

Engineered Porosity-Induced Burn Rate Enhancement in Dense Al/CuO Nanothermites

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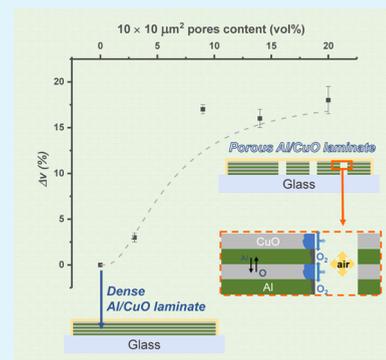
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ABSTRACT: This work investigates the combustion of porous Al/CuO thermites, that is, nanolaminates fabricated with various densities of micron-sized air-filled pores in the range of 0–20 vol %. High-speed videography and pyrometry of the high-temperature propagating flame were used to analyze the effect of porosity on propagation velocity. Incorporating micron-sized pores in Al/CuO nanolaminates results in a faster burn rate (burn rate enhancement of 18% for a pore loading of 20 vol %) while the flame temperature remains the same. Microscopic observations of the flame front in porous nanolaminates show hotspots around each pore upstream of the flame but no advection. Conduction remains the dominant heat transfer mechanism in dense thermite configuration (80% theoretical maximum density) and the causes of burn rate enhancement when pores are embedded into the nanolaminate are found to be the convection of the trapped air inside the pores upon heating together with a possible modification of the reaction chemistry leading to a lowering of the ignition threshold of the thermite around each micron-sized pores. Indeed, this hot gaseous O_2 species trapped into the pores diffuse and react with solid Al on the inner wall of the pores to form Al_2O_3 . This gas-phase mediated reaction mechanism in the pores occurs at a lower temperature than the diffusion-based mechanism of the aluminum cations and oxide anions across the alumina shell as in fully dense Al/CuO nanolaminates. The critical size of the pores beyond which their beneficial effect disappears is difficult to estimate, but this study showed that $100 \times 100 \mu m^2$ pores have almost no effect on the combustion with an average burn rate increase of only $\sim 4\%$ compared to the fully dense nanolaminate part.

KEYWORDS: nanothermites, porous nanolaminate, Al/CuO, combustion, flame propagation, heat transfer, advection, convection



1. INTRODUCTION

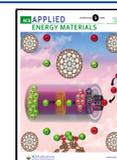
Since the 1990s, progress in nanomanufacturing¹ has led to a new class of solid energetic materials commonly referred to as nanoscale composite energetic materials or simply nano-energetics. These materials include nanothermites composed of nanosized metals (Al, Mg, Ti, and B) and metal oxides (CuO, Fe_2O_3 , Bi_2O_3 , MoO_3 , etc.), which both participate in a highly exothermic and self-propagating redox reaction.^{2,3} Much research in nanothermites has focused on the Al/CuO systems due to their high energy density,^{4,5} and because they allow fabricating thermite systems with varying shapes/geometries, that is, multilayered,^{6,7} core/shell,^{8,9} 3D assembled particles,^{10,11} and 3D porous nanostructures.¹² It has been observed that the formulation and deposition method greatly affect the energy transfer mechanisms and combustion behavior, which depend on several factors, such as reactant intimacy, material confinement, and gas generation. This performance tunability in addition to the high energy density makes nanothermites promising for joining or welding¹³ tunable generators of biocidal-agents,^{14,15} actuation in initiators/detonators,^{16,17} and in single-use miniaturized microelectromechanical systems^{18–21} such as microthrusters.^{22,23}

Despite the over 3 decades of experimental and theoretical research in the field of nanothermites, relatively little is known about the energy transfer mechanisms governing the self-propagation of the reaction front. They depend on several factors such as the gas products generated; the heat transfer mechanisms, that is, conduction (transport of heat within the material itself), convection (transfer of heat by the physical movement of hot masses of gas), and advection (physical movement of solid or molten aggregates); and the activation energies of the reactive components and material confinement. In confined environments and in low-density thermite configurations [powder with compaction $< 50\%$ of the theoretical maximum density (TMD)], convection of hot gases and ballistic advection of condensed phase aggregates^{24,25} are the dominant heat transfer mechanisms during flame

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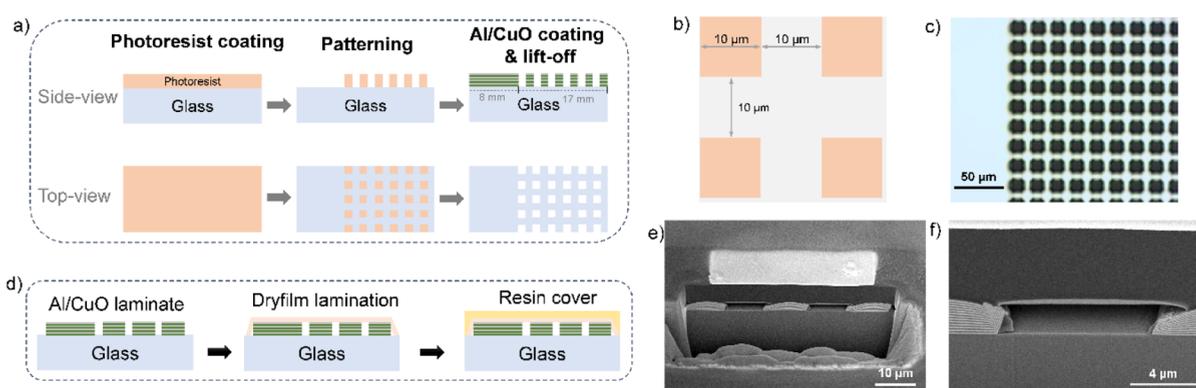


Figure 1. (a) Schematic of the process developed to obtain air cavities (pores) within Al/CuO sputter-deposited nanolaminates; (b) zoom of the photolithography mask pattern used to obtain 20% porosity; (c) optical top view image of an Al/CuO nanolaminate with 20% porosity; (d) schematic of the encapsulation process to obtain the porous laminates, that is sealed with a dry epoxy film and covered with a resin layer; (e, f) SEM cross-section images of a sealed Al/CuO nanolaminate with 20% porosity.

propagation, whereas pure conduction (or normal deflagration) prevails at higher densities. This was supported by experimental findings showing that loosely packed nanothermite powders propagate from ~ 100 m/s to $\sim \text{km/s}$ ^{26–29} against $\sim \text{cm/s}$ to $\sim \text{m/s}$ for fully dense laminated nanothermites.³⁰ No data is yet available on heat transfer mechanisms governing the self-propagation of dense thermite configurations, that is, powder with compaction $>75\%$ TMD, due to technical impossibility to obtain nanopowders at that compaction rate.

