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► **To cite this version:**

Vidushi Singh, Tao Wu, Erik Hagen, Ludovic Salvagnac, Christophe Tenailleau, et al.. How positioning of a hard ceramic TiB₂ layer in Al/CuO multilayers can regulate the overall energy release behavior. *Fuel*, 2023, 349, pp.128599. 10.1016/j.fuel.2023.128599 . hal-04099141

HAL Id: hal-04099141

<https://laas.hal.science/hal-04099141>

Submitted on 16 May 2023

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How positioning of a hard ceramic TiB₂ layer in Al/CuO multilayers can regulate the overall energy release behavior

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Abstract

This study reports on a new ternary thermite comprising of Al-TiB₂/CuO multilayers, designed to take advantage of the high ignitability of titanium (Ti), high volumetric density of boron (B), and low melting point of aluminum (Al). Results demonstrate synergetic effects leading to an energetic layer outperforming single fuel counterparts, Al/CuO or TiB₂/CuO, while being safe to handle. The additive TiB₂ not only lowers the ignition energy by 100%, but also enhances the burn rate by more than a factor of two compared to the single fuel samples (Al/CuO and TiB₂/CuO). The thermite reaction sequences and synergy of Ti, B and Al oxidation, examined by thermo-analytical analyses coupled with X-ray spectroscopy and high-resolution electron energy loss spectroscopy, demonstrate the strong affinity of TiB₂ to oxygen that catalyzes CuO decomposition at temperatures as low as 380 °C; followed by a dual-step TiB₂ oxidation: first to TiO, and then to TiO₂ led by a reaction limiting step of oxidizer availability. Finally, Al undergoes oxidation via liquid boron oxide as well as gaseous oxygen. This study also underlines the crucial effect of the nanolayer morphology in the thin-film technology: when Al is sputter-deposited onto the TiB₂ layer, Al ions penetrate into the grain boundaries penalizing the TiB₂ reactivity. The results demonstrate the advantages of using TiB₂ fuel to improve the ignitability and combustion performance of Al based thermite and offers some means to finely tune their energetic properties.

Keywords: Titanium diboride, ternary nanothermites, thin-films, reactive materials

1. Introduction

Metal-based reactive materials have long been explored and developed as the next-generation energetic materials and may benefit various applications that includes additives to propellants and pyrotechnics¹⁻⁴, high temperature material synthesis^{5,6} as well as micro-initiation⁷⁻¹³. One of the most promising reactive materials emerged in the 2000s is nanothermite which combines a metal and a metal oxide at nanoscale to chemically release large amounts of heat. These nanoscale energetic materials possess high volumetric energy densities (up to 80 kJ.cm⁻³), high adiabatic flame temperatures (>2600 °C) and improved combustion properties by several times¹⁴⁻¹⁹ compared to microscale counterparts. A number of factors, in addition to the components' (metal and metal oxide) nature, influence the combustion properties of these reactive materials: they include the components' size, their intimacy, the metal/metal oxide interfacial layer's nature and thickness, as well as the metal and metal oxide mass ratio, thus providing quite a few ways to manipulate the overall energetic performance. Aluminum (Al) is still predominantly the metal of choice because of its high oxidation enthalpy, non-toxic nature, abundance and low cost²⁰⁻²⁴. However, its low melting point leads to sintering process prior the thermite initiation curtailing the reaction surface area²⁵⁻²⁹, and, the presence of native alumina on aluminum fuel negatively impacts its ignitability. To overcome these shortcomings, a variety of alloys or binary fuels i.e. a combination of Al and a second metal such as Zr, Mg, Ti and B chosen for their gravimetric or volumetric energy density, have been examined³⁰⁻³³ with significant interest to ignition/combustion characteristics.

For example, ignition temperatures of Al-Zr or Al-Mg binary fuels are significantly lower than those of pure Al of similar sizes due to the exothermic reactions of formation of intermetallic phases (Al+Mg and Al+Zr) that drives the thermite ignition at very low temperatures (~ 350 °C)

^{34,35}

Compared to Al-Zr and Al-Mg binary fuels, Al-Ti ones offer the potential for very low ignition thresholds, higher gravimetric heats of combustion, and lower costs. For example, Shoshin et al. found that ball-milled Al-Ti powders burn relatively faster than their pure counterparts of similar sizes³⁶. Very recently Wu et al. reportedly established the strong oxygen affinity of Ti at low temperature (300 °C) together with extreme sensitivity³⁷ which makes Ti based thermite difficult to handle safely. Another fuel to have attracted a lot of attention is Boron (B) due to its very high volumetric and gravimetric energy density^{38,39}, sustainability and low cost.

Undoubtedly, a combination of B and Ti with Al fuel should lead to promising new thermite composition by coupling the advantage of each material (**Table S1, Supplementary Information**). The technological objective of this paper is to develop a thin-film technology to produce ternary fuel thermite nanolaminates, e.g. Al-TiB₂/CuO multi-layers, with controlled bilayer spacing and featuring reduced ignition delays, shorter burn times, higher combustion temperatures, compared to traditional single fuel Al/CuO nanolaminates⁴⁰⁻⁴⁵ while being as safe to handle. CuO was chosen for its strong oxidizing nature. The scientific objectives are two-fold: (i) examine the initiation and combustion behavior of CuO/TiB₂-Al and CuO/Al-TiB₂ nanolaminates, using high-resolved and high-speed visible and infrared camera; and, (ii) depict the sequential reactional steps combining thermal analysis, X-ray diffractometry, high-magnification Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM), with a High-Angle Annular-Dark-Field (HAADF) mode, to probe with ultra-high spatial resolution the different interfaces chemical and structural evolution upon heating. The advantages of using Al-TiB₂ fuel are clear in terms of its capability of tuning both ignitability and combustion which can be altered by TiB₂ incorporation in the multilayer stack. Moreover, the position of TiB₂ nanolayer in the thin film stack only has a slight effect on the ignition and combustion properties.

2. Materials and methods

2.1 Sample preparation

CuO, TiB₂, Al nanolayers were deposited using Direct Current (D.C.) magnetron sputtering from Neyco, France purchased 99.99% purity, 8 by 3 square inches and ¼ inch thick Cu, TiB₂ and Al targets in an equipment from Thin Film Equipments (TFE), Italy. Prior to the deposition of each nanolayer, the chamber was pumped down to 2×10^{-7} torr followed by the introduction of the gases. The gas flow was set via percent-flow control as described in our previous works⁴⁶. Briefly, the argon flow was set to 100% during each of the sputtering event, except CuO, wherein the percent flow of each of the two gases, oxygen and argon was set to 50% resulting in 22.5 s.c.c.m. Ar gas flow and 32 s.c.c.m. oxygen gas flow. The sputtering process conditions are summarized in **Table S2, Supplementary Information**. The unbiased sample holder was centered 15 mm away from the target. The chamber was pumped down, and a cooling time for the sample holder was applied prior to each subsequent sputtering event.

