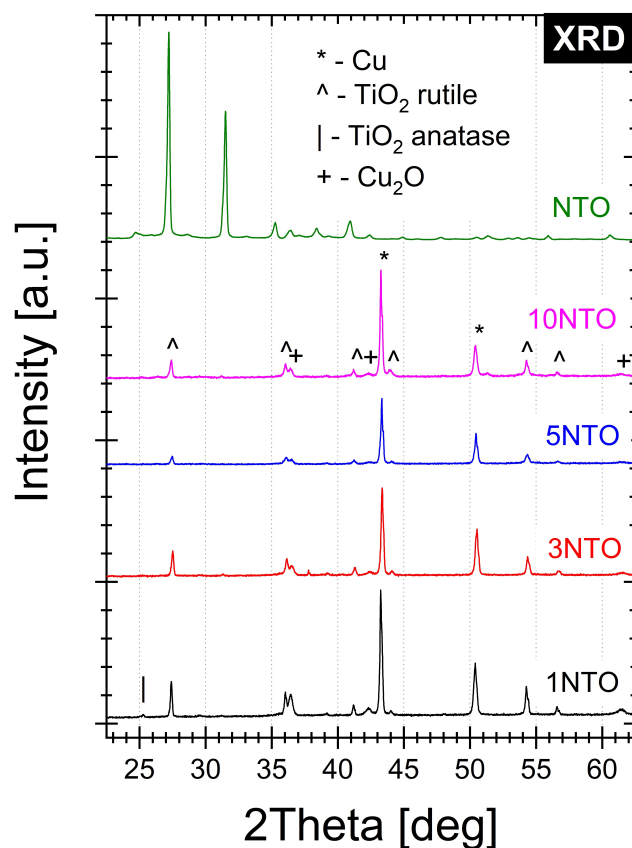


Figure 8. X-ray diffraction patterns of NTO and decomposition products 1NTO, 3NTO, 5NTO and 10NTO.

3.5. DSC/TG Tests

In Figure 9, the DSC/TG curves for pure NTO and 1NTO composition are presented. In the case of NTO, a single exothermic peak is present, with a maximum temperature equal to 283.06 °C and heat of reaction equal to 946 J/g, whereas the mass loss process starts at approximately 190 °C.

In each run for NSTEX composition, a decrease in mass is observed, with an analogous course for all tested samples (Figure 10). The initial slight decrease in mass (up to about 150 °C) is related to the removal of adsorbed water and residual solvent from the electrospraying process. The subsequent rapid decrease in mass in the temperature range of 15–400 °C (with a sharp drop of about 330 °C) is related both to the decomposition of nitrocellulose and nitrotriazolone, as well as to reactions occurring in the Ti-CuO system in the 300–400 °C to, due not only to the decomposition of CuO to Cu_2O , Cu and O_2 , but also to the reaction between the fuel and oxidising agent.

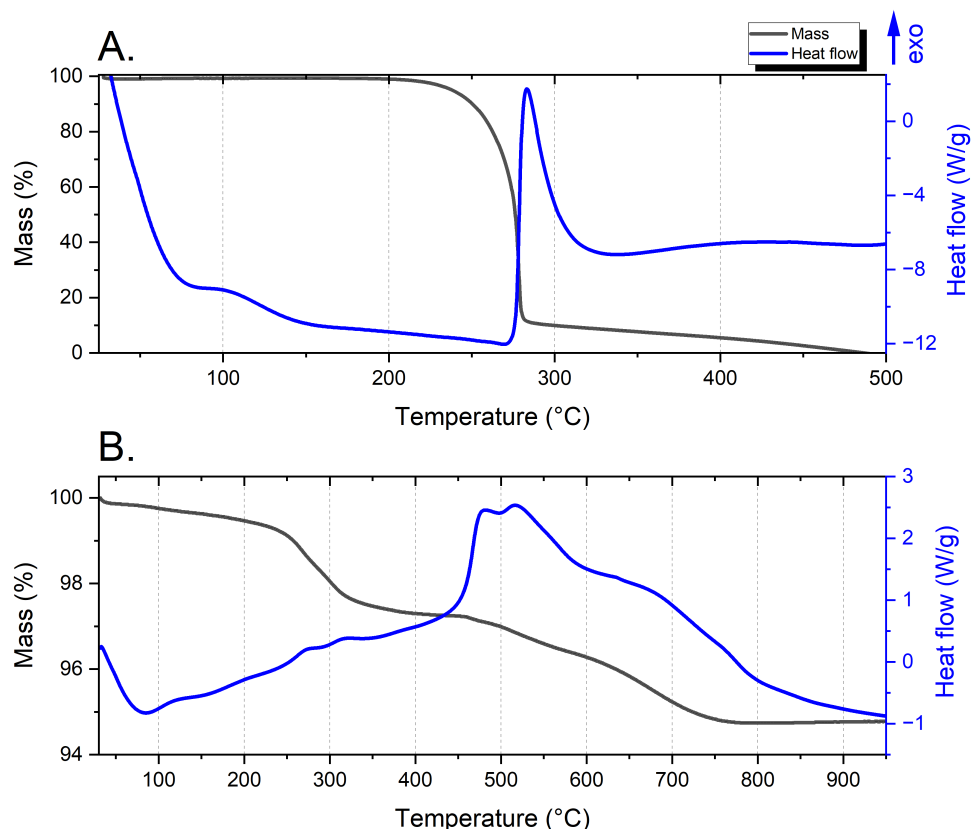


Figure 9. DSC/TG curves for (A) NTO and (B) 1NTO composition.

Subsequently, in the temperature range of 400–750 °C, the uniform mass decrease is related to the oxidising agent decomposition and reactions between the metallic fuel and oxidising agent (Figure 11). The uniform mass decrease is noteworthy, independent of the thermal effects occurring. Above this temperature, a stabilisation of the mass of all the samples can be observed, or a slight increase in the case of the 10NTO composition, which is due to the reaction of titanium with the atmospheric air from the back-pressure air flows generated in the apparatus chamber.

The overall decrease in mass is consistent with the NTO content of the compositions. The mass decrease in the first stage shows an analogous trend, which indicates the correctness of the assumptions made above. Additionally, the value of the mass decrease is greater than the NTO and NC content of the compositions, indicating the presence of the CuO decomposition and reaction in the thermite system. The discrepancy between the mass decrease and the theoretical NTO and NC content increases with increases in their content in the system. The further decrease in mass is quite similar, however, a noticeable downward trend is observed with increasing NTO content, indicating that the CuO decomposition reaction and the thermite reaction are facilitated with increasing NTO content. This difference is particularly pronounced for the 10NTO composition (Figure 10).

For all compositions, the observed thermally induced transformations are relatively similar, with compositions 1NTO and 3NTO showing three distinct exothermic peaks and compositions 5NTO and 10NTO showing a small exothermic fourth peak.

The first reaction occurs in the temperature range of about 250–320 °C. The heats of these reactions increase rapidly with increasing NTO content (36; 81; 121; and 217 J/g). The curves themselves indicate a two-stage reaction, where the breakdown is more pronounced with increasing NTO content.

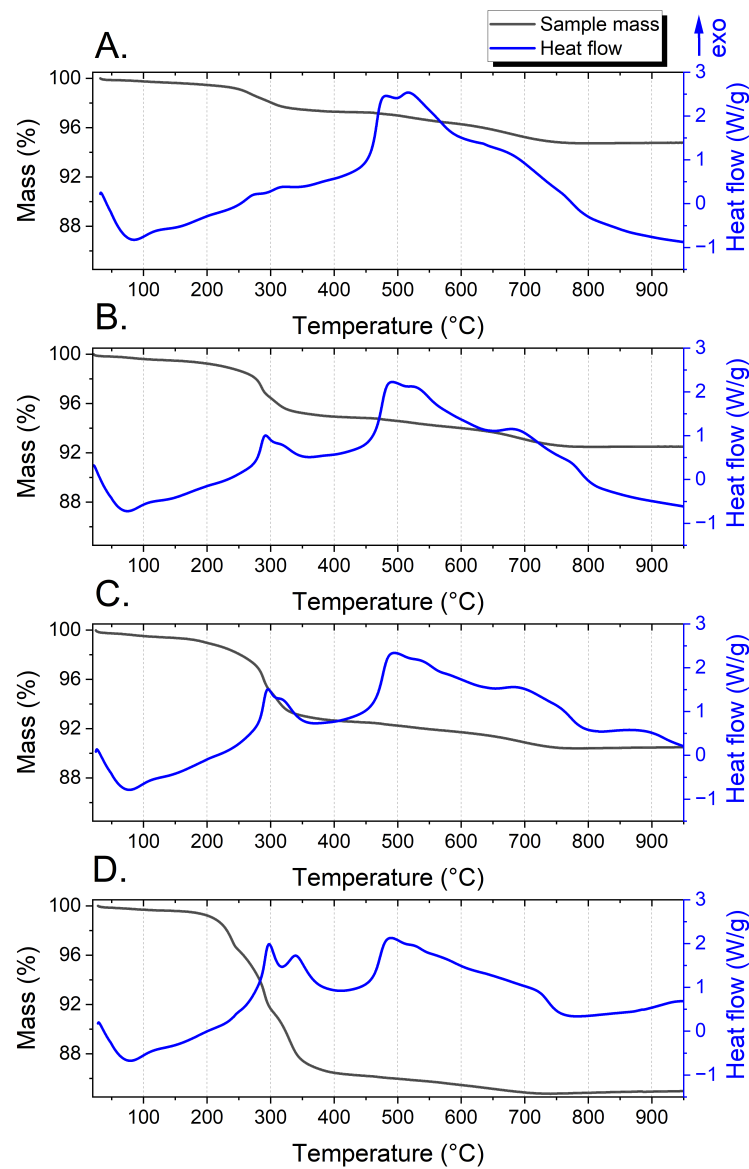


Figure 10. DSC/TG analysis for the tested compositions: (A) 1NTO; (B) 3NTO; (C) 5NTO; (D) 10NTO.