The objective of this paper is both to examine the effect of porosity on the combustion in high-density thermite configurations ($>75\%$ TMD), and to elucidate which of the heat transfer mechanisms among conduction, convection, and advection is dominant in such configurations. For that purpose, controlled porosity, that is, a controlled quantity of air-filled pores, $10 \times 10 \mu\text{m}^2$ in size, are embedded into fully dense Al/CuO nanolaminates through a simple photolithography approach. The self-propagation of the reaction front in such prepared materials containing various fractions of pores in the range of 0–20 vol %, is observed at the macro and microscale and compared with fully dense nanolaminates. It is found that a small fraction (~ 20 vol %) of $10 \times 10 \mu\text{m}^2$ pores within the nanolaminate accelerates the burn rate by $\sim 18\%$. Operando microscopic observations of the confined burning flame front show the formation of hotter zones (hotspots) in and around the pores, whereas no advection is observed through them. Therefore, the formation of hotspots in the upfront is supposed to be a result of two mechanisms: (1) the convection of the heated air trapped inside the pores enhancing the heat transfer to unreacted nearby material; (2) the interaction of diffused free-molecular oxygen species from the trapped air with solid Al on the inner wall of the pores to form Al_2O_3 . This gas-phase reaction pathway is kinetically more favorable than the purely condensed phase reaction mechanism occurring at the Al/CuO interface in fully-dense thermite systems.³¹ This study also outlines that the beneficial effect of air-filled pores is greatly reduced when increasing the pore size up to $100 \times 100 \mu\text{m}^2$ as the mass of trapped air in the pore becomes too large to be heated at a sufficient temperature to establish convection.

2. MATERIALS AND METHODS

2.1. Porous Nanolaminate Sample Fabrication. Lines of nanolaminates with dimensions of ~ 30 mm (length) \times 4 mm (width) were sputter deposited onto a ~ 31.75 mm (length) \times 17.75 mm (width) \times 500 μm (thick) glass slide (Figure S1). Titanium

filaments were patterned at both nanolaminate ends, underneath the nanolaminate line, to resistively heat the multilayer to ignition (Figure S1). The nanolaminates used in this work consist of 13 Al/CuO bilayers deposited using a direct current (DC) magnetron-sputtering system from Thin Film Equipment (Italy). Al and CuO were sputtered from Al and Cu targets (8 by 3 inch square sides and 1/4 inches thick) using a base pressure of 5×10^{-7} mbar. O_2 and Ar gas flow rates of 16 and 32 cm^3/min were used for CuO deposition with a partial pressure of 10^{-2} mbar. The Ar partial pressure during Al deposition was maintained at 5×10^{-3} mbar. The sample was cooled at ambient temperature for 600 s at the end of the deposition process. The percentage of porosity added into the fully dense Al/CuO nanolaminate was controlled by varying the volume loadings of $10 \times 10 \mu\text{m}^2$ cavities into the material, as depicted in Figure 1a–c. As the first step, a negative photoresist (NLOF2070, MicroChemicals, 20 μm) was spin coated onto the glass wafer to obtain a 10 μm thick NLOF layer. This photoresist layer was soft baked at 110 $^\circ\text{C}$ for 2.5 min and cooled down to room temperature. The photoresist layer was then patterned by exposing it to UV light (A6 Gen4 SUSS MicroTec, 360 mJ/cm^2) through a contact mask defining the porosity patterns. After a post-bake at 125 $^\circ\text{C}$ for 3 min, the pattern was then transferred to the photoresist layer by developing the exposed photoresist using an MF-CD-26 developer for 130 s, followed by rinsing in deionized water and drying under N_2 . Then, the Al/CuO nanolaminate was sputter-deposited. To remove the photoresist pillars and reveal the pore, the sample was put into an acetone bath for 3 h followed by another 10 min of sonication. After this step, we end up with Al/CuO nanolaminates embedding open cavities as shown in Figure 1c. The next steps consist in the hermetic sealing of the air into the cavities to produce close pores. A 5 μm thick dry film (DF 1005, SU8 epoxy-based photoresist) was laminated onto the Al/CuO nanolaminate by a laminator (Shipley 3024) with a rolling speed of 1 $\text{m}\cdot\text{s}^{-1}$, a rolling pressure of 2.5 bars, and a temperature of 90 $^\circ\text{C}$. Then the DF coated nanolaminate was exposed to UV light and followed by development to remove the extra DF part on the chip in order to expose the ignition contacts. Then the DF-sealed Al/CuO nanolaminate was covered with a layer of resin (Pack resin MA2+, PRESI, France) (Figure 1d). Scanning electron microscopy (SEM) cross-sections of the sealed Al/CuO nanolaminate with 20% porosity are shown in Figure 1e, f showing the cavities sealed by the DF and resin covers. The dimensions of the pores are measured to be $9 \times 9 \mu\text{m}^2$ instead of $10 \times 10 \mu\text{m}^2$. Four porosity configurations are considered in this study: 3, 9, 14, and 20% loading (Table S1). For comparison purposes, required for results analysis, an additional set of samples was prepared in which the dimension of the pores was increased to $100 \times 100 \mu\text{m}^2$ keeping the fraction at 20%. If not specified, the Al/CuO bilayer thickness is set at 300 nm with an Al to CuO equivalence ratio of 2:1 (fuel-rich configuration), that is, Al and CuO thicknesses of 150 nm.