Various multilayers were prepared to perform a head-to-head comparison. Each stack was composed of 10 bilayers (BL) of CuO/Me {Me: TiB₂-Al, Al-TiB₂, TiB₂, Al}, the latter two respectively serving as the reference samples. All the multilayers began with CuO followed by the deposition of metallic layer. TiB₂-Al signifies the deposition of TiB₂ (over CuO) followed by that of Al on TiB₂, whereas Al-TiB₂ notation represents the deposition of Al (over CuO) followed by that of TiB₂ on Al. In each multilayer, a fuel rich configuration ($\phi = 2$) was used and the CuO layer thickness was set to 200 nm. ϕ is defined as the molar ratio between the fuel (Al/TiB₂) and the oxidizer (CuO). Hence, the corresponding thicknesses of TiB₂ (in CuO/TiB₂) and the respective thicknesses of TiB₂ and Al (in CuO/TiB₂-Al and CuO/Al-TiB₂) are 100 nm, 62 nm and 80 nm. As for the remaining reference sample, the resultant Al layer thickness is 200 nm.

In addition, one bilayer of CuO/TiB₂-Al and CuO/Al-TiB₂ finished with a CuO layer on top was prepared on Si substrate to perform the interface analysis. The thickness of each nanolayer is carefully controlled via a calibration process preceding each full stack deposition. Additionally, 2 BL samples of CuO/Me were prepared on Si substrate to perform annealing experiments. CuO-TiB₂-Al-CuO and CuO-Al-TiB₂-CuO multilayers were also sputter deposited on Si substrate to analyze the microstructural evolution of the two systems close to each of the interfaces.

For combustion tests, lines of 10 BL CuO/Me with dimensions of 25 mm (length) x 2 mm (width) were sputter deposited through a shadow mask onto a 500 μm thick glass slide and ignited using a resistively heated titanium (Ti) filament. Prior to thermite deposition, a photolithography process was used to pattern 300 nm thick Ti resistors on 4-inch glass wafers. Au (800 nm thick) was evaporated onto the surface and patterned thereafter to define the Ti filament as well as the Au electrical contact pads. For ignition tests, a similar fabrication process was followed except the multilayers were deposited using a different shadow mask, with an active thermite area of 5.6 x 6.7 mm².

Finally, free standing 10 BL of CuO/Me were also fabricated for ignition threshold characterization and thermal analysis. A silicon wafer was subjected to plasma cleaning following which a layer of photoresist (NLOF, 5 μm) was spin-coated. Succeeding a post-exposure 110 °C baking (PEB) step, the multilayers were sputtered onto the wafer. The multilayer foils were then released by dissolving the photoresist in acetone.

2.2 Material characterization

The crystallographic structure of each nanolayer and the phase was determined using SIEFERT XRD 3000 TT X-Ray diffractometer with Cu-Kα radiation ($\lambda = 1.5406 \text{ \AA}$) fitted with a diffracted beam graphite monochromator. The 2θ X-Ray Diffraction (XRD) measurements were performed

from 10° to 60° with a step of 0.04° . The morphology and the chemical composition of the multilayers were analyzed by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Scanning Transmission Electron Microscopy (STEM) and Electron Energy Loss Spectroscopy (EELS) using a JEOL cold-FEG JEM-ARM200F operated at 200 kV equipped with a probe Cs corrector reaching a spatial resolution of 0.078 nm. EELS data were acquired on a Gatan imaging filter quantum (energy resolution of 0.3 eV) using a dispersion of 0.5 eV/channel, a collection angle of 29.4 mrad and a semi convergence angle of 14.8 mrad. The spatial resolution was estimated at 0.5 nm. FEI Helios NanoLab DualBeam FIB-SEM was used to acquire morphological images as well as perform Focused Ion Beam (FIB) technique to prepare the cross-sectional lamellae.

The heat released during each step of the chemical reaction in the multilayers is characterized by thermal analysis performed in Ar atmosphere using a Differential Scanning Calorimetry (DSC) carried out in a NETZSCH DSC 404 F3 Pegasus system equipped with a DSC-Cp sensor type S and a Platinum furnace. The diffractogram, normalized to the foil mass (typically ~ 10 mg), was recorded at a constant heating rate of $10^\circ\text{C}/\text{min}$ up till 950°C and then baselined manually.

The slow annealing experiments were performed in high metals tube furnace (AET Technologies) at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ (same as that of DSC) and a cooling rate of $2^\circ\text{C}\cdot\text{min}^{-1}$ under an inert N_2 atmosphere.

2.3 Ignition tests

Auto ignition temperature: A hot plate was utilized to understand the effect of high heating rate on the ignition event in the thermites and involved instantly heat the free-standing 10 BL CuO/Me foils. This method involves placing ~ 1 mg of foils specimen in contact with the hot surface and observing the reaction (spark emission). Samples that fail to ignite when heated at

that temperature do not emit a burst of light. Note that for each test, the hot-plate is held at a constant temperature and fresh multilayer specimens are dropped onto its surface. Enough time is allowed for the plate temperature to stabilize before each testing event. The test setup and the snapshots from the tests are shown in **Figure S1, Supplementary Information**.

Ignition energy: The multilayers were ignited using externally applied direct current pulse resistively heating the Ti filament in ambient atmosphere. For each test, the current was adjusted so as to keep same dissipated power (6.125 W). The ignition delay was measured using a photodiode (VISHAY, BPV10) biased at 5 V placed a few centimeters away from the sample and capable of detecting the optical flash emitted from the ignition event. A 1 k Ω dummy resistance was used to measure the photocurrent. The electrical setup is shown in **Figure S2, Supplementary Information**. All electrical signals were acquired on a digital oscilloscope and processed using in-house programs. Several tests were performed, and a mathematical average value of ignition delay (ms) was constituted. Results are then reported in terms of ignition energy calculated as the integral of power over time (up to initiation). The ignition delays can be found in **Table S3, Supplementary Information**.