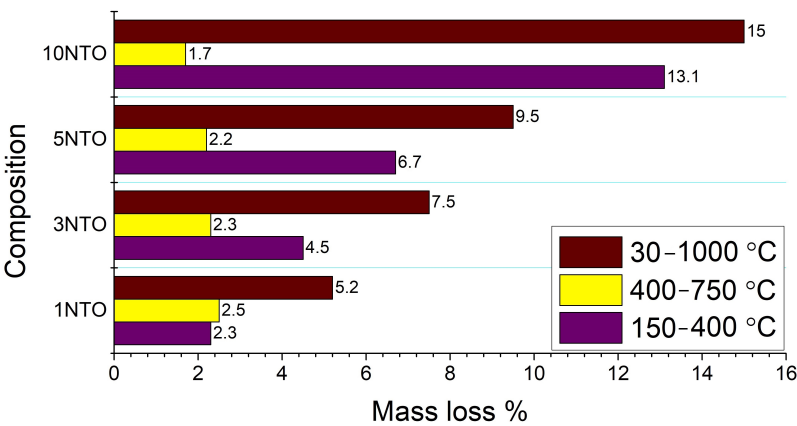


Figure 11. Mass loss for tested compositions.

In this stage, the decomposition of NTO ($268.2\text{ }^{\circ}\text{C}$ [47], $274\text{--}288\text{ }^{\circ}\text{C}$ [48]) takes place. However, given the mass drop values, there is also an initial reaction of the nanothermite itself, or at least the decomposition of the oxidising agent.

The subsequent reaction, occurring in the temperature range $400\text{--}500\text{ }^{\circ}\text{C}$ is characterised by the highest heat and is the main reaction of the nanothermite system. The presence of the double peak is dependent on NTO content, the lower it is, the more pronounced the peak. This indicates that the titanium–copper oxide reaction is limited by the intermediate products of combustion (titanium oxides) and that the amount of gases evolving upon combustion of the composition has a strong influence on the combustion mechanism itself, with a large amount of gaseous products facilitating permeation through the titanium oxide layer into the reactive core of the Ti grains. The heat of the reaction reaches a maximum for the 3NTO composition and decreases rapidly with further increases in NTO content.

Another process, occurring in the temperature range of $600\text{--}700\text{ }^{\circ}\text{C}$, shows analogous trends, with a maximum heat release for the 3NTO composition. This process is most likely related to consecutive reactions of the Ti/CuO system to more stable products.

The percentage contributions of the individual reactions to the total decomposition heat of the composition are presented in Figure 12.

With increasing NTO content, the contribution of reaction 1 increases at the expense of reactions 2 and 3. Considering the total reaction heats (525 ; 625 ; 439 ; and 372 J/g in function of NTO content), this indicates not only the influence of NTO, which increasingly dominates the reaction mechanism, but also a reduction in the reactivity of the composition. As a limiting composition, the 5NTO composition should be distinguished, where the contribution of reaction II is still dominant; at the same time, the other decomposition stages are characterised by similar values.

As mentioned previously, the mass loss observed below $400\text{ }^{\circ}\text{C}$ is higher than stemming straight from the NC and NTO content in the compositions, where this difference rises with NTO content. Based on the contribution of the first process on the net reaction heat, an initial reaction between Ti and CuO takes place.

The minor addition of gas-generating compounds was expected to enhance the nanothermite reaction, due to the formation of reaction “micro-clusters”. In this case, the evolving gaseous decomposition products of NTO and NC constitute a pressure wave that prevents sintering. The hindered sintering process allows maintaining the nanometric size of reacting particles, leading to a more efficient combustion. Simultaneously, the presence of gaseous species influences the heat transfer in the combustion zone, due to their facile migration through the bulk of the nanothermite composition.

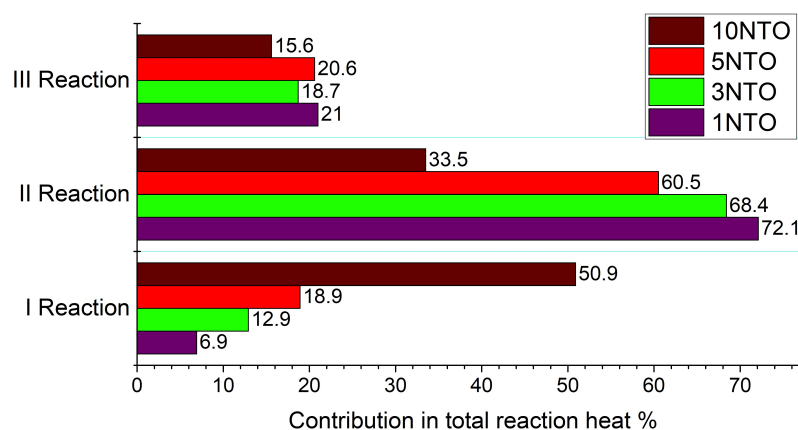


Figure 12. Contribution of reactions in total reaction heat.

In the case of samples containing larger shares of NTO, the unit volume of evolving gases may be sufficient to disperse the solid components of the formulations, simultaneously obstructing solid–solid reactions and facilitating the escape of oxygen from the reaction zone. In such an event, combustion via the reactive sintering mechanism is no longer viable, leading to combustion via a typical diffusion mechanism, limited by gaseous products. This will disrupt the equivalence ratio of the components in subsequent reactions and result in significantly lowering the net heat of combustion.

3.6. Closed Vessel Combustion

The pressurization rate observed for the nanothermite samples (Figure 13) appears to be directly correlated with the system [49]. The pressurization rate (dP/dt) of the entire system reaches the maximum for 3 wt.% NTO.

This is due to the fact that the reactions occurring during combustion provide the greatest amount of heat, as shown in the section above. By increasing the NTO content, the composition is shifted to a state of oxidising agent deficiency, resulting in a reduced oxidation of Ti by CuO. Interestingly, the $P_{\max}$ for the tested compositions does not correspond to the net heat of combustion.

Nevertheless, the reaction of NTO occurs with the generation of a large amount of gas, resulting in an increasing maximum pressure value as the amount of NTO in the composite increases. The total combustion time of the compositions tested is fairly constant, with the exception of 3NTO, for which it is equal to approximately 64 ms.

Based on the obtained results, it can be concluded that NSTEX composition with 3 wt.% NTO is an optimal formulation in terms of energetic performance. Ranking the compositions in terms of decreasing pressurization rate, the sequence of 3NTO > 5NTO > 10NTO > 1NTO is obtained.

3.7. Thrust Force

The results of the thrust force measurements are presented in Figure 14.

Initially, the addition of NTO results in increasing the maximum thrust force, but exceeding 3 wt.% NTO in the composition results in a rapid decrease in the thrust force. Although the increasing NTO content contributes to the amount of gases evolving from a unit mass of the composition, it also prolongs the combustion of the sample, resulting in a significantly lower thrust force. This is due to the fact that thrust is significantly affected by the mass flow rate and velocity of the exhaust gases [50]. Conversely, the total impulse decreases to a much lesser extent, due to the higher combustion times and high gas emission for samples containing larger amounts of NTO contents.

The increase in combustion time points to the decelerating effect of NTO addition on the ignition process. Nevertheless, the rise in gas production allows the maximum thrust to reach higher values for compositions with 1–3 wt.% of NTO.

3.8. Open-Air Combustion

Open-air combustion tests were conducted for loosely poured samples (Figure 15) that were not confined in any way. Consequently, higher experimental variance was encountered than in the case of other described experiments, making the in-depth analysis of the results unreliable. Nevertheless, the obtained top-level information provides a significant insight into the behaviour of the compositions.

Firstly, increasing the NTO content up to 3 wt.% results in prolonging the time required for igniting the composition, but further NTO content increases do not significantly increase ignition times. This is in line with the aforementioned postulate that NTO decelerates the ignition and combustion development of the investigated compositions. Secondly, several combustion stages can be identified for all compositions. Initially, point ignition develops into rapid combustion with high brightness and narrow flame. This stage transitions into a deformed hot-gas zone, surrounded by spallating solid particles, that continue to combust during this process. The duration of the main combustion stage of the investigated NSTEX

samples indicates stabilization of combustion process. The full combustion develops more rapidly for compositions containing lower amounts of NTO (Figure 16). Conversely, the time of the entire combustion process is relatively similar for all samples except 10NTO, for which it is noticeably longer. Usually, however, the afterburning of scattered solid particles lasts longer than the combustion of gases.

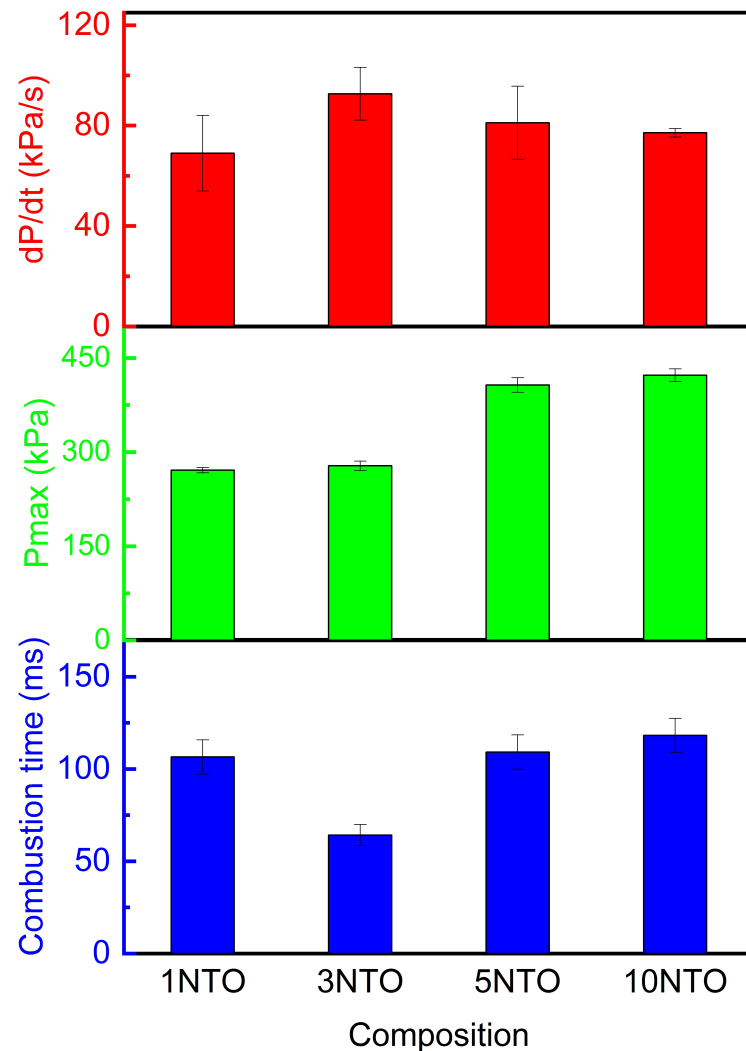


Figure 13. Closed-vessel test results.