It has to be noted that, for all samples, the first third of the nanolaminate length, 10 mm long, does not contain pores and allows for

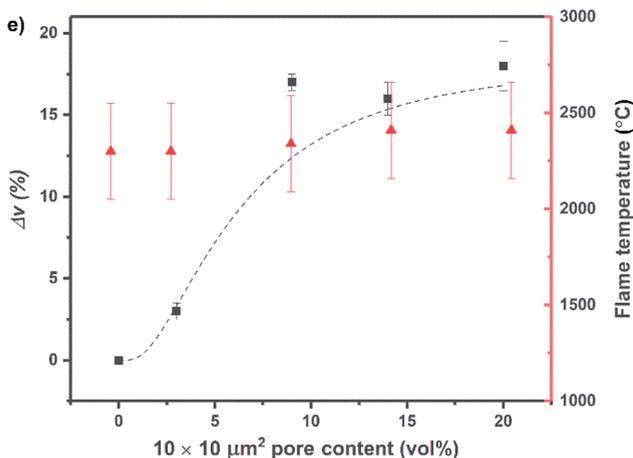
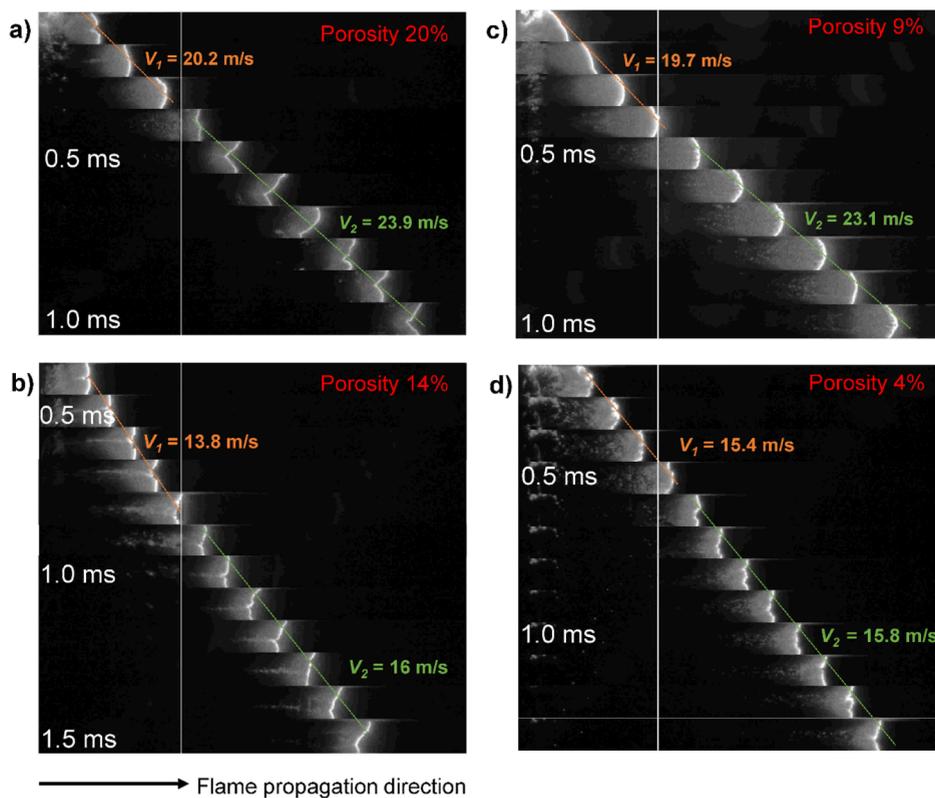


Figure 2. High-speed images of the propagating flame front for Al/CuO nanolaminates with (a) 20, (b) 14, (c) 9, and (d) 4% porosity; (e) corresponding percentage of propagation speed changes and flame temperatures. Al to CuO equivalent ratio is 2:1. White vertical lines on the video images delimit the fully dense (left-side) to porous part (right side).

the measurement of a reference burn rate (i.e., a fully dense Al/CuO nanolaminate average burn rate). The other two-thirds (20 mm) of the nanolaminate length contains pores and thus constitutes the porous part.

2.2. Characterizations. **2.2.1. Material Observations.** The structures and compositions of the Al/CuO laminates as well as the reaction products were characterized by SEM (FEI Helios 600i Nanolab), coupled with energy-dispersive X-ray spectroscopy (EDX). The post-product was characterized by SEM (Hitachi, S-4800) and EDX. The particles sizes were measured by ImageJ over 50 particles on several SEM images. The working distance is 8 mm, with an in-lens SE/BSE detector (TLD) and an accelerating voltage of 5 kV.

2.2.2. Macro-Scale Combustion Tests. To evaluate the flame propagation speed of the Al/CuO nanolaminates, referred to as the average burn rate, the prepared samples were imaged with a high-speed

camera (25 cm) (Phantom VEO710L-18GB-M, USA) at 94,000 frames/s. Around six burn rate experiments were carried out per sample configuration and all experiments were performed in a constant-pressure air atmosphere. An average burn rate was then calculated by tracking the distance traveled by the reaction front as a function of time by Phantom Camera Control software (6 positions in the flame front were used for each burn rate experiment and then an average value was obtained). Furthermore, for each sample configuration, two average burn rates were calculated: v_1 and v_2 , in the fully dense part and in the porous part of the nanolaminate, respectively. Then, the flame propagation speed percentage deviation (Δv) is deduced using eq 1.