2.4 Macro and microscopic imaging of combustion and flame temperature

The flame propagation speed was evaluated using a high-speed camera (VEO710, Phantom, USA) recording at 48000 frames per second with a resolution of 512 \times 64 pixels. The videoed films from multiple samples of each type were processed using Phantom Camera Control (PCC) Software to report statistical values of average macroscopic burn rate. Briefly, 6 two-points measurements were performed to determine the propagation speed for each device across each of the four CuO/Me thermite stacks. Two devices from each configuration were tested. The macroscopic burn rate is then reported as a mathematical average for each multilayer. The setup

to determine the front thickness and the flame temperature is comprised of a high-speed camera (Phantom VEO710L, USA) coupled with a long-distance microscopic lens (Infinity Photo-optical Model K2 DistMax, CF-4 Objective). At a pixel/distance ratio of $\sim 2 \mu\text{m}/\text{pixel}$, the propagation of the flame front was recorded at 60,000 frames per second. The thickness of the front is obtained from the optical micrograph recorded during the propagation event. The tool is calibrated to a blackbody source (Mikron M390) for color pyrometry to estimate the reaction temperatures. Further information about the pyrometry measurement can be found in previous studies ¹⁹. Concisely, a raw temperature map is extracted using a three-color (RGB) channel and an average value of the flame temperature is obtained from several such points on the front. The error threshold on the reported values is about 200 – 300 K.

3. Results and discussions

3.1 Ignition, burn-rate and flame front characteristics

The first two columns of **Table 1** give the ignition energy and global burn rate measured for CuO/TiB₂-Al and CuO/Al-TiB₂ stacks compared to CuO/Al and CuO/TiB₂ reference multilayers samples. The ternary systems CuO/TiB₂-Al and CuO/Al-TiB₂ demonstrated much higher burn rates of $8.2 \pm 0.31 \text{ m}\cdot\text{s}^{-1}$ and $10.8 \pm 0.52 \text{ m}\cdot\text{s}^{-1}$ respectively, in comparison to the reference samples: CuO/Al and CuO/TiB₂, which burn at $4 \pm 0.1 \text{ m}\cdot\text{s}^{-1}$ and $2.3 \pm 0.04 \text{ m}\cdot\text{s}^{-1}$, respectively. The additive TiB₂ not only enhances the burn rate by $\sim 50\%$ compared to the CuO/Al reference sample but also exhibited $\sim 100\%$ lower ignition energy of 1.3 mJ (CuO/TiB₂-Al) and 0.033 mJ (CuO/Al-TiB₂) in comparison to unary fuel-based reference nano-thermites. Clearly incorporating TiB₂ with Al (mass ratio 1:1) proved to be more reactive than both single fuel systems.

It is interesting to note that despite a lower auto-ignition temperature (~ 285 °C), CuO/TiB₂ possesses quite low burn rate indicating the thermite reaction is likely to be dominated by condensed phase thus inhibiting the forward energy transfer. The V-shaped flame front of CuO/TiB₂ burns dimly with little to no creation of particles (**Figure 1b**), while the burning front of CuO/Al is characterized by particle emissions and intense bright light (**Figure 1a**). This implies a higher flame temperature as well as more gas generation⁴⁷ in the latter samples. Certainly, the flame temperature of CuO/Al is measured at 3500 °C, much higher compared to that of CuO/TiB₂ measured at 1800 °C, the latter being (**Table 1**) well below the melting point of TiB₂ (3230 °C), bringing another indication in of its combustion behavior in the condensed phase. The CuO/TiB₂ flame front thickness is also much thicker (~ 590 μm) compared to that of CuO/Al (64 μm) further supporting that the combustion is extended in the condensed phase that remains active long after the passing of the flame front. **Figure 1b** shows the CuO/TiB₂ thermite still burning even after the passing of the flame front with no visible gas generation.

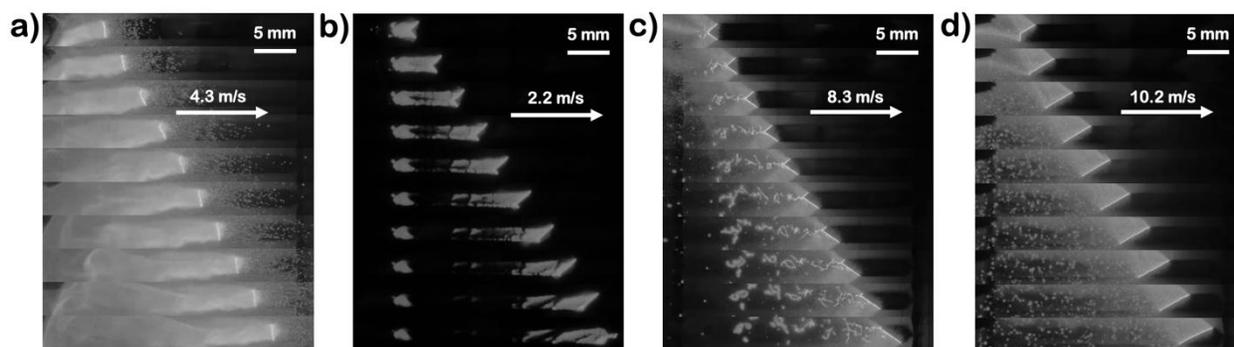


Figure 1: Snapshots from propagation of 5 BL CuO/Me {Me: **a**) Al, **b**) TiB₂, **c**) TiB₂-Al and **d**) Al-TiB₂}

In bi-fuel thermites (TiB₂-Al and Al-TiB₂), we clearly distinguish two combustion stages as shown by the thin sharp well-defined V or slant-shaped front (**Figure 1c-d**) strikingly different from slightly curved Al flame front. The first combustion stage is dominated by combustion of Al

in the vapor phase, followed by the condensed phase combustion of TiB_2 . Another observable characteristic difference is less intense gas generation in the burning of bi-fuels compared to Al/CuO burning: the bi-fuels exhibit particles tearing away from behind the flame front as it progresses. Among TiB_2 -Al and Al- TiB_2 fuels, it seems that Al- TiB_2 displays superior reactivity than TiB_2 -Al in that the propagation of the flame front generates more energy that then ejects smaller more uniform particles as opposed to larger string like solid emissions from TiB_2 -Al. This points to a faster transfer in Al- TiB_2 than that in TiB_2 -Al, even though the flame front characteristics are very similar. CuO/ TiB_2 -Al and CuO/Al- TiB_2 feature similar flame front thicknesses ($\sim 80 \mu\text{m}$) and flame temperatures ($\sim 3000 \text{ }^\circ\text{C}$). We speculate that the likely cause of very low initiation points in bi-fuel thermites (CuO/ TiB_2 -Al and CuO/Al- TiB_2) may be the first stages of reaction, when the first oxides (TiO_x and B_xO_y) in contact with the CuO are formed, thus ensuing the reaction with the exposed fuel. In order to understand the nature of the exothermic events, foils from each configuration (CuO/ TiB_2 -Al, CuO/Al- TiB_2) as well as the reference samples (CuO/Al, CuO- TiB_2) were analyzed by DSC with a heating ramp of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under a constant flow of Ar.