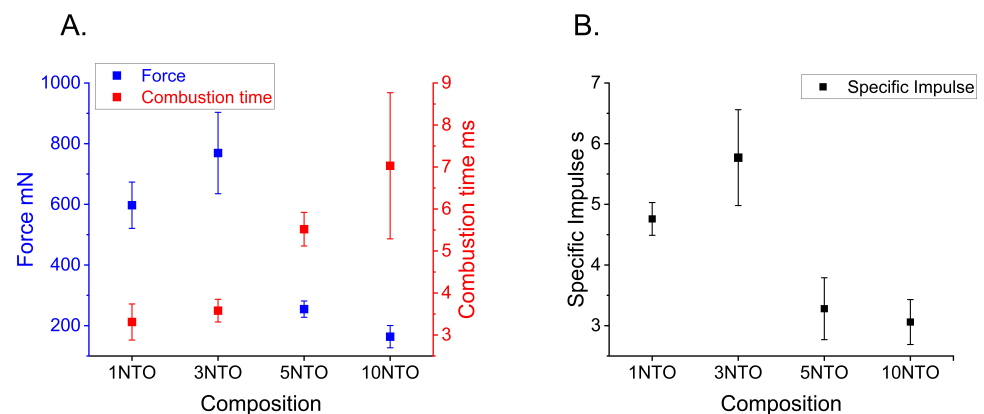


Figure 14. (A) Thrust force and combustion time; (B) specific impulse of tested compositions.

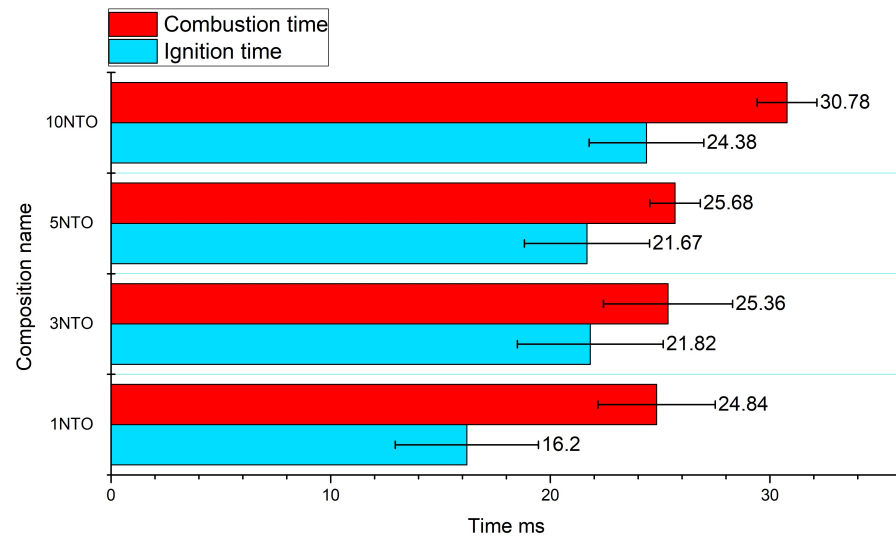


Figure 15. Results of open-air combustion tests.

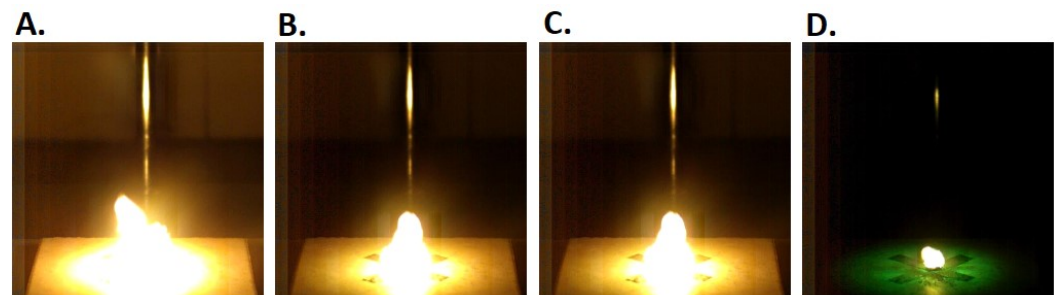


Figure 16. Open-air test snapshots 3.1 ms from ignition for (A) 1NTO; (B) 3NTO; (C) 5NTO; (D) 10NTO.

3.9. Combustion Velocity

Contrary to the results of open-air and thrust force tests, combustion velocity measurements (Figure 17A) revealed the lack of any significant dependence on NTO content (i.e., minor combustion velocity increase upon the transition from 3NTO to 5NTO) on the measured values. A significant dependence on the density, in relation to TMD, was observed, with increasing density resulting in a sharp decrease in combustion velocity, as expected for nanothermites.

High-speed camera image analysis allowed the development of ignition in the compositions to be followed, along with the formation of a gaseous piston that thickens the composition on the head of the combustion front (Figure 18), initially resulting in a slower ignition and combustion development. At a certain point, the initiation of the combustion front occurs behind the thickened area and the rapid development of the combustion process, combined with the simultaneous combustion of the aforementioned area, become apparent.

A significant curvature of the combustion front is also apparent, resulting from the area in which the composition has re-ignited. Most likely, the observed thickening effect is connected with a pressure wave propagating before the flame front [51]. A similar phenomenon was observed for all tested compositions, indicating the occurrence of a two-step combustion development process: main ignition of the composition, associated with the initial initiating stimuli, leading to the formation of a gas piston; second ignition behind the initial flame front that rapidly develops into stable combustion.

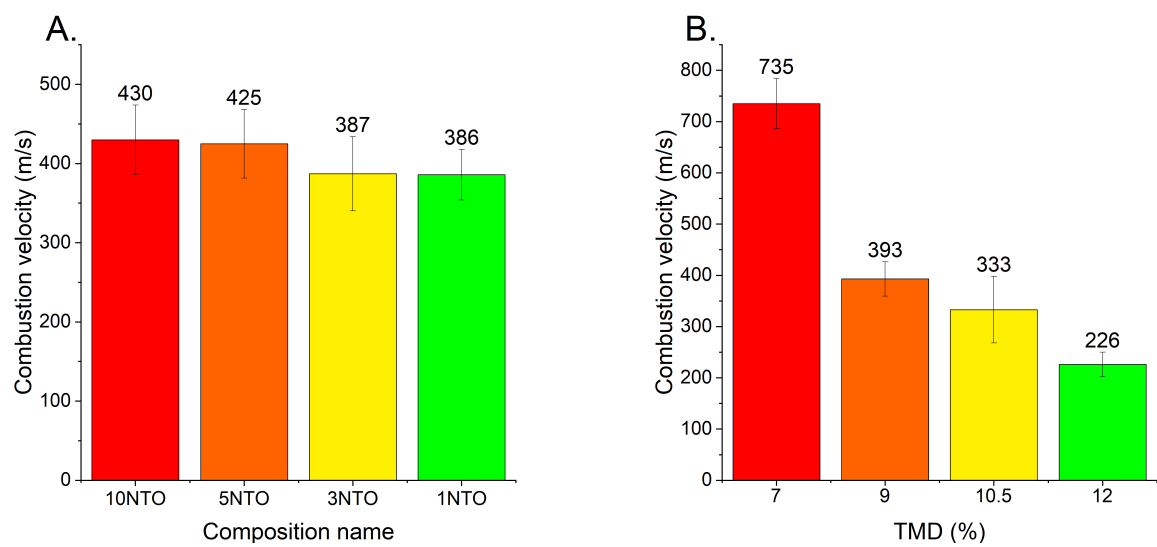


Figure 17. Effects of the (A) NTO content and (B) density of the 3NTO composition (%TMD) on the combustion velocity of the tested NSTEXs.