$$\Delta v(\%) = \frac{v_2 - v_1}{v_1} \times 100 \quad (1)$$

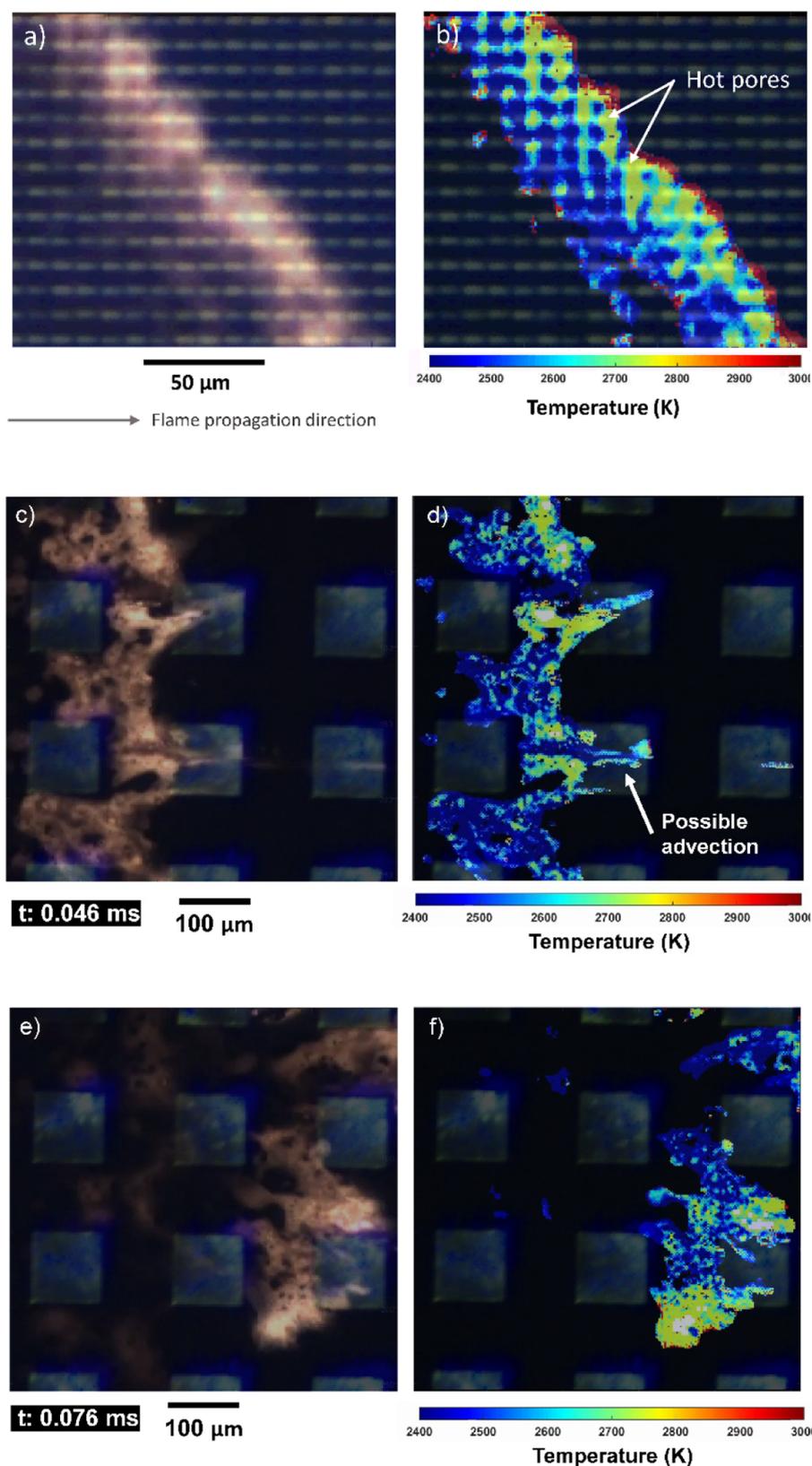


Figure 3. Microscopic imaging of the propagating flame front for Al/CuO nanolaminates with (a,b) 20 vol % of $10 \times 10 \mu\text{m}^2$ pores and (c–f) 20 vol % of $100 \times 100 \mu\text{m}^2$ pores; zoomed-in images of two $100 \times 100 \mu\text{m}^2$ air-filled pores where (c,d) some advection is visible and (e,f) without advection. The Al to CuO equivalent ratio is 2:1.

2.2.3. High-Speed Microscopy/Pyrometry. The details of the flame front propagation of the Al/CuO nanolaminates were observed in operando using a high-speed microscopic imaging system. Detailed

information can be found in previous studies.^{32–34} In short, a high-speed camera (Vision Research Phantom VEO710L, USA) coupled with a long-distance microscope (Infinity Photo-Optical model K2

DistaMax, USA) provides a pixel/distance ratio of $2.2 \mu\text{m}/\text{pixel}$ to observe the flame front propagation (77,000 frames/s). The high-speed microscope apparatus has also been calibrated with a blackbody source for color pyrometry to estimate the temperature of the reaction. The detailed information about the color ratio pyrometry could be found in the previous study.³⁴ The temperature uncertainty is estimated to be 200–300 K.

3. RESULTS AND DISCUSSION

3.1. Enhanced Average Burn Rate of Porous Al/CuO Laminates. The flame propagation of Al/CuO nanolaminates with various pore fractions (3, 9, 14, and 20%) was investigated by high-speed videography. Steady-state propagation is achieved within ~ 3 mm of the nanolaminate length. Figure 2a–d shows the typical time-resolved snapshots of their propagation in both the fully dense reference and the porous fraction; to be noted is that the burn rates were not determined from those frames (see Section 2.2 for details). Importantly, for all four laminates regardless of their pore content, the porous material burns slightly faster than the fully dense reference one. The samples with 20% porosity burn at an average rate of $\sim 23.9 \pm 2.0 \text{ m}\cdot\text{s}^{-1}$, which corresponds to a $\sim 18\%$ increase compared with the reference ($\sim 20.2 \pm 1.8 \text{ m}\cdot\text{s}^{-1}$). However, the flame temperature is measured at ~ 2410 °C in the porous part, that is, similar to that of the fully dense Al/CuO case (~ 2300 °C). The propagation speed variation versus pore content is plotted in Figure 2e: an increase of pore content from 3 to 9% causes the burn rate change to rapidly rise from ~ 3 to $\sim 17\%$, before plateauing at $\sim 20\%$ pore content. Importantly, the snapshots show that the reaction front, approximately $200 \mu\text{m}$ thick for all samples, becomes corrugated when entering into the porous side of the sample. The front generally adopts an “L” or “V” shape, with the front edges pointing to the flame front. The corrugation, which is defined by the ratio of the total geometrical length of the flame to the width of the sample in the direction perpendicular to propagation, increases with the pore content from 1.2 to 2. Corrugation is meant to characterize the degree of roughness of the flame front. Similar to what was reported in ref 34, we observe that corrugation goes with an increase in the average burn rate. Considering that the flame propagation behavior, that is, its corrugation, is dependent on how fast energy is generated (kinetics of the reaction) and how fast that released energy can be transferred to the unreacted area (heat transfer mode), the corrugation of the flame front obtained on porous nanolaminates is the consequence of either a lowering of the ignition threshold by the presence of free molecular oxygen in the pores or an enhancement of heat transfer through the pores by advection and/or convection; indeed, we can imagine that the heat would be transferred through the air-filled cavities by the movement of condensed phase aggregates traveling through the cavities and/or the air trapped inside the pores, thus preheating or initiating the upfront (side and opposite sidewalls of microcavities) faster than the thermal wave by conduction. To probe if advection/convection occurs during combustion in porous nanolaminates, we now turn our attention to a microscopic view of the flame front with a resolution of $\sim 2.2 \mu\text{m}/\text{pixel}$.