Table 1: Ignition energy (mJ), burn rate ($\text{m}\cdot\text{s}^{-1}$), ignition threshold (K) and flame characteristics of 10 BL CuO/Me {Me: Al, TiB_2 , TiB_2 -Al, Al- TiB_2 }

10 BL stacks	Ignition Energy (mJ)	Burn rate ($\text{m}\cdot\text{s}^{-1}$)	Flame temperature ($^\circ\text{C}$)	Auto-ignition point ($^\circ\text{C}$)	Flame thickness (μm)
CuO/Al	102.1 ± 15.6	4.3 ± 0.1	3500	700 ± 5	65
CuO/ TiB_2	5.9 ± 1.1	2.3 ± 0.04	1800	285 ± 1	592
CuO/ TiB_2 -Al	1.3 ± 0.7	8.3 ± 0.3	3000	380 ± 1	83

CuO/Al-TiB₂	0.3 ± 0.2	10.8 ± 0.5	3100	445 ± 1	85
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3.2 Thermo-analytical analysis

DSC traces of CuO/TiB₂-Al and CuO/Al-TiB₂ are plotted in **Figure 2** with those of CuO/Al and CuO/TiB₂ samples, obtained under the same conditions. DSC traces show exotherms of subsequent oxidation reactions of Al and TiB₂ with CuO without the contribution of oxygen from the surrounding environment. The total heat of reaction is indicated across each plot. To supplement the understanding of the different reaction steps, CuO/TiB₂-Al sample was annealed at 475 °C, 550°C and 950°C while CuO/Al-TiB₂ sample was annealed at 375 °C, 480 °C and 950 °C corresponding to the main peaks recorded in the DSC scan and their respective compositions were analyzed by XRD. The composition of each sample after annealing steps is summarized in **Table 2** while the XRD diagrams can be found in **Figure S3, Supplementary Information**.

Even though the respective total heats of reaction of CuO/Al and CuO/TiB₂ exceed that of CuO/TiB₂-Al and CuO/Al-TiB₂, the phenomenon must be carefully analyzed as important differences in the occurrences of the exotherms when TiB₂ is added to CuO/Al multilayer are observed. Therefore, each of these ternary systems is systematically compared and analyzed with the former reference samples as follows.

CuO/TiB₂-Al system: The DSC scan (**Figure 2**, black trace), shows a tiny exothermic peak (onset temperature of ~200 °C) attributed to the reactions occurring prior to ignition indicated in the pre-ignition region (PIR) that lead to the formation of TiO_x starting at 300 °C³⁷. As a matter of fact, at 200 °C, condensed-phase oxygen transfer is thought to occur until CuO begins to decompose at ~350 °C⁴⁸. At ~ 375–550 °C (**Figure 2**, region R₂), an apparent exothermic double peak (onset temperature of ~ 380 °C) is seen, which is due to the oxidation of TiB₂

forming two oxide layers liquid B_2O_3 and TiO_2 , as the oxygen atoms migrate outwards following the release from the decomposition of CuO . The XRD of samples annealed at $475\text{ }^\circ\text{C}$ confirms the presence of TiO_2 , B_2O_3 and Cu_2O , the latter confirming the early decomposition of CuO (**Table 2**). This exothermic double peak is a succession of two exotherms, corresponding to the oxidation of TiB_2 resulting in two adjacent native oxides ($TiO_x-B_2O_3$), separated by the melting of boric oxide at $\sim 450\text{ }^\circ\text{C}$. It is noteworthy that as the sample approaches the melting temperature of B_2O_3 , some of the released heat is consumed in melting the oxide bringing the exotherm down. Further temperature increase leads to the second peak of this first exotherm at $505\text{ }^\circ\text{C}$ (onset at $470\text{ }^\circ\text{C}$) which is the continuation of TiB_2 oxidation. XRD analysis after annealing at $550\text{ }^\circ\text{C}$ stages the presence of TiO_2 , Cu_2O and Cu . Overall, this two-step TiB_2 oxidation produces 79.5% of the total heat released in the ambient – $950\text{ }^\circ\text{C}$ range, i.e., $1116\text{ J}\cdot\text{g}^{-1}$ of $1400\text{ J}\cdot\text{g}^{-1}$ total released heat. Next, region R_3 relates to the main CuO - Al oxidation reaction ⁴⁶. It releases much lower heat compared to the reference CuO/Al sample. This might be due to the tendency of Ti atoms to rapidly react and consume oxygen compared to that of Al ³⁷ as previously reported. As for the last peaks in region R_4 , similar to CuO/Al , the exotherm simply relates to the Al oxidation in both gas and condensed phase ⁴⁹. It should be noted that a Cu signal is observed in XRD (**Figure S3b-c, Supplementary Information**) that evidently supports the superior reactivity of TiB_2 - Al as well as Al - TiB_2 bi-fuel systems in that the main reaction is catalyzed compared to Al -only thermite. The peaks corresponding to boric oxide are quite low intensity which is likely due to its materialistic nature.