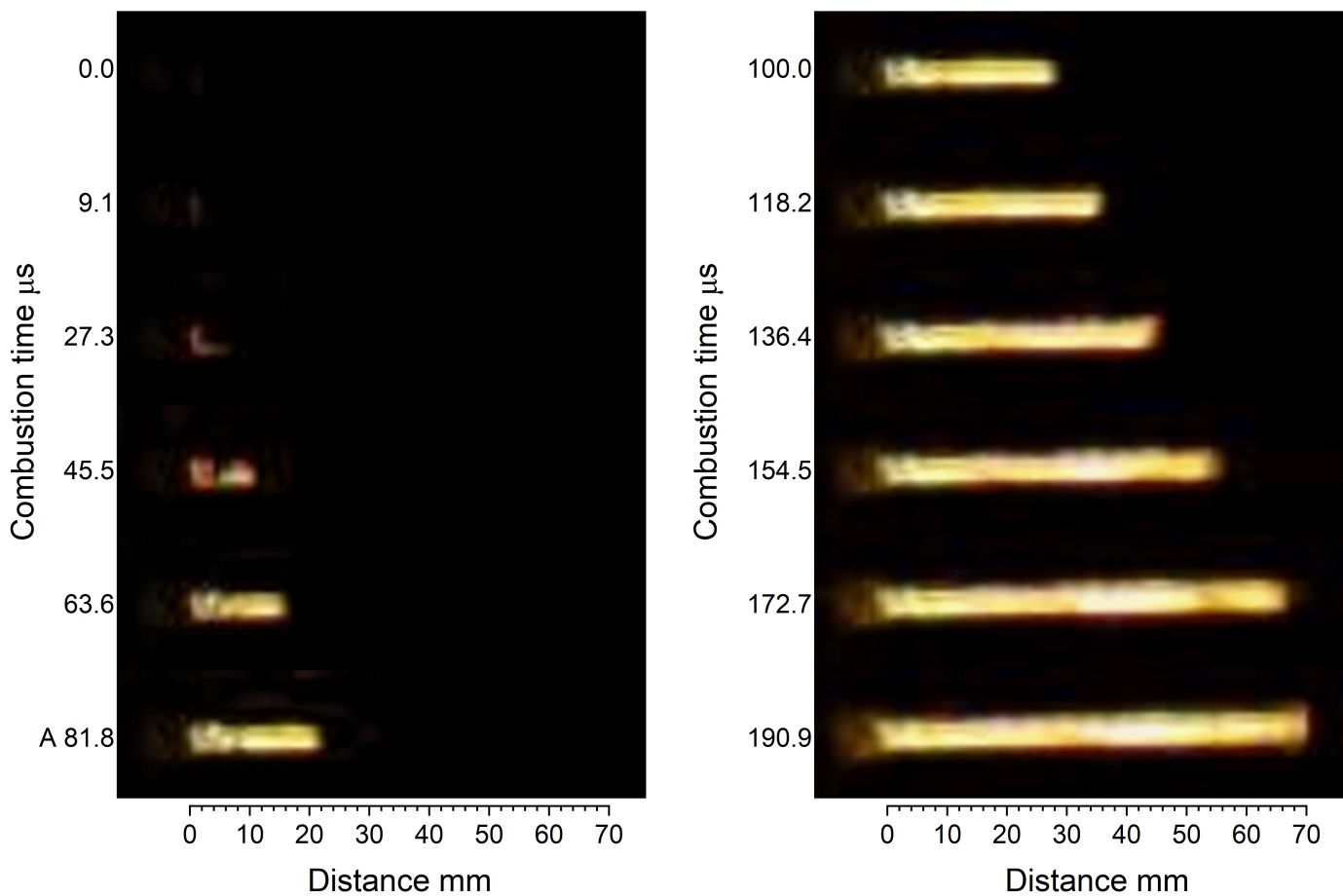


Figure 18. Snapshots from 1NTO composition combustion. The sequence of frames is split into two parts for clarity.

Contrary to the effect of the NTO content in the compositions, increasing their density (expressed in relation to the theoretical maximum density, TMD) brings about a significant decrease in the measured combustion velocity. This inversely proportional relationship between combustion velocity and density is typical of nanothermites and compositions based on them [52]. This effect is related to the limitation of mass and heat transfer through a system, where the porosity decreases with increasing density. The studied compositions produce relatively high amounts of gaseous products upon combustion, hence, their contribution to the combustion process will become increasingly strong with increasing NTO content. Simultaneously, hindering gas permeation is expected to have a more significant effect on the achieved combustion parameters.

4. Conclusions

The tested NSTEX compositions show high safety parameters, i.e., they are completely insensitive to impact, show minor sensitivity to friction, their radiation sensitivity is moderate and inversely proportional to the NTO content. The compositions are readily prepared via electrospraying and are highly uniform in both component distribution and morphology, even though the latter is dependent on the presence and amount of NTO. The increasing NTO content results in the NSTEX becoming composed of increasingly larger and progressively less porous particles.

In terms of performance, the change in NTO content significantly influences the combustion mechanism. This is manifested as both changes in the contribution of the individual reactions taking place during thermally induced decomposition and changes in the combustion parameters observed in closed and open systems.

The total reaction heat was the highest for samples containing 3 wt.% NTO. Analogous conclusions were derived from the closed vessel combustion and thrust force tests—the pressurization rate, thrust force and specific impulse achieved maxima for a NTO content of 3 wt.%. Open-air combustion confirmed the radiation sensitivity tests results and proved the occurrence of multi-stage combustion for the studied compositions.

Conversely, combustion velocity measurements indicated that increasing NTO content also increases the linear combustion velocity of the tested compositions. This points to the crucial role of hot gases in the combustion of these NSTEXs, as evolving gases drive the reaction via heat exchange through convection.

It should be noted that the performed investigations were conducted with the limitation of at most 10 wt. % NTO in the NSTEX formulations, as the secondary EM may not constitute a large share of the NSTEX. Further increasing the NTO content may rapidly change the combustion mechanism, up to a detonation regime.

Overall, the investigated NSTEXs, based on the Ti/CuO nanothermite system supplemented by NTO, provide favourable performances (e.g., a combustion velocity of up to 735 m/s), while maintaining high safety parameters. This makes them extremely promising materials for application in e.g., igniters and pyrotechnic relays.

Due to the fact that this report is devoted to the novel NSTEX system, we have also limited our investigation of the microstructure of the produced NSTEX samples. This is the next logical step in describing the Ti/CuO/NC system, as fine-tuning this microstructure will likely lead to maximising the performance of these NSTEXs. This, however, requires an in-depth study and optimisation of the electrospraying process used for the preparation of samples and will necessitate its own dedicated report.

Future investigations of the tested compositions should be dedicated to deepening understanding of the initially proposed combustion mechanism, including kinetic factors and actual application of these compositions in blasting devices, such as igniters or fuses.

Author Contributions: Conceptualisation: A.S.; methodology: A.S. and T.J.; investigation: M.P. (Mateusz Polis), A.S., K.S., B.L., M.P. (Marcin Procek), S.S., T.G., Ł.H. and T.J.; data curation: M.P. (Mateusz Polis) and A.S.; writing—original draft: M.P. (Mateusz Polis), A.S., K.S., B.L., T.G., Ł.H. and T.J.; writing—review and editing: A.S. and T.J.; supervision: A.S. and T.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research was co-financed by the Ministry of Science and Higher Education of Poland under Grant No. DWD/4/21/2020—51/003. A.S. acknowledges the scientific and innovative merit grant, no. 04/040/RGJ24/0275, of the Rector of Silesian University of Technology. T.J. acknowledges the scientific and innovative merit, grant no. 04/040/RGJ24/0278, of the Rector of Silesian University of Technology.

Data Availability Statement: The data presented in this study are available upon request from the authors.

Acknowledgments: This work benefited from facilities and research infrastructure provided by the Department of Optoelectronics Silesian University of Technology, which receives support under project NLPQT—National Laboratory for Photonics and Quantum Technology, POIR.04.02.00-00-B003/18. M.P., A.S. and T.J. acknowledge the support of the M-ERA.NET 3 Room temperature hydrogen sensors based on polycarbazole and their derivatives, “HydroSens” project (no. 9150, M-ERA.NET3/2021/93/HYDROSENS/2022).

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Appendix A.1. Laser Sensitivity

Table A1. Ignition times for various radiation powers of tested compositions.

Composition	300 mW	250 mW	200 mW	150 mW
C3-1NC-1NTO	32.09 ± 2.36	42.55 ± 2.95	76.85 ± 12.80	222.46 ± 76.07
C3-1NC-3NTO	39.11 ± 3.65	68.70 ± 2.58	99.05 ± 15.00	233.44 ± 22.76
C3-1NC-5NTO	52.97 ± 3.40	68.22 ± 4.48	103.09 ± 12.03	232.68 ± 18.99
C3-1NC-10NTO	49.82 ± 2.19	71.66 ± 5.71	129.10 ± 3.36	311.18 ± 37.94

In each test, a 15 mg sample of tested composition was poured into a copper shell, which in turn was placed inside a positioning alumina ring. The distance between the sample surface and collimator was fixed at 250 mm; therefore, the radiation affected the sample on an area equal to 2.2 mm². All tests were repeated at least five times. Samples insensitive for given radiation power were exposed for 3 min (with three repeats) to confirm insensitivity.

Appendix A.2. SEM-EDS Tests

The following figures show the morphology of the combustion products of the analysed compositions. Taking into account the increase in the NTO composition content, a modification in the morphology of the analyzed materials is noticed. The ashes become more and more porous, formed of spherical, hemispherical and jagged multi-walled crystals. The images indicate that the sintering process occurred. In any case, the particles with irregular shape are significantly smaller than spherical and hemispherical particles. A complex structure is especially visible for the 3NTO composition and 5NTO composition. In many cases, crushed particles with irregular or spherical shapes are also visible.

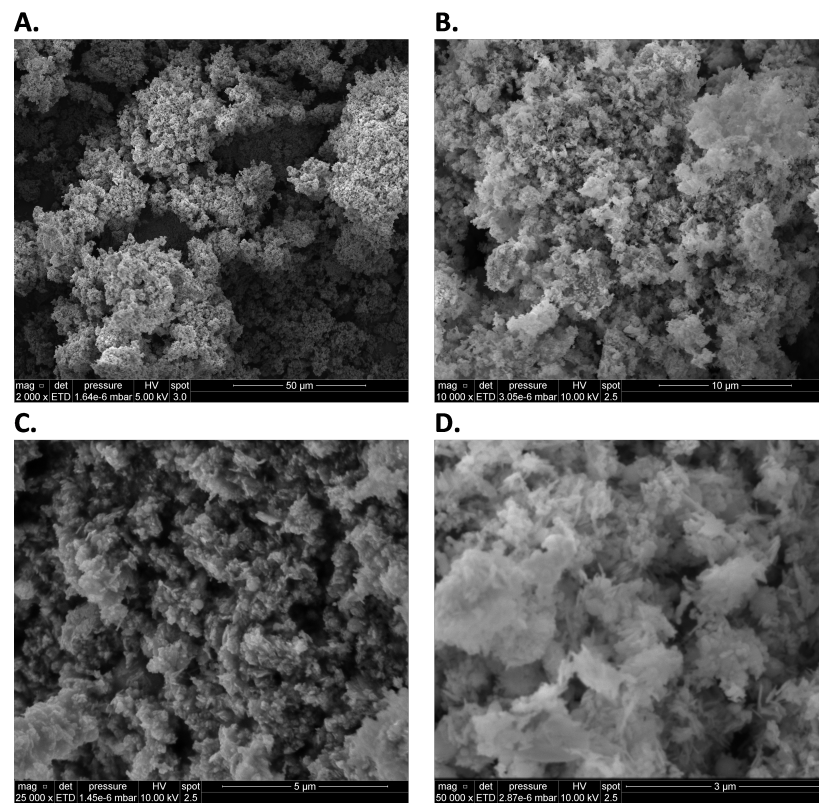


Figure A1. Result of SEM analysis for sample 1NTO with different magnification. (A) $\times 2000$; (B) $\times 10,000$; (C) $\times 25,000$; (D) $\times 50,000$.