3.2. Microscopic Imaging of the Flame Front with Pyrometry. The propagating flame front in the porous region was observed around the air-filled cavities using a much higher spatial ($\sim 2.2 \mu\text{m}/\text{pixel}$) and temporal (μs) resolution coupled with pyrometry. Figure 3a,b, the snapshots obtained from samples with 20% porosity, confirm that the front is corrugated

when entering into the porous region and the temperature is confirmed at 2410 °C. The shape of the confined flame front in Figure 3b shows that the whole pores are hotter (~ 500 °C) than the surrounding fully dense Al/CuO, which implies the air trapped inside the pores in the flame front are heated and convection of hot air could play a role in propagation. However, high-speed microscopy images do not allow distinguishing advection of particles of burning matter flying away through the cavities. Because the size of the pores is near the limit of our optical resolution, and the propagation is so fast that we could only obtain 1–3 frames, which is insufficient to accurately capture any advection events. We therefore produce nanolaminates with pores size $100\times$ larger, that is, $100 \times 100 \mu\text{m}^2$ keeping the same volume fraction (20%), and probe the flame front propagating around the air-filled pores.

Images in Figure 3c,d show that some advection does appear in only a few large pores ($\sim 20\%$). Figure 3e,f further indicates that the flame preferably propagates through the dense thermite without advection. However, interestingly the pores are not hotter than the Al/CuO bulk as observed in samples with $10 \times 10 \mu\text{m}^2$ pores (Figure 3b) and the average burn rate of porous nanolaminates with embedded $100 \times 100 \mu\text{m}^2$ pores does not increase much compare with the reference material (only 4% increment). Results thus suggest that the influence of advection on the flame propagation in this material is negligible.

In the absence of advection, hot-zones around $10 \times 10 \mu\text{m}^2$ pores seen on microscopic observations of the flame front that may indicate faster burn rate would result from 2 joint effects: (1) the establishment of convection of the trapped air (and possibly gaseous copper because its boiling point is in the order of the flame temperature) inside the pores, thus improving the heat and mass transfer to unreacted laminate nearby; (2) a modification of the redox reaction pathway lowering the ignition threshold at the pore edges. Note that the “hot” air trapped inside the pores is a strong oxidizer and thus will react with exposed Al following a gas-phase or gas-surface exothermal reaction mechanism. In the literature³¹ upon investigating arrested reactive milled Al/CuO nanocomposites containing nanovoids, the authors showed that incorporation of micron-sized pores into dense Al/CuO thermites lowers the ignition threshold compared to a fully dense composite. The authors conjectured that gaseous O_2 species diffuse through the pores and react readily upon adsorbing to the exposed Al or Al_2O_3 . Importantly, this work highlighted that the reaction scenario of the free molecular O_2 reaction with exposed solid Al or Al_2O_3 leading to the formation of Al_2O_3 and Cu is more thermodynamically favored compared to the purely condensed phase mechanism dominating the reaction at the interfaces of Al and CuO³⁵ as in a fully dense Al/CuO laminates.^{4,6,36,37}

Observations differ in porous laminates embedding $100 \times 100 \mu\text{m}^2$ pores (Figure 3e,f): convection failed to establish in the pores as they remain at the same temperature as the bulk Al/CuO. The energy delivered by the burning reaction front is insufficient to heat up the trapped air mass (increased by $\times 10$ compared to small pores) over 650 K. In addition, the large pores feature larger inert surface areas (top resin and bottom glass covers); therefore, the heat loss for each individual pore is more significant than the smaller pores. However, the burn rate of porous laminates with large pores (20 vol %) is enhanced by 4% compared to bulk Al/CuO: this increment may be the contribution of the lowering of the ignition threshold at the pore edges due to the presence of a gaseous oxidizer.

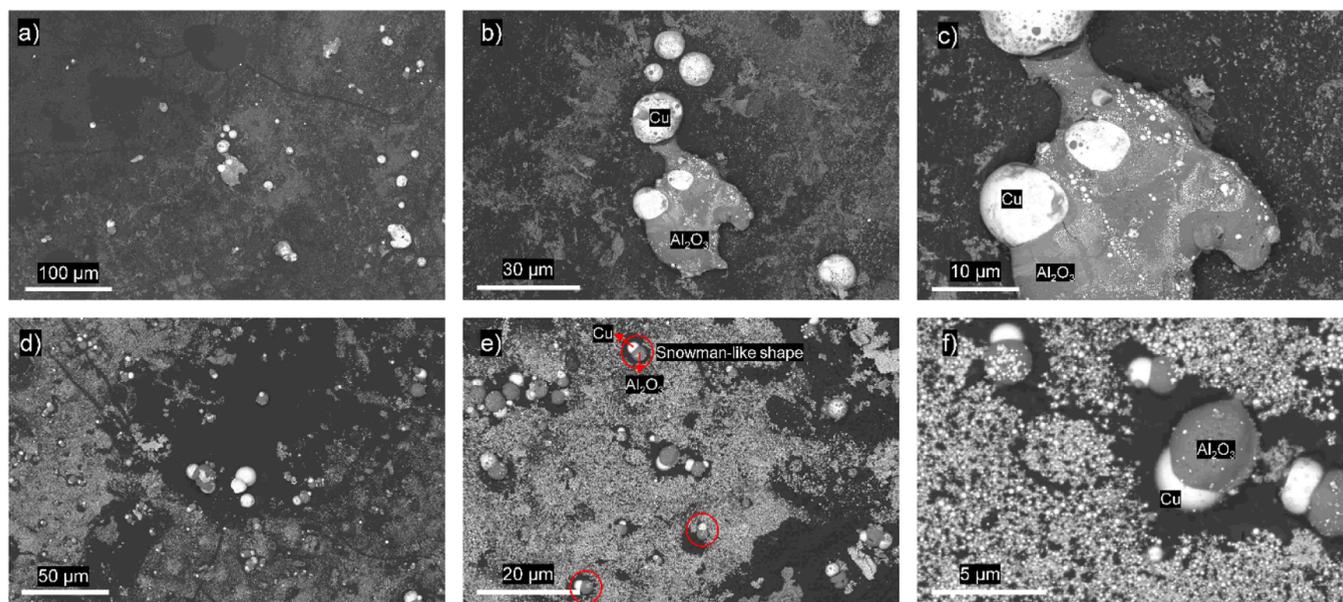


Figure 4. SEM images of combustion residues collected after the combustion of (a–c) 1:1 Al/CuO nanolaminate with 20% air-filled porosity, (d–f) fully dense 1:1 nanolaminate.