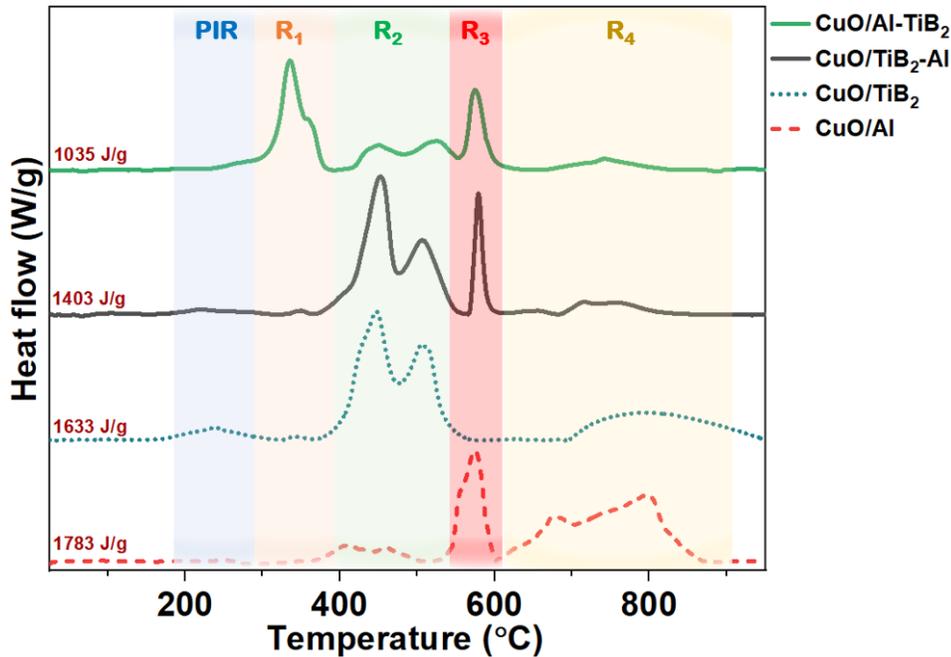


Figure 2: DSC traces of 5 BL CuO/Me {Me: Al, TiB₂, TiB₂-Al}. The traces are baseline subtracted manually and are offset in Y to provide clarity. The plot is divided into 5 regions: a pre-ignition region (PIR), regions R₁, R₂, R₃ and R₄

CuO/Al-TiB₂ system: A noteworthy feature of CuO/Al-TiB₂ (**Figure 2**, green plot) is the major low temperature exotherm (onset of ~ 230 °C) (region R₁) which produces ~ 45% of the total heat of reaction (455 J.g⁻¹ of 1035 J.g⁻¹ total released heat) and the quenched subsequent exothermic double peak (region R₂). This first exotherm is attributed to the rapid consumption of oxygen atoms released as a result of CuO decomposition by TiB₂ to form TiO_x. XRD analysis at the end of the first exotherm (380° C) shows the presence of Cu₂O and TiO₂ which in turn confirms this event. Quite conspicuously, the presence of TiB₂ between each Al/CuO bilayer seems to catalyze the oxygen release from CuO slightly faster than its presence sandwiched between CuO and Al. This low temperature exotherm seems to be responsible for the lowest ignition onset in this system (ignition point measured at 285 °C, **Table 1**). With most of TiB₂ already oxidized in the PIR + R₁ region, there is less oxygen atoms to further diffuse through native oxides of TiB₂ to

oxidize the core leading to the first peak of region R₂ around the same temperature as CuO/TiB₂-Al system. Similarly, the following exotherm in this region post B₂O₃ melting results in the remaining of the oxidation event. Finally, region R₃ represents CuO-Al oxidation reaction. Post annealing at 550°C, unlike CuO/TiB₂-Al system, XRD of CuO/Al-TiB₂ reveals the presence of elemental boron and severe Cu-Ti alloying. The presence of Cu₂O upholds the ongoing CuO/Al thermite reaction at this stage (Region R₃, **Figure 2**). Region R₄ is characterized by low heat events attributed to little to no presence of the oxidizer, as well as alloying of Ti and Cu.

Finally, for both samples, CuO/Al-TiB₂ and CuO/TiB₂-Al, more intense the low temperature peaks, less is the high temperature Al oxidation exotherms (**Figure 2**, region R₃ and R₄), confirming a lower availability of Al during this last event, as it was consumed during the first low temperature events.

Table 2: Summary of chemical constituents of as deposited (AD) and annealed CuO/Me {Me: Al, TiB₂, TiB₂-Al}

Sample	Constituents at different temperatures			
	AD	475 °C	550 °C	950 °C
CuO/TiB₂	CuO, TiB ₂	TiO ₂ , Cu ₂ O	Ti _x Cu _y , Cu ₂ O, Cu	Ti _x Cu _y , Cu
CuO/TiB₂-Al	CuO, Al, TiB ₂	TiO _x , Cu ₂ O, AlTi, Al, Cu	B, Al, TiO ₂ , Cu ₂ O, Cu, Ti _x Cu _y	Ti _x Cu _y , Cu
CuO/Al-TiB₂	CuO, Al, TiB ₂	TiO ₂ , Cu ₂ O, B ₂ O ₃ , Cu	TiO ₂ , Cu ₂ O, B ₂ O ₃ , B, Cu, Ti _x Cu _y	Ti _x Cu _y , Cu

Table 3: Approximate heats of reaction determined from the DSC scans

Sample	Heat of reaction (J/g)		Total heat of reaction (J.g ⁻¹)
	< 550 °C	<650 °C	
CuO/Al	179 ± 3	602 ± 10	1580
CuO/TiB ₂	740 ± 4	1196 ± 5	1536
CuO/TiB ₂ -Al	764 ± 11	1116 ± 19	1403
CuO/Al-TiB ₂	730 ± 6	940 ± 7	1035

Overall, the analysis of the exothermal events brings about three salient findings:

(i) Addition of TiB₂ to Al/CuO modifies the low temperature reaction steps, i.e. those occurring below Al melting, which explains the superior reactivity in term of prompter initiation of bi-fuels compared to CuO/Al (**Table 1**). Indeed, the low temperature exothermic events (below Al melting) releases more heat compared to that of CuO/Al multilayers: the heat released below 550 °C represent 79.5% and 70.5% of the total heat in CuO/TiB₂-Al and CuO/Al-TiB₂ systems against only 23% of the total heat in CuO/Al (**Table 3**). The Al_xO_y interface growing in CuO/Al at 400°C (**Figure 2**, region R₂) is therefore a better oxygen diffusion barrier than the native TiO/TiO₂ layer³⁷.

(ii) Exothermic occurrences in CuO/TiB₂-Al and CuO/Al-TiB₂ multilayer are a superposition of the individual reaction steps recorded in the two reference multilayers, CuO/Al and CuO/TiB₂ (**Figure 2**, dotted plots) which also happens to be the multilayers releasing maximum heat of reaction: 1780 J.g⁻¹ and 1630 J.g⁻¹ for CuO/Al and CuO/TiB₂, respectively. This indicates that ‘hidden’ endothermic reactions such as phase transformations which are not detected by XRD

occur within the ternary thermite reaction process. Furthermore, some liquid B_2O_3 may be reduced to B (detected at ~ 550 °C) when reacting with Al.