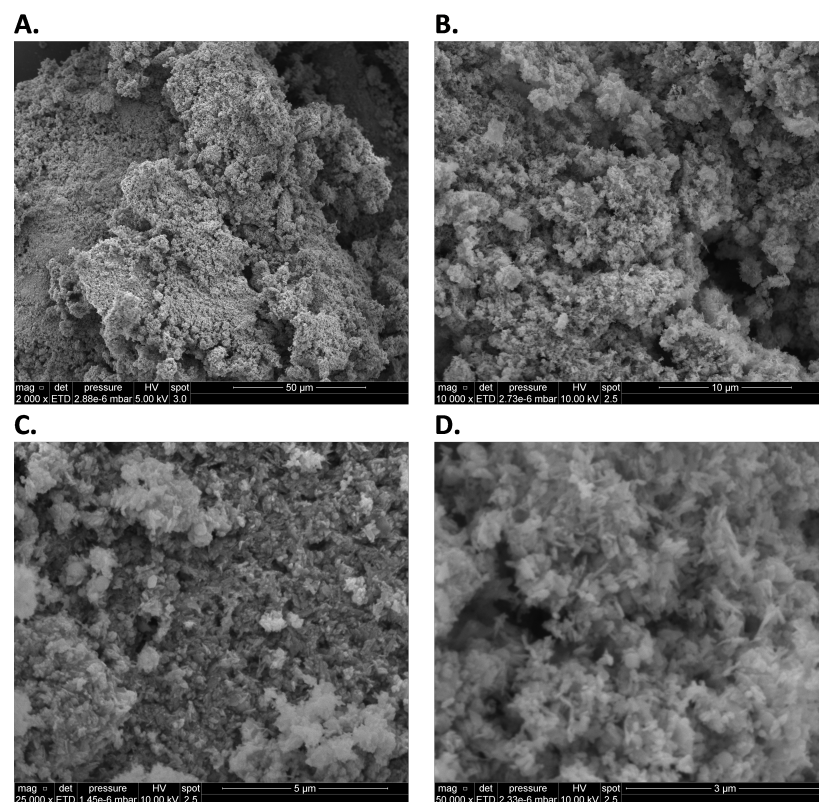


Figure A2. Result of SEM analysis for sample 3NTO with different magnification. (A) $\times 2000$; (B) $\times 10,000$; (C) $\times 25,000$; (D) $\times 50,000$.

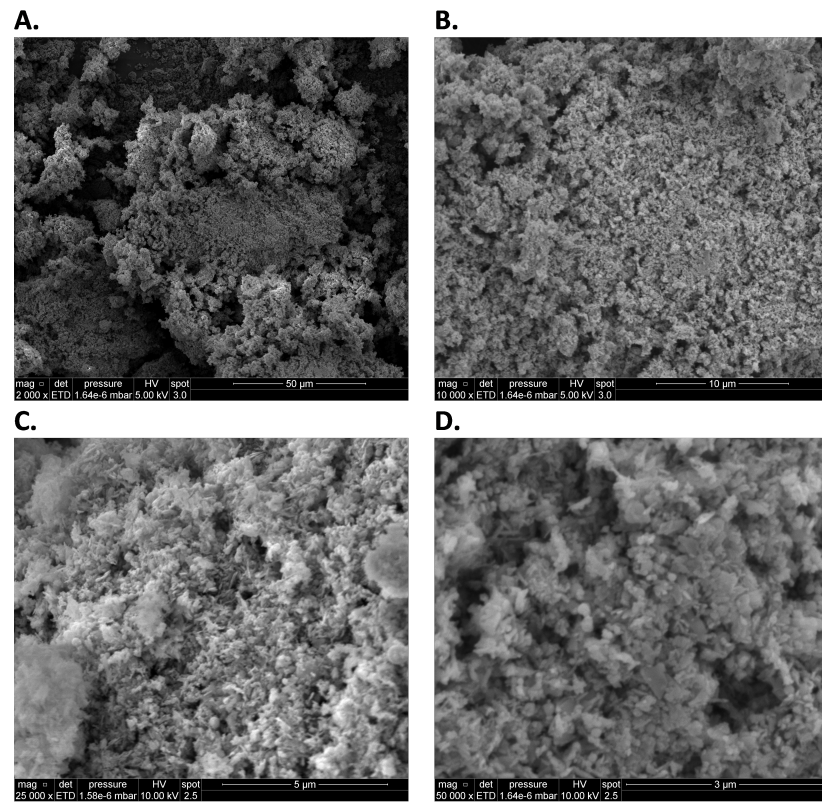


Figure A3. Result of SEM analysis for sample 5NTO with different magnification. (A) $\times 2000$; (B) $\times 10,000$; (C) $\times 25,000$; (D) $\times 50,000$.

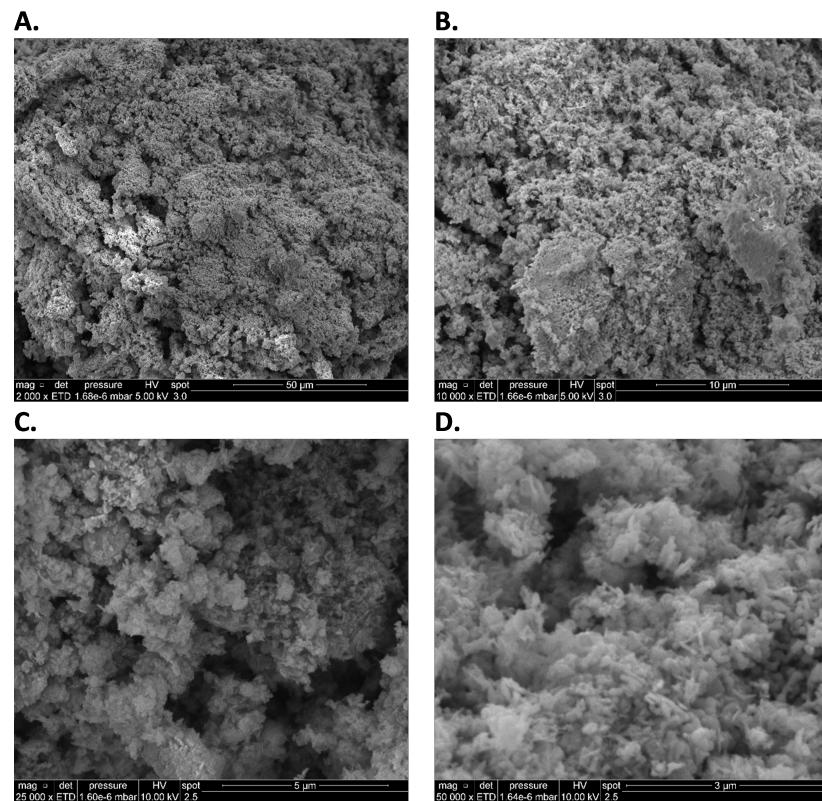


Figure A4. Result of SEM analysis for sample 10NTO with different magnification. (A) $\times 2000$; (B) $\times 10,000$; (C) $\times 25,000$; (D) $\times 50,000$.

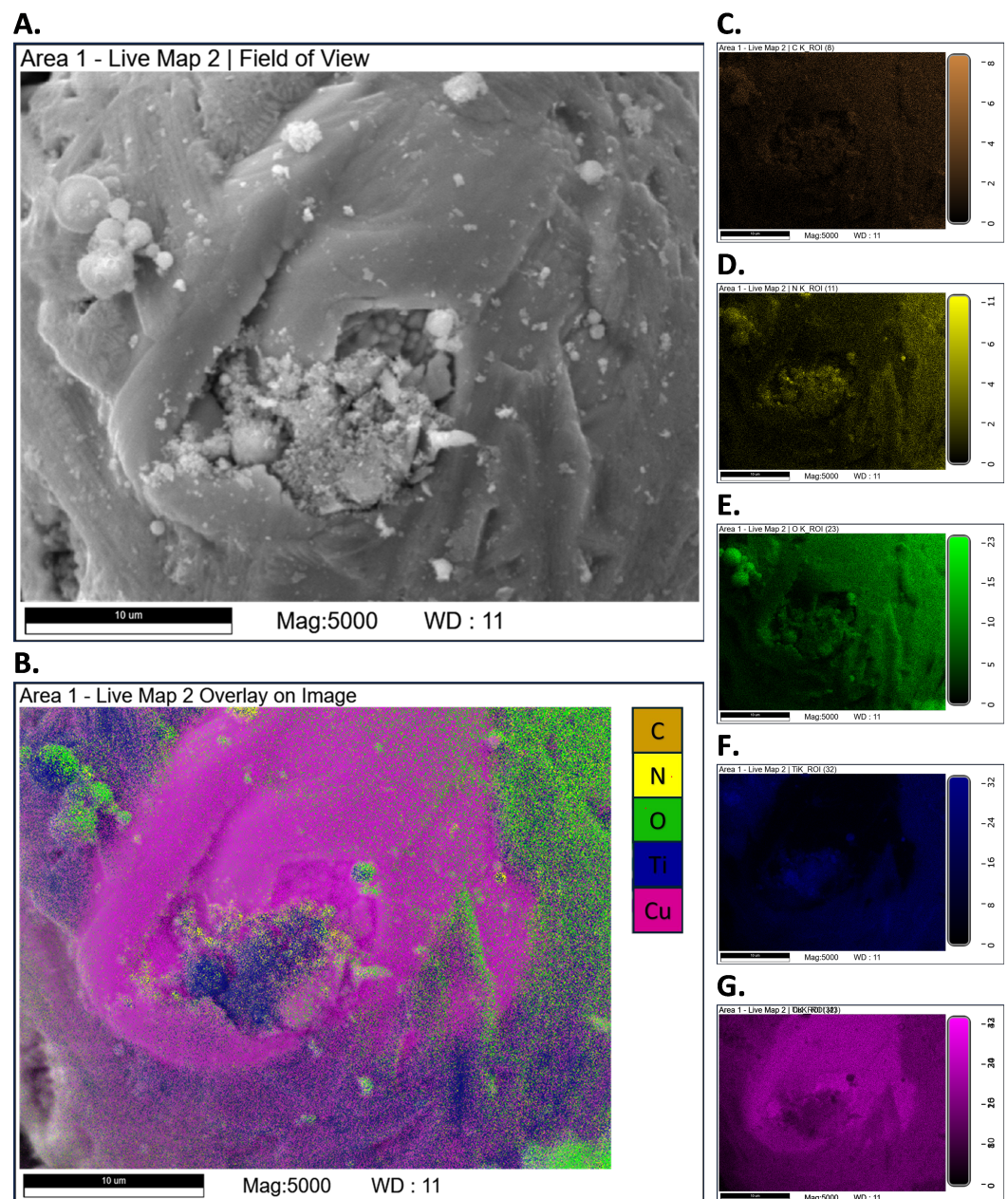


Figure A5. Result of SEM-EDS analysis for combustion products of sample 1NTO. (A) SEM picture; (B) EDS map; (C) EDS map for C; (D) EDS map for N; (E) EDS map for O; (F) EDS map for Ti; (G) EDS map for Cu.