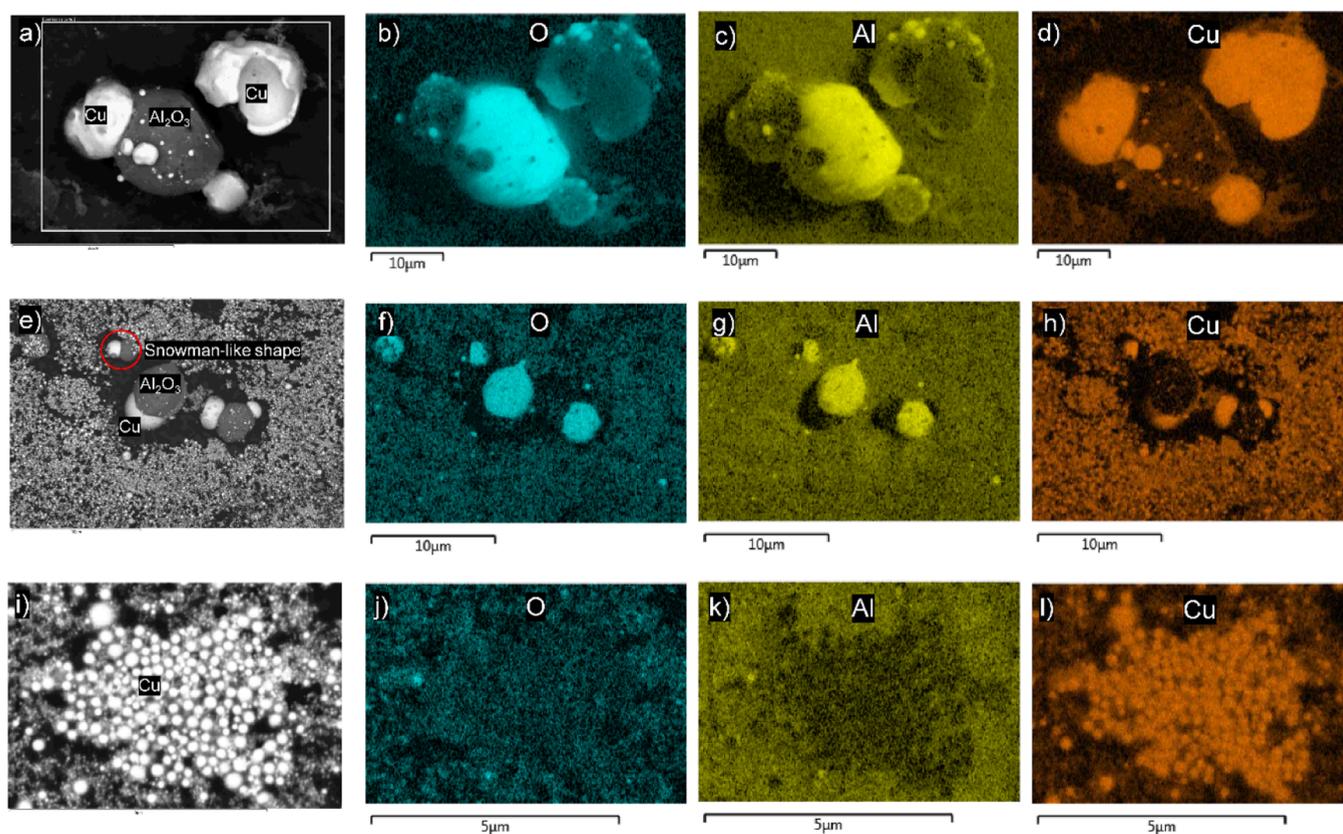


Figure 5. EDX mapping results of post-combustion products collected from (a–d) 1:1 Al/CuO nanolaminate with 20% air-filled porosity, (e–h) fully dense 1:1 nanolaminate, (i–l) nanoparticles from fully dense nanolaminate.

3.3. Post-combustion Product Analysis. To further analyze the relevance of this conjecture, the post-combustion products collected from fully dense and porous (containing 20 vol % of $10 \times 10 \mu\text{m}^2$ pores) 1:1 nanolaminates (Al thickness 100 nm and CuO thickness 200 nm) were retrieved by a carbon tape and then characterized using scanning electron microscopy. Figure 4 shows the different particle morphologies from the

collected post-combustion residues. In all SEM images, the brighter spherical particles are identified as Cu and the grey as Al_2O_3 , based on the corresponding EDX analysis shown in Figure 5. Interestingly, for all samples, post-combustion products are composed of two different populations: large micron-sized particles (size given in Table 1) and clusters of aggregated nanoparticles being 100–400 nm in size. EDX

Table 1. Summarizing Size Distributions of Post-combustion Products (Large Particles Only)

<!--Col Count:3F0E0post-combustion products	size (μm)	
	Cu	Al_2O_3
porous nanolaminate	8.5 ± 5.1	16.2 ± 8.5
fully dense nanolaminate	1.6 ± 0.8	2.5 ± 1.0

analysis of the nanoparticles identifies them as individual Cu and Al_2O_3 nanoparticles (Figure 5i–l). These nanoparticles collected in both laminates are condensed reaction products (Cu and Al_2O_3), which were able to be accessed because the whole combustion event happened within a sealed space, whereas laminates burning in an open atmosphere³⁰ produce only large particles of Al_2O_3 , Cu, or Al/Cu alloys.