(iii) Finally, while the main exothermic reactions in both samples are attributed to the oxidation of titanium, boron, and aluminum, their onset temperature and intensity vary with the deposition sequence: either TiB_2 nanolayer deposited prior to Al onto CuO (CuO/ TiB_2 -Al configuration), or TiB_2 deposited onto Al over CuO (CuO/Al- TiB_2 configuration). This indicates that the nature and the thickness of the interfaces has a significant impact on the ternary thermite reaction process.

Deeper understanding on the reaction of the ternary systems necessitates a morphological as well as chemical analysis, which is addressed next by coupling TEM and EELS, at selected annealing steps. The target temperature for annealing were set at 475 °C and 550 °C for CuO/ TiB_2 -Al and 375 °C and 480 °C for CuO/Al- TiB_2 system because of the DSC traces.

3.3 Morphology and chemical analysis of the bi-fuel samples

3.3.1 As deposited

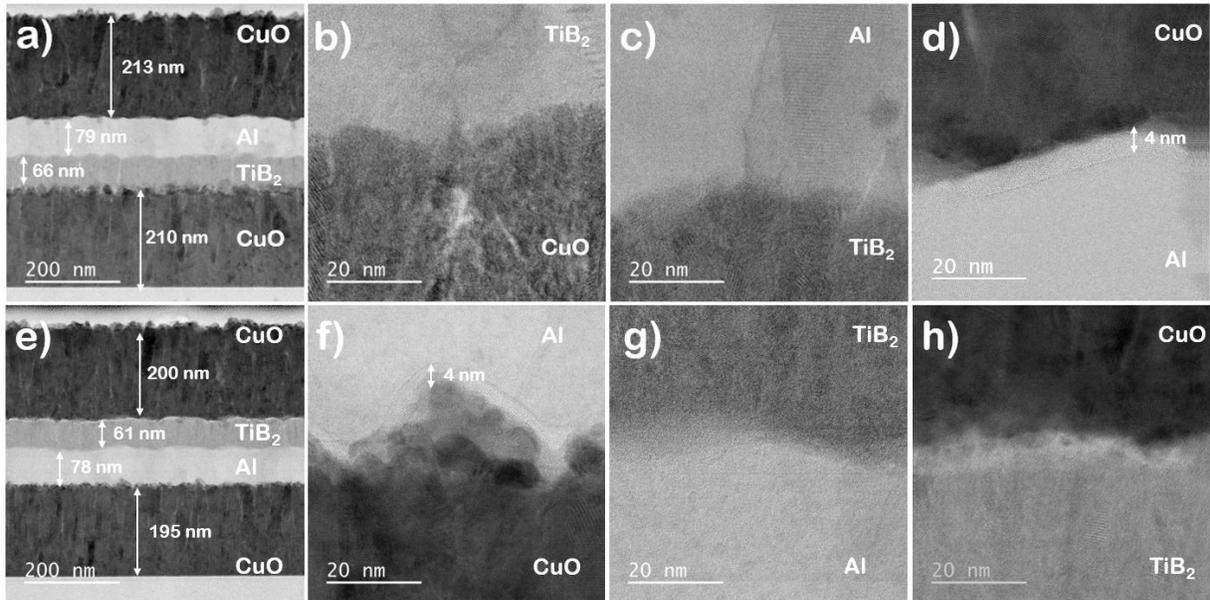


Figure 3: STEM images showing as deposited multilayers and the corresponding interfaces: **a)** CuO-TiB₂-Al-CuO **b)** CuO-TiB₂ **c)** TiB₂-Al **d)** Al-CuO and **e)** CuO-Al-TiB₂-CuO **f)** CuO-Al **g)** Al-TiB₂ **h)** TiB₂-CuO. All interfaces are observed to be quite dense with no delamination.

The **Figure 3a** and **Figure 3e** show the STEM images of CuO-TiB₂-Al-CuO and CuO-Al-TiB₂-CuO stacks indicating the respective thicknesses of each layer. CuO layer possesses a thin columnar structure and quite rough surface morphology. The consonant EDX maps of the CuO-TiB₂-Al-CuO and CuO-Al-TiB₂-CuO stacks (**Figure S4, Supplementary Information**) do not show any severe intermixing close to the interfaces. **Figure 3b-d** and **Figure 3f-h** show the high-resolution STEM micrographs of each of the resultant interfaces. No voids or delamination are observed between each layer. Al-CuO interface features a 4 ± 0.2 nm thick native alumina formation observed previously⁴⁶. It is worth noting however that the deposition of Al over CuO results in more jagged projections at the interface compared to a relatively smoother interface

formed as a result of the deposition of CuO over Al. It has been previously reported that more is the contact surface damage, lower is the probability of quicker oxidation onset⁴⁷. The CuO-TiB₂ and TiB₂-CuO interfaces are less defined. The inability to discern the formation of a native interface between CuO and TiB₂ suggest remarkable resistance of TiB₂ to oxidation at room temperature. Note that the deposition of CuO over TiB₂ results in less rough interface compared to otherwise. This is attributed to the rough uneven surface of CuO created as a result of columnar growth, into which TiB₂ tends to penetrate filling any spaces. The hardly distinguishable Al-TiB₂ and TiB₂-Al interfaces are observed to be rather compact, the former however being more uniform. Next, the chemical nature of the interfaces is determined by Electron Loss Near Edge Structure (ELNES). Cu L_{2,3}-edges at 931-951 eV, O K-edge at 536 eV, B K-edge at 188 eV, Ti L_{2,3}-edges at 456-462 eV and Al K-edge at 1560 eV were acquired near and across the unexplored interfaces namely CuO-TiB₂, TiB₂-CuO, TiB₂-Al and Al-TiB₂. EELS core loss edges were background subtracted using a power law fit before being plotted in **Figure S5, Supplementary Information**.

Across CuO-TiB₂ interface (**Figure S5a**) and close to CuO, sharp B peak at 194 eV along with a second peak at ~204 eV indicates the presence of B-O (as in B₂O₃) and Ti-B bonds (as in TiB₂). Because TiB₂ always has two native oxides to its sort, we conjecture the presence of TiO_x as well. Indeed, Ti L_{2,3} edges at 453-465 eV back this occurrence up. Since the two peaks do not show any splitting, they can be attributed to a mixture of Ti²⁺ and Ti³⁺, which could either be a Ti-B bond or Ti-O bond³⁷. The presence of O K-edge however confirms some oxidation in the vicinity of CuO-TiB₂ interface.