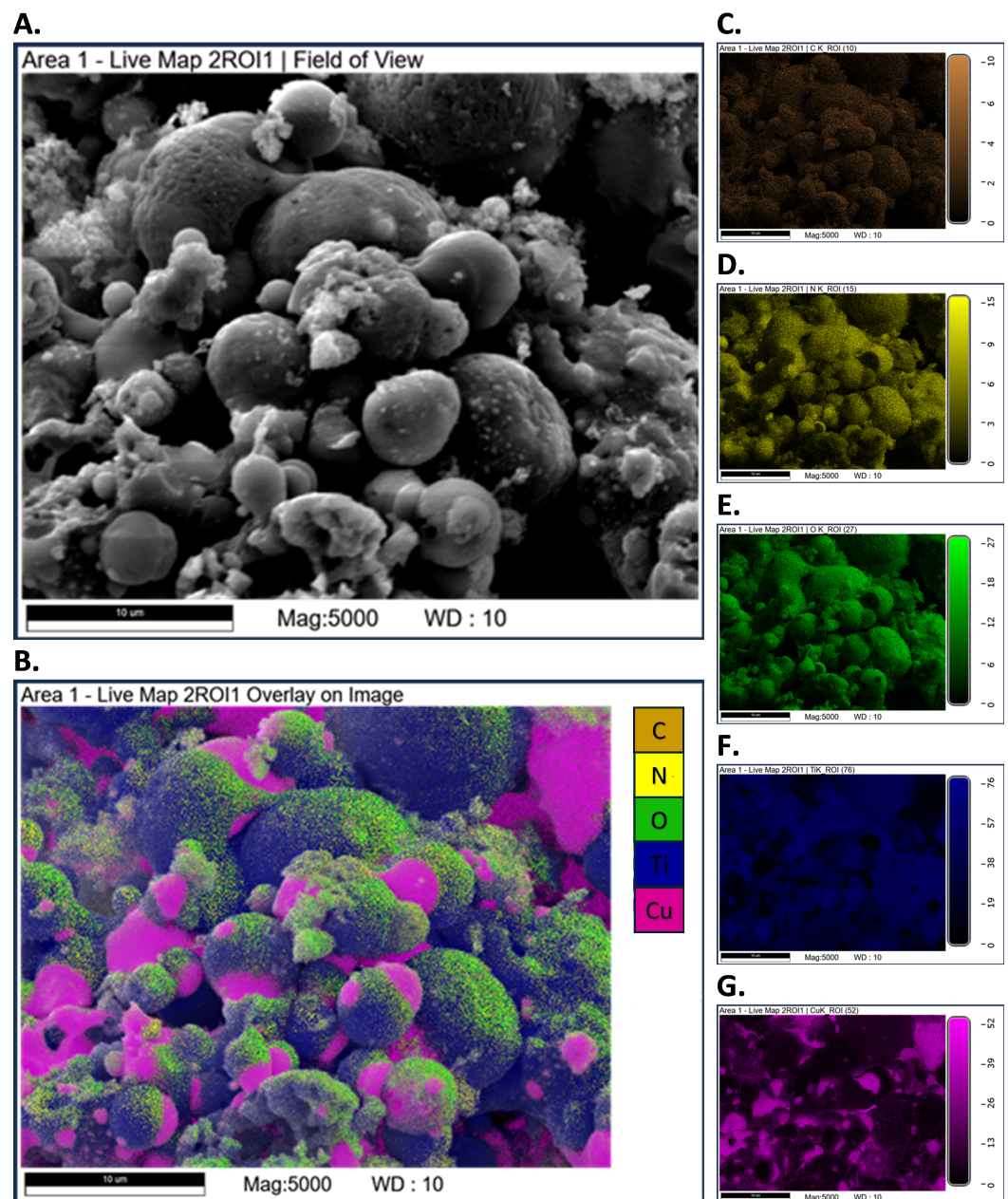


Figure A6. Result of SEM-EDS analysis for combustion products of sample 3NTO. (A) SEM picture; (B) EDS map; (C) EDS map for C; (D) EDS map for N; (E) EDS map for O; (F) EDS map for Ti; (G) EDS map for Cu.

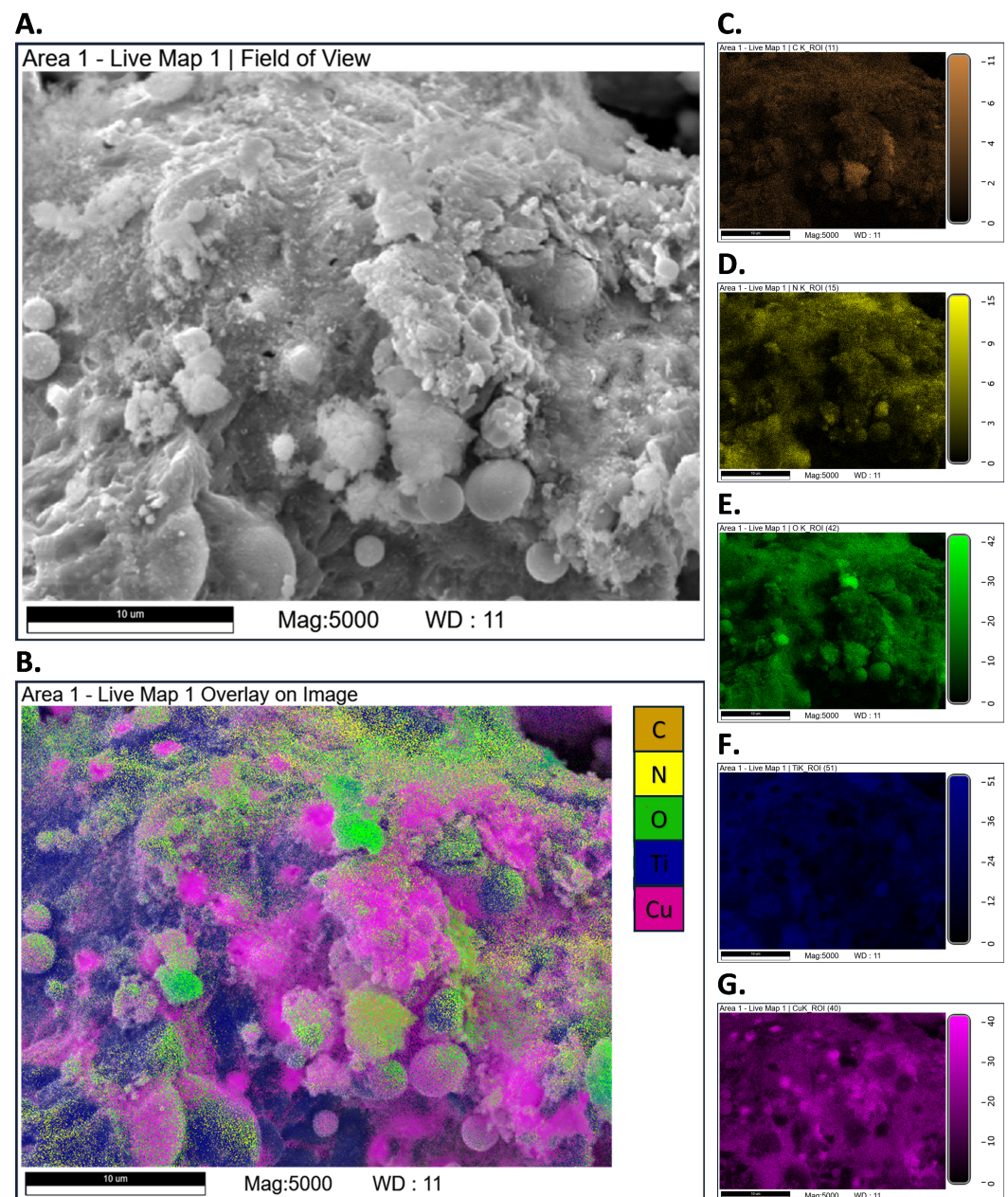


Figure A7. Result of SEM-EDS analysis for combustion products of sample 5NTO. (A) SEM picture; (B) EDS map; (C) EDS map for C; (D) EDS map for N; (E) EDS map for O; (F) EDS map for Ti; (G) EDS map for Cu.