Two major differences can be highlighted on large residues collected from porous and fully dense laminates. First of all, Cu and Al_2O_3 products after combustion of the fully dense laminate feature a snowman-like shape (usually Cu on top and Al_2O_3 at the bottom). By contrast, Cu and Al_2O_3 products after combustion of porous laminate are mostly separated particles with some Cu particles deposited on the surface of Al_2O_3 . Second, both Cu and Al_2O_3 products collected from the porous laminates feature larger sizes than the ones collected from the fully dense samples, as summarized in Table 1.

Although the analysis of residues size and composition does not give direct evidence of the convection of trapped air inside the pores and/or the lowering of the ignition threshold, the observations are aligned with the previous comments regarding the overall reaction scenarios. In the fully dense nanolaminate, condensed phase reaction at the Al/Cu interface seems to dominate the reaction because the produced Cu particles are always attached to Al_2O_3 particles. Noticeably, there are much fewer Cu/ Al_2O_3 agglomerates in the combustion products of porous laminates. Obviously, introducing $10 \times 10 \mu\text{m}^2$ pores within the laminate reduces the reactant and product agglomeration which in turn enhances the burn rate of nanothermites as already observed in refs³² and ³⁸. The size enlargement observed in porous zones is also consistent with the following two facts: (1) there is more space available for the products to eject to in the porous zones; (2) the trapped air inside the pores can potentially facilitate the oxidation of Al and improve the overall burn rate.

3.4. Flame Propagation Modeling in Porous Nanolaminates. As a final step of this study, a two-dimensional (2D) and time-dependent heat diffusion model (eq 2) was built to explore the effect of porosity on the burn rate considering the two possible scenarios: molten-product advection through pores and formation of hot-zones upstream of the flame due to a local enhancement of the reactivity, that is, earlier redox reaction

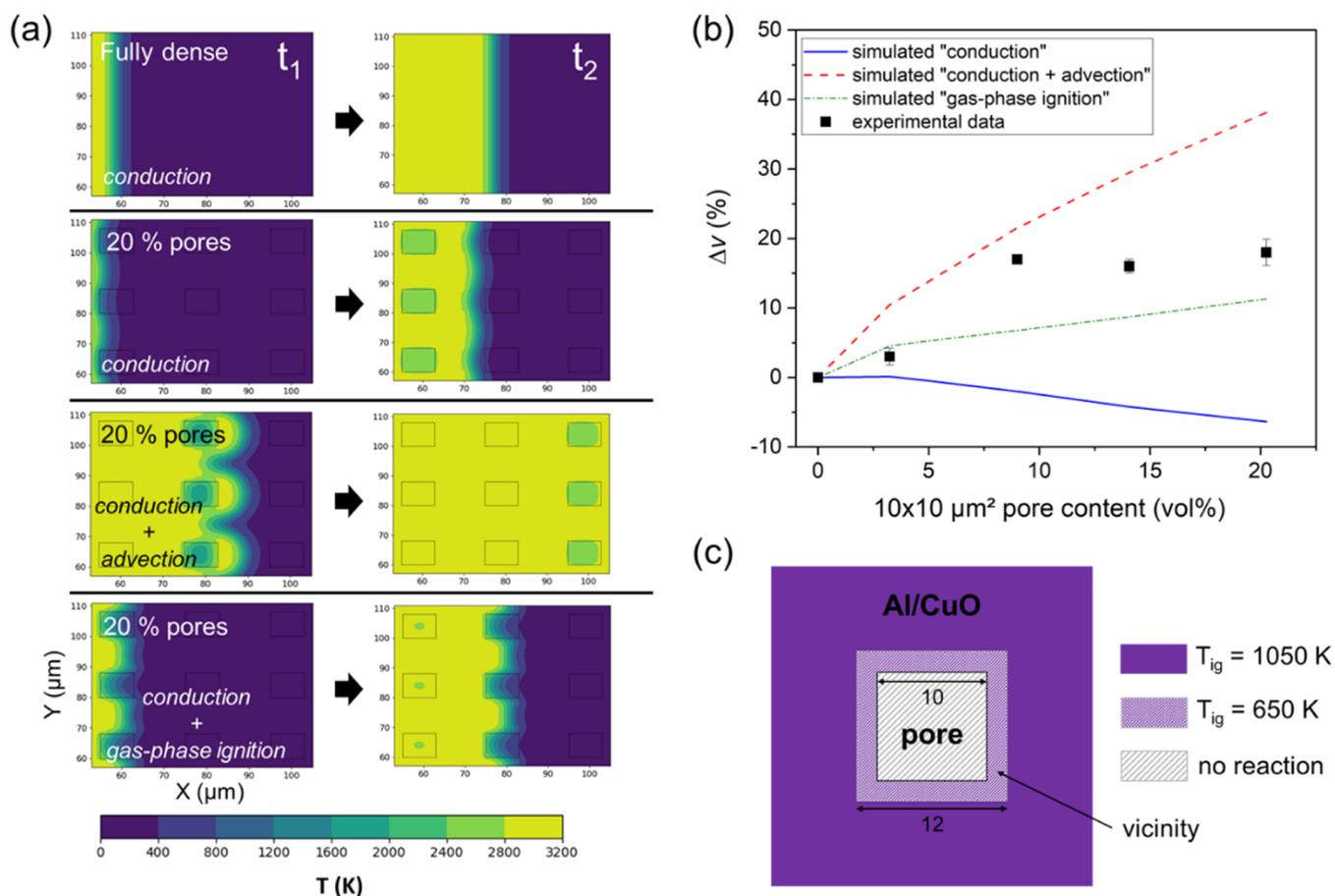


Figure 6. (a) 2D maps of the temperature taken at two different times (t_1 and t_2) of the simulation for fully dense and porous nanolaminates with 20% volume fraction considering pure conduction (conduction + advection) in pores or gas-phase ignition at the vicinity of pores. (b) Simulated propagation speed enhancement at 20% pore content with different configurations: pure conduction (solid blue line), (conduction + advection) in pores (dashed red line), and (conduction + "gas-phase ignition") (dashed green line). Black squares represent the experimental data. (c) Illustration of "gas-phase ignition" configuration, showing the spatial distribution of the ignition temperature T_{ig} in the "vicinity" of the pores.