Interestingly, across the TiB₂-CuO interface (**Figure S5b**), slight shift of Ti L₂ edge from 456 eV to 457 eV and slight splitting of the oxygen peak points to the formation of a mixture of Ti²⁺ and Ti³⁺ as well. In the vicinity of CuO, a pre-oxygen peak at 529 eV normally attributed to the

presence of molecular oxygen is recorded. In addition, B K edges at 194 eV and a further peak at 204 eV confirms the presence of B-O bond across this interface. This is attributed to the slow outward diffusion of oxygen from CuO as seen previously across CuO-TiB₂ interface.

In summary, the CuO-TiB₂ and TiB₂-CuO interfaces display similar chemical behavior at room temperature except the presence of gaseous oxygen in the latter.

Across TiB₂-Al and Al-TiB₂ interfaces (**Figure S5b, Supplementary Information**), the L₂₋₃ edges at 456-462 eV are attributed to Ti-B bond. While the Al-TiB₂ interface features a sharp and clear transition from TiB₂ to Al with no detectable elemental intermixing, the TiB₂-Al interface shows some Al, Ti and B intermixing. During the sputtering of Al over TiB₂ (less compact than Al), the former tends to fill into any empty spaces in TiB₂ columns henceforth giving rise to low intensity ELNES of Al, Ti and B in the vicinity of the interface, which is an important difference between both bi-fuel configurations.

3.3.2 Annealed

To investigate the change in microstructure of each layer as well as the evolution of the interfaces, the two bi-fuel samples were annealed at 475 °C and 550 °C for CuO/TiB₂-Al multilayer; and at 375 °C and 480 °C for CuO/Al-TiB₂ multilayer based off of the DSC traces. The resulting observations are discussed below.

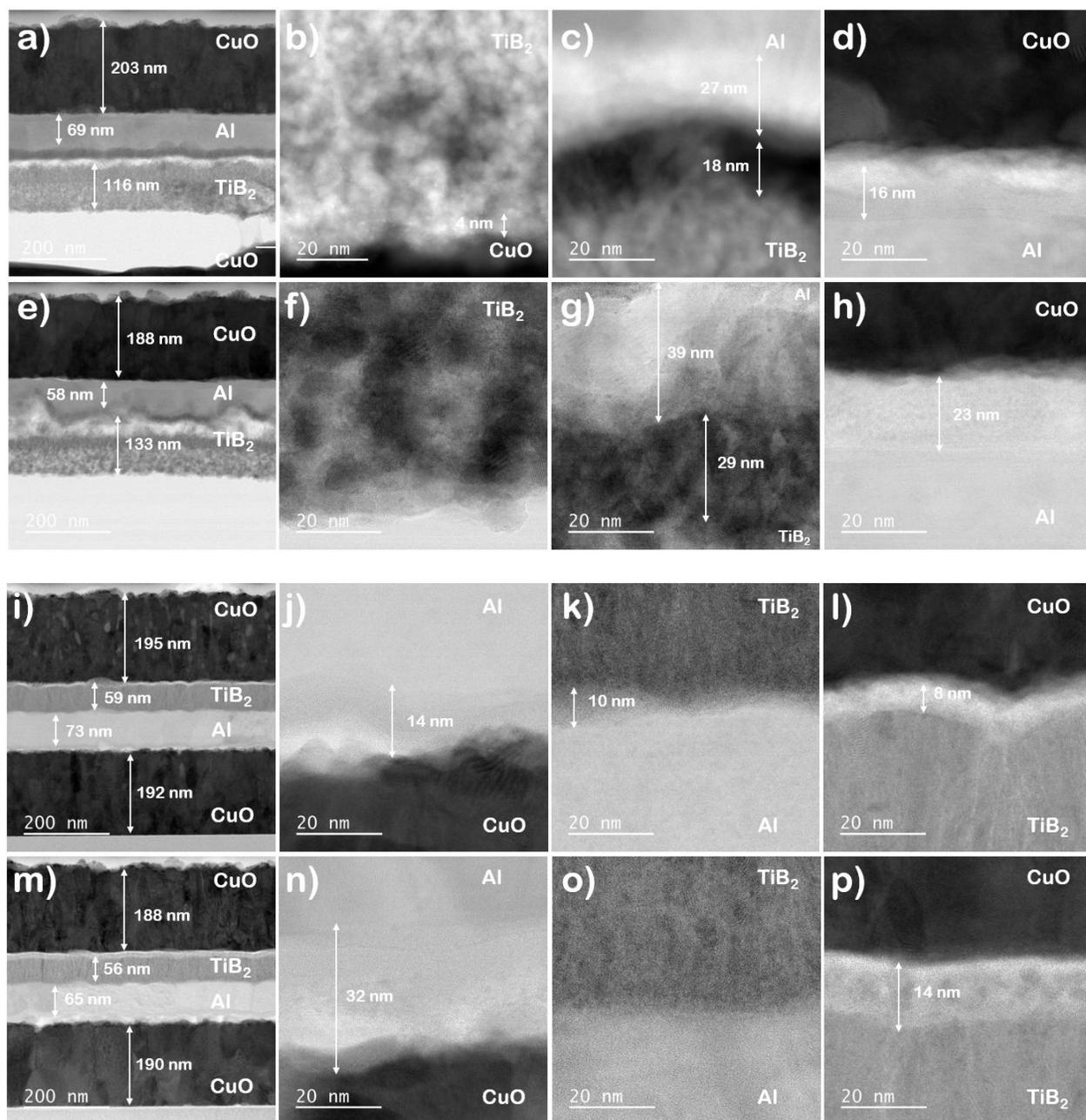


Figure 4: STEM images showing annealed multilayers and the corresponding interfaces: **a)** CuO-TiB₂-Al-CuO annealed at 475 °C and its interfaces (**b-d**), **e)** CuO-TiB₂-Al-CuO annealed at 550 °C and its interfaces (**f-h**), **i)** CuO-Al-TiB₂-CuO annealed at 375 °C and its interfaces (**j-l**), **m)** CuO-Al-TiB₂-CuO annealed at 480 °C and its interfaces (**n-p**)