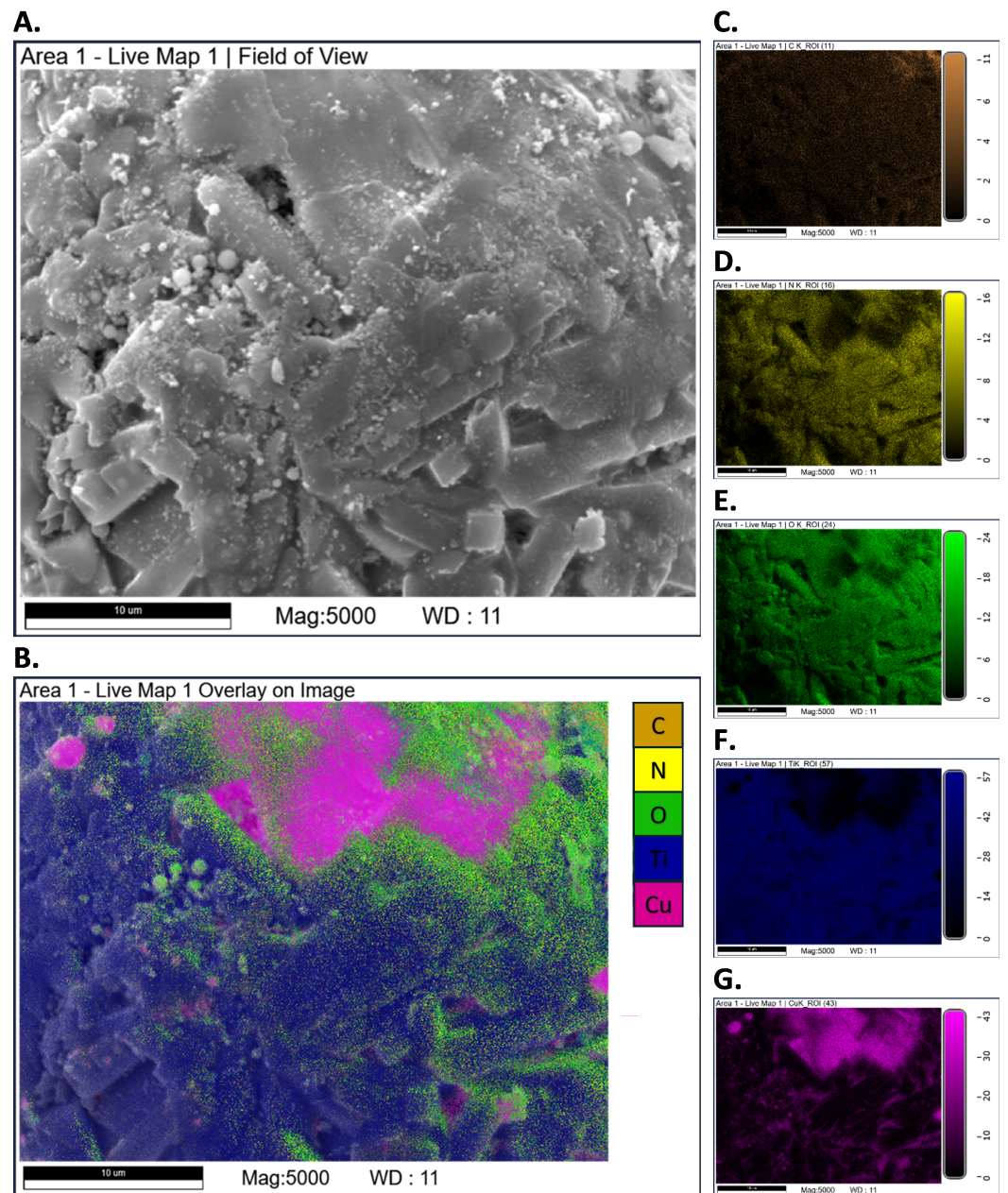


Figure A8. Result of SEM-EDS analysis for combustion products of sample 10NTO. (A) SEM picture; (B) EDS map; (C) EDS map for C; (D) EDS map for N; (E) EDS map for O; (F) EDS map for Ti; (G) EDS map for Cu.

Appendix A.3. Closed-Vessel Combustion

Table A2. Closed-vessel test results.

Composition	Combustion Time [ms]	$P_{\max}$ [kPa]	$\frac{dp}{dt}$ [$\frac{kPa}{s}$]
C3-1NTO	106.5 ± 9.32	271.1 ± 4.27	69.0 ± 15.08
C3-3NTO	64.2 ± 5.75	278.1 ± 7.47	92.6 ± 10.52
C3-5NTO	109.2 ± 9.31	406.7 ± 11.54	81.1 ± 14.54
C3-10NTO	118.2 ± 9.22	422.5 ± 10.23	77.13 ± 1.69

Appendix A.4. Thrust Force

The experimental set-up consisted of a force sensor (PCB Piezotronics 208C02) that was connected with massive steel support with a double-threaded bolt. With the threaded connector, the upper part of the sensor was connected with a cylindrical shell slot. In each case, 15 mg samples of NSTEX were poured inside a copper shell (4.93 mm inside diameter, 4.30 mm inside depth, 0.32 mm wall thickness). The copper shells, in next step, were placed inside a cavity in the shell slot and sealed with a cylindrical nozzle (4.93 mm inside diameter, 5.90 mm long). Directly over the sample, the optical collimator connected with a laser pulse generator was mounted, sheltered with a 2 mm PMMA plate placed between the nozzle and collimator. All samples were ignited via laser pulse, with a 520 nm laser, power of 700 mW, pulse time of 50 ms and spot diameter equal to 1 mm. The force sensor was connected with a PCB Piezotronics 480E09 signal conditioner and digital oscilloscope Tektronix TBS2401B, with 12.5 MS/s sampling. The tests were repeated five times for each composition.

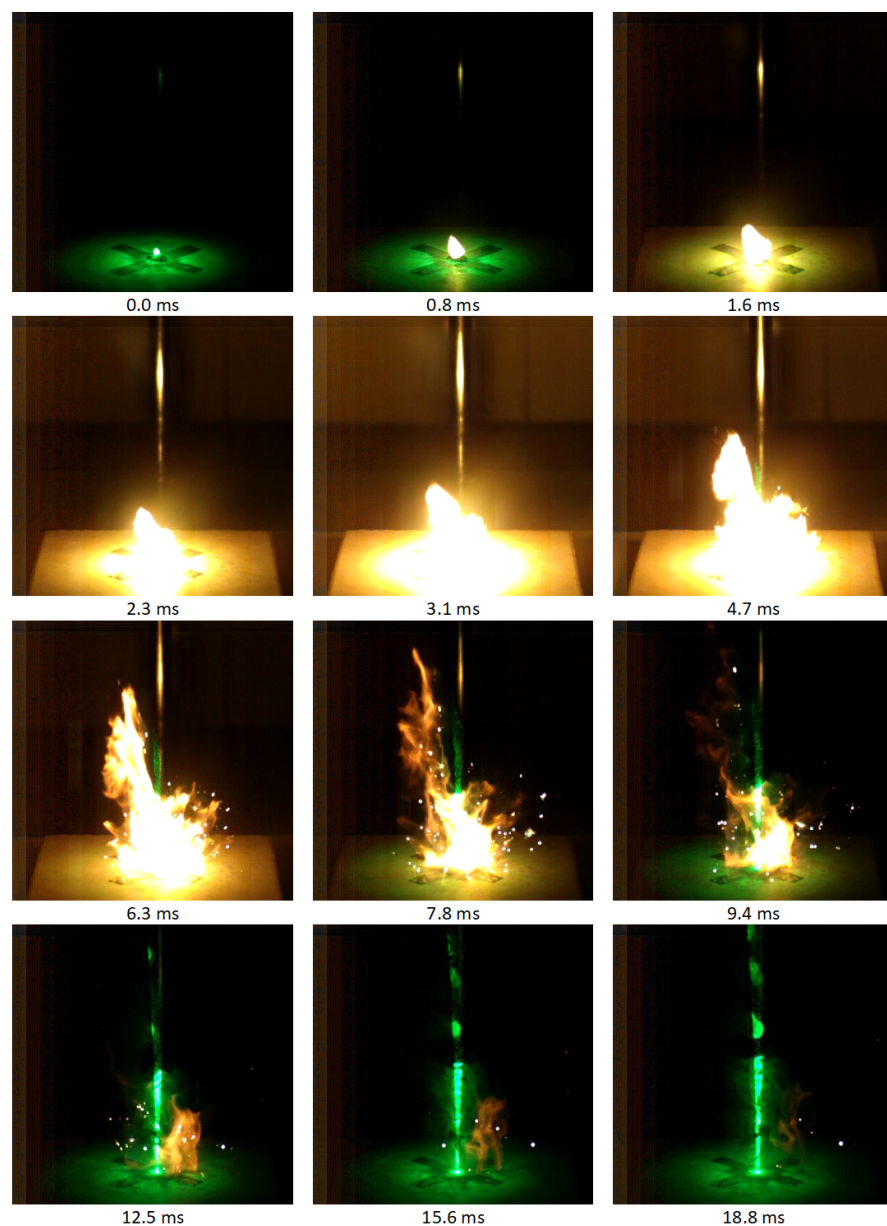
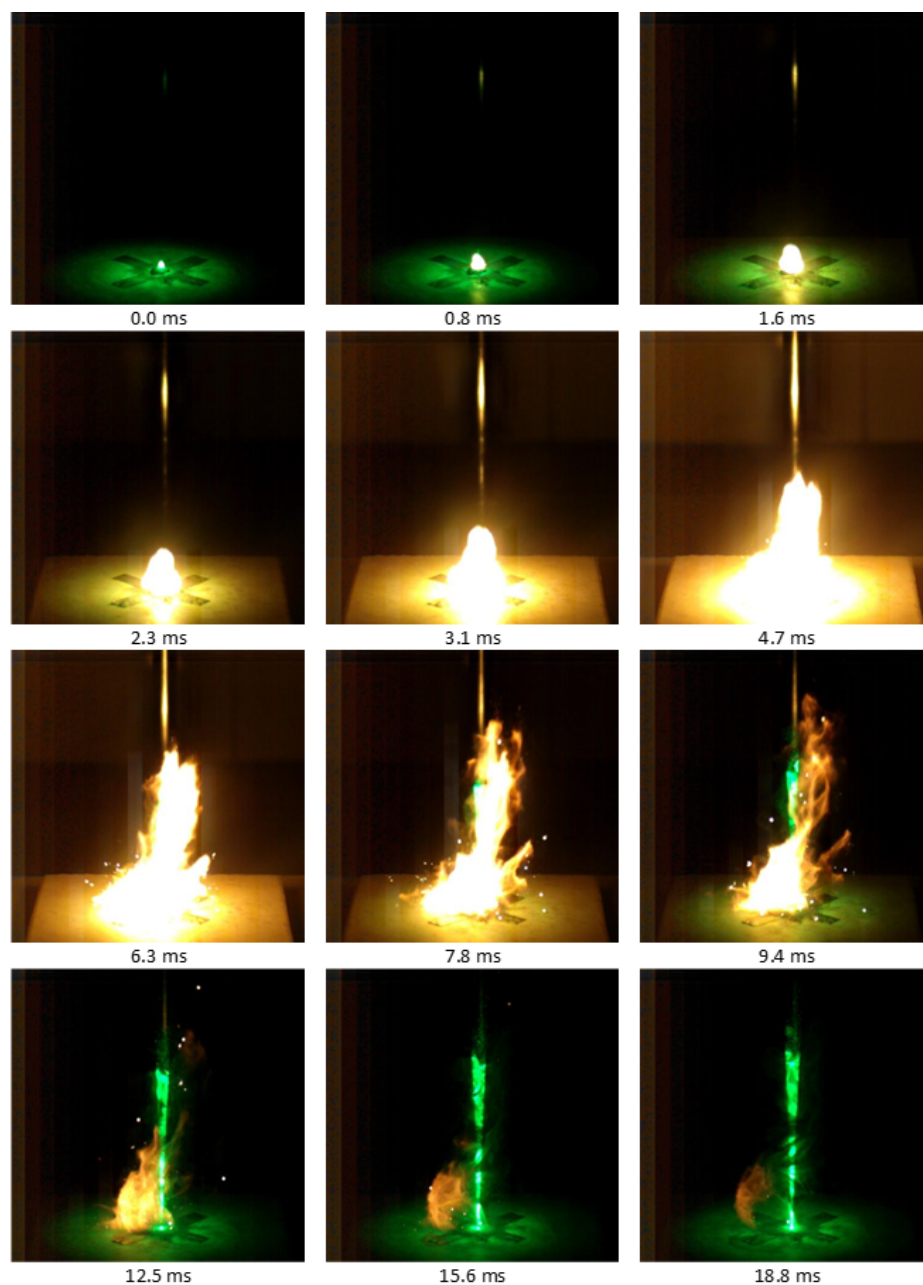