ignition at pore edges. The flame propagation in dense nanolaminate being a purely conductive process, a purely conductive model is employed as in ref 39. For simplicity, the exothermic Al + CuO reaction is simulated by a source term, and the model assumes that no exothermic self-heating reaction occurs prior to the ignition point, assumed to occur at a certain temperature, as discussed below. To be noted is that the reaction kinetic, which corresponds to the time the material takes to react after being heated to its ignition temperature, is not considered. Then, the system is described by the time-dependent diffusion equation

$$\frac{\partial T}{\partial t} - \alpha(\Delta T) = \frac{S}{\rho c} \quad (2)$$

where ρ , c , and α are the density, specific heat, and thermal diffusivity of the Al/CuO nanolaminates, respectively. For each node (i,j) , the thermal properties are calculated as $\lambda_{i,j}$, $\rho_{i,j}$ and $c_{i,j}$. Then, for each time step n , the node temperature is calculated by a finite element method. As the initial condition, the nanolaminate is ignited at the left ($i = 0$), that is, a temperature of 2843 K is set at the left boundary, corresponding to the adiabatic temperature of the Al/CuO reaction and copper vaporization point. In other words, $T_{0,j}^0 = 2843$ K, while in the rest of the laminate, $T_{i \neq 0,j}^0$ is initially set at the ambient temperature, 298 K. Because the goal of this study is not to quantify burn rates but rather support qualitatively the experimental tendencies, no heat loss is considered. The heat source term, $S_{i,j}$ is also arbitrarily set at $2 \times 10^5 \text{ W}\cdot\text{m}^{-3}$ in order to fit the experimental burn rate measured on the fully dense Al/CuO nanolaminate reference region: $\sim 20 \text{ m}\cdot\text{s}^{-1}$. $S_{i,j}$ is null inside the pores. The average thermo-physical properties and condition parameters used in the calculations are given in Tables S2 and S3. Simulation outputs are the 2D temperature field/map for each condition (only thermal conduction, advection added in pores, and lower ignition threshold around pores) and at different simulation times, as shown in Figure 6a. The average burn rate is then determined as the distance between the points where the temperature reaches the flame temperature (2843 K) and the minimum temperature (ambient). The predicted average burn rate is plotted in Figure 6b for nanolaminates with porosity varying from 4 to 20% considering the two distinct scenarios:

- (1) the ignition threshold is lowered around each pore to simulate a possible reduction of the activation energy of oxygen diffusion due to the convection of gaseous O_2 in the pores. In other words, the ignition temperature is set at 650 K at the vicinity of the pores, whereas it is set at 1050 K in the bulk, according to a previous work⁴⁰ (Figure 6c, green dashed line). In this paper, the vicinity is defined by a ring around the hole; considering a $10 \mu\text{m}^2$ pore, a ring of $1 \mu\text{m}$ wide is set around the hole, which is the vicinity of this pore.
- (2) heat transfer is enhanced through the cavities by advection of molten products. Thus, a spontaneous transmission of the heat from the wall in contact with the flame front to the other walls (two sides walls plus the opposite one) is implemented (Figure 6c, black dashed line). Note that this is a simplification of the real advection processes as we consider the time of flight of potential aggregates throughout the cavities to be equal to zero, but it aims at evaluating the order magnitude of the flame speed change as a function of the pore fraction.

Simulation results show that the advection mechanism has a much greater effect on burn rate enhancement than chemistry: with an increase of the air-filled pore content from 4 to 20%, the propagation speed rapidly increases from ~ 10 to $\sim 40\%$ when advection is added, against less than 10% if we consider that the presence of free molecular oxygens inside the pores reacts with surrounding Al at a lower temperature than in a purely condensed phase reactional mechanism, that is, when occurring at the fully dense Al/CuO interface. Increasing the size of pores to $100 \times 100 \mu\text{m}^2$ leads to an increase of burn rate of 70% against $\sim 1.5\%$ (not plotted in the graph of Figure 6b) considering an earlier ignition threshold at pore edges. This also corroborates qualitatively with the experimental findings and highlights the fact that convection plays a role in burn rate enhancement.

4. CONCLUSIONS

Incorporating micron-sized pores in fully dense Al/CuO nanolaminates results in a faster burn rate (burn rate enhancement of 18% for a pore loading of 20 vol %) while the flame temperature remains the same. Interestingly and unexpectedly, microscopic observations of the burning front in porous nanolaminate show hotspots around each pore upstream of the flame but no advection could be observed as the first conclusion conduction remains the dominant heat transfer mechanism in dense thermite configuration (80% TMD). The cause of burn rate enhancement when pores are embedded into the nanolaminate can be explained by two possible effects: (1) the establishment of convection of the trapped air inside the pores, thus improving the heat and mass transfer to unreacted material. This effect is also supported by the fact that by increasing the pore size, the air does not heat up much, and the burn rate does not increase much; (2) a modification of the reaction chemistry around each micron-sized pores leading to a lowering of the ignition threshold. The air inside the pores also acts as an oxidizer as it can diffuse and react readily upon adsorption into the exposed Al or Al_2O_3 . This gas-phase mediated reaction mechanism occurs at a lower temperature than the diffusion-based mechanism of the aluminum cations and oxide anions across the alumina shell as in the fully dense Al/CuO nanolaminates. The critical size of the pores beyond which their beneficial effect disappears is difficult to estimate, but, this study showed that $100 \times 100 \mu\text{m}^2$ pores have no effect on the combustion with an average burn rate increase of only $\sim 4\%$ compare to fully dense nanolaminate part.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.1c03805>.

Optical image of a typical Al/CuO laminate with air-filled pores; corrected configurations of laminates with different porosities; thermo-physical properties used in the model for Al/CuO laminates and air-filled pores; and condition parameters used in the model to simulate the reaction (PDF)

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Author Contributions

T.W. prepared all samples and performed all characterization measurements. T.W. and C.R. drafted the manuscript. B.J. performed and drafted the flame propagation model and assisted T.W. in EDX analysis. H.W. performed high speed in operando microscopy/thermometry. S.P. assisted T.W. in thermite deposition. M.Z. and A.E. provided support for the manuscript preparation. C.R. supervised this research.

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Notes

The authors declare no competing financial interest.

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