CuO/TiB₂-Al system: Annealing up to 475 °C reduced the thickness of Al by ~13% to 69 ± 2 nm with little morphological changes (**Figure 4a**). Interestingly, the thickness of TiB₂ went up by ~76% to 116 ± 2 nm introducing porosity in the layer. EDX (**Figure S3b, Supplementary Information**) maps reveal the presence of oxygen throughout TiB₂ layer marking the ongoing oxidation process. XRD at this stage showed the presence of TiO₂ (**Figure S7a-f, Supplementary Information**). One interesting result of this annealing is the shrinkage of CuO by ~37% to 134 ± 20 nm accompanied by the rapid reduction of CuO to Cu, aggressive enough to create ~70 nm deep uneven void (**Figure S6a, Supplementary Information**). This is confirmed by the EDX map (**Figure S7a-f, Supplementary Information**) showing the presence of Cu and no oxygen in the bottommost layer as well as by XRD showing signals from metallic Cu. The oxygen gas liberated as part of this decomposition is quickly adsorbed by TiB₂ causing prompt oxidation and release of most of the heat (**Figure 2**, region R₂). More interestingly, Cu diffused through the multilayer ascending to TiB₂ and Al layers concentrating at CuO-TiB₂ and TiB₂-Al interfaces (**Figure S3b and Figure S7e, Supplementary Information**). A thinly undefined ~4 nm CuO-TiB₂ interface was left at some areas of contact, while 45 ± 5 nm TiB₂-Al interface exhibited an amorphous dual interfacial formation (**Figure 4b-c**). The denser bottom layer of this dual interface is concentrated with Cu while the top features the presence of mainly Ti and O, and some Al (weak signals from AlTi seen in the XRD). Al-CuO also featured a 16 ± 1 nm thick amorphous alumina interface formed as a result of slow Al oxidation (**Figure 4d**). The ELNES of B, Ti, O, Cu and Al acquired across the TiB₂-Al interface annealed at 475 °C (**Figure S9a, Supplementary Information**) confirm the presence of glassy B₂O₃ as well as oxygen rich TiO (major shift of Ti L_{2,3} edges to 460-466 eV and O K-edge at 532 eV) in accordance with the XRD analysis. Upon closer examination, right at the bottom of TiB₂ (near the initially present CuO-TiB₂ interface), there is a slight splitting of Ti L edges confirming the occurrence of TiO₂

^{37,50}. Nevertheless, most of TiB₂ happens to be oxidized to TiO. It is only across the TiB₂-Al interface that some existence of B is detected closer to Al layer.

Annealing to 550 °C features further reduction of bottom CuO augmenting the void to about 1 μm in depth (**Figure S6b, Supplementary Information**). Cu is not detected in either TiB₂ or Al nanolayers anymore. Any oxygen released hereafter is rapidly consumed by TiB₂, which features severe porosity furthering its thickness to 133 ± 4 nm. As shown in the EDX maps, diffused O spans the thickness of TiB₂. Additionally, Ti also diffuses through the interfacial oxides into Al causing some intermixing (**Figure S7g-l, Supplementary Information**). Al and the top CuO layers curtailed by 16% and 7% to 58 ± 16 nm 188 ± 8 nm respectively. The TiB₂-Al and Al-CuO interfaces, widen following a similar nature as observed at lower temperature. It should be noted that B is too light to be detected accurately by EDX but is identified by EELS (**Figure S9b, Supplementary Information**).

CuO/Al-TiB₂ system: The microstructural changes in CuO/Al-TiB₂ system annealed at 375 °C (**Figure 4i-l**) and 480 °C (**Figure 4m-p**) show strikingly different progression of the reaction. While the bottom CuO shows a mere 2% (to 192 ± 3 nm at 375°C) and 3% (to 190 ± 2 nm at 480°C) reduction in its thickness, the top CuO reduces by 3% at 375°C and 6% by 480°C. Its microstructure changes from columnar to slightly granular. The CuO-Al interface features an amorphous alumina confirmed by the EDX maps (**Figure S8c and Figure S8f, Supplementary Information**), thickness of which increases from an initial 14 nm to 32 nm showing that Al oxidation did in fact begin at a temperature lower than previously observed ⁴⁶. A faster oxidation and subsequent growth at the interface lead to the formation of voids at this interface (**Figure S8g, Supplementary Information**). The thickness of Al reduced by 6% to 73 ± 3 nm at 375 °C and further by 16% to 65 ± 2 nm at 480 °C. TiB₂ hardly diminished until 375 °C but depreciated

by 8% to 65 ± 2 nm at 480 °C. Al-TiB₂ interface is observed to be quite dense with no distinguishable interface, except a ~10 nm interface can be sporadically defined (**Figure 4k**). A very well defined TiB₂-CuO interface mainly composed of Ti and O grows from an initial 8 nm (at 375 °C) to 14 nm (at 480 °C). The ELNES of B, Ti and O acquired across Al-TiB₂ interface, at 375 °C and 480 °C (**Figure S10a-b, Supplementary Information**), indicate a change in Ti bonding to Ti-O from an initial Ti-B (high energy-loss shift of Ti L edges to 458-464 eV from an initial 457-462 eV). In addition, there is no oxygen signal picked up close to Al layer suggesting any diffused oxygen is consumed by the adjacent TiB₂. ELNES of Ti indicate the formation of TiO₂ and Cu₂O at this interface (shift in Ti L edges to 460-466 eV with slight peak splitting in the vicinity of CuO and shift in Cu L edges to higher energy-loss). Close to top CuO, it is worth noting that there is a low intensity B L-edge (onset at 198 eV) as well, but no O K-edge supporting the formation of B₂O₃. Thus, it may be attributed to elemental B as a result of reaction of B₂O₃ with Al to produce B and Al₂O₃. Further annealing to 480 °C, no formation of B₂O₃ is seen, boron oxide is therefore reduced. The low intensity O K-edges however mark the beginning of oxidation at this interface via outward oxygen ion diffusion from the oxidizer. Quite remarkably, TiB₂-CuO interface not only displays the thickening of the interface but also Ti L edges' splitting pointing to the presence of Ti⁴⁺. The corresponding splitting in O K edge confirms the presence of stoichiometric TiO₂ at this interface. In the vicinity of top CuO, a shift of Cu L edges to higher binding energy indicates the presence of Cu₂O, a product of the ongoing redox reaction (**Figure 2**, region R₂). As TiO₂ is one of the final reaction products, it seems like unlike CuO/TiB₂-Al, CuO/-Al-TiB₂ reaches completion stage faster. It has been shown previously that the presence of TiO₂/B₂O₃ mixture is capable of enhancing oxidation rate by creating alternative oxygen diffusion pathways⁵¹. Reportedly, CuO/Ti undergoes a two-step redox reaction, first forming TiO at lower temperature and finally to TiO₂ at ~500°C³⁷. It seems