Figure A9. Snapshots from 1NTO composition combustion.

Table A3. Results of thrust force measurement.

Composition	$F_{\max}$ [mN]	Combustion Time [ms]	Total Impulse [s]
C3-1NC-1NTO	597.2 ± 76.3	3.31 ± 0.43	4.76 ± 0.27
C3-1NC-3NTO	769.2 ± 134.1	3.58 ± 0.27	5.77 ± 0.79
C3-1NC-5NTO	254.6 ± 26.9	5.52 ± 0.40	3.28 ± 0.51
C3-1NC-10NTO	163.8 ± 36.7	7.03 ± 1.74	3.06 ± 0.37

**Figure A10.** Snapshots from 3NTO composition combustion.

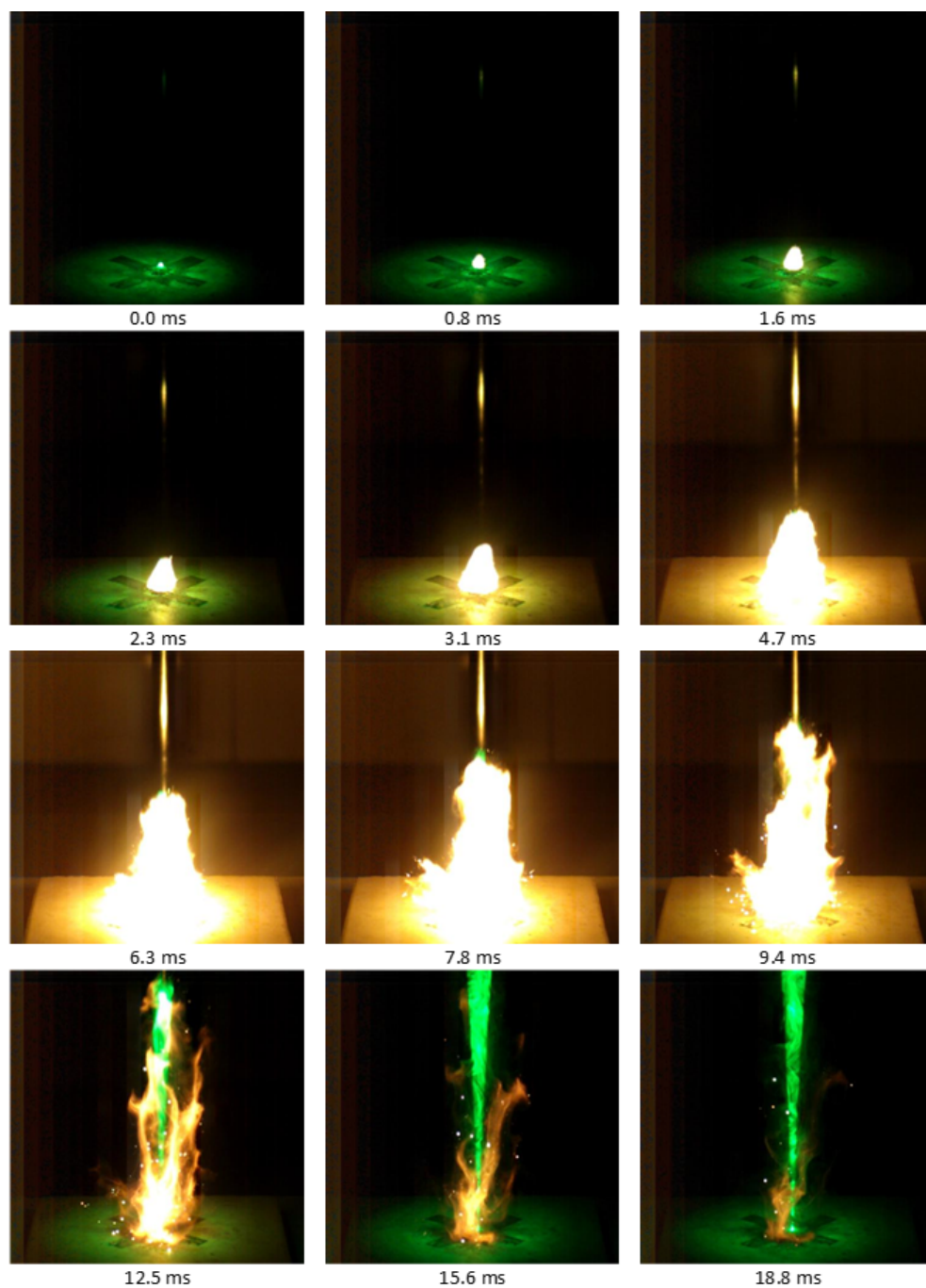


Figure A11. Snapshots from 5NTO composition combustion.

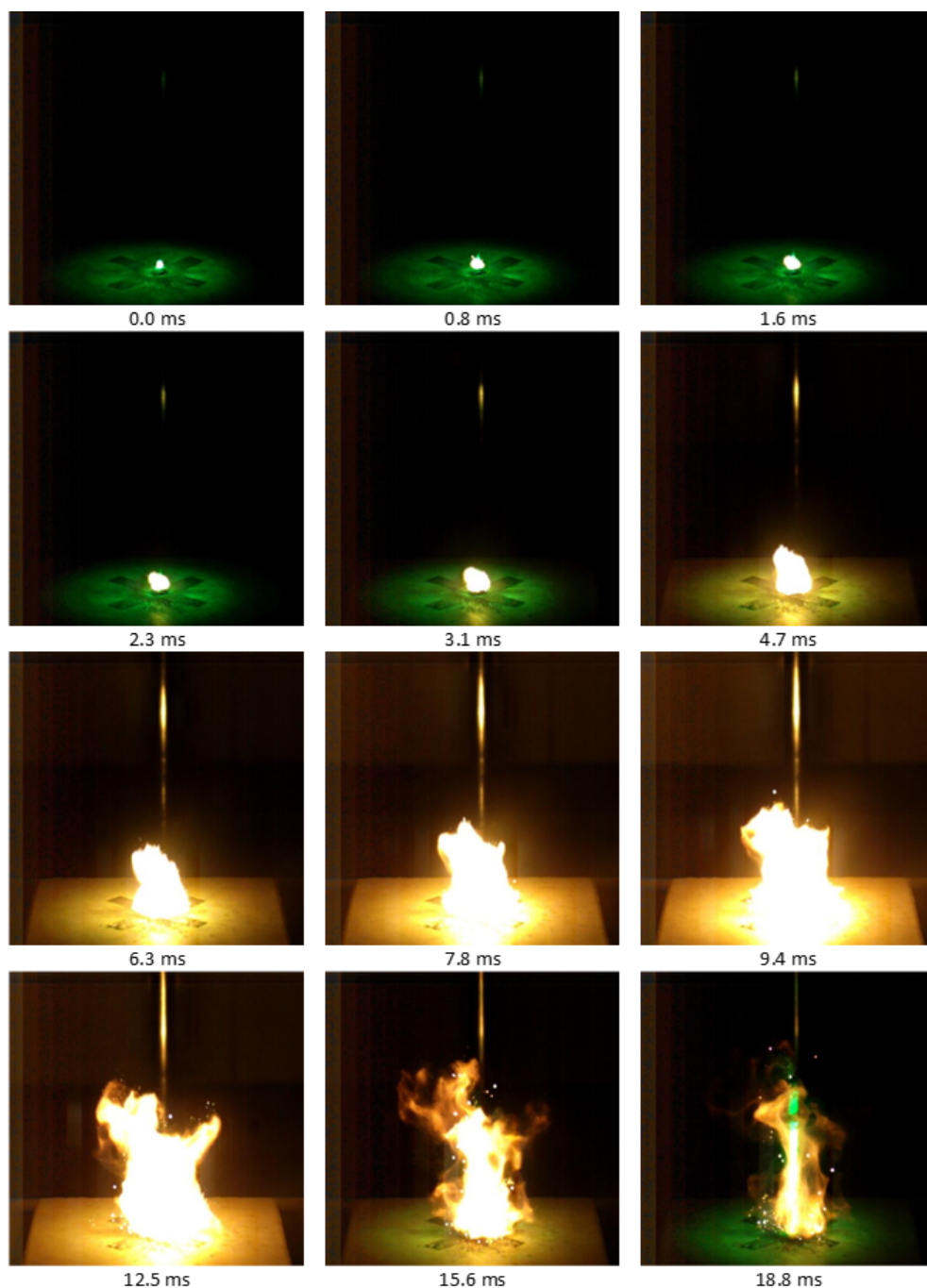


Figure A12. Snapshots from 10NTO composition combustion.

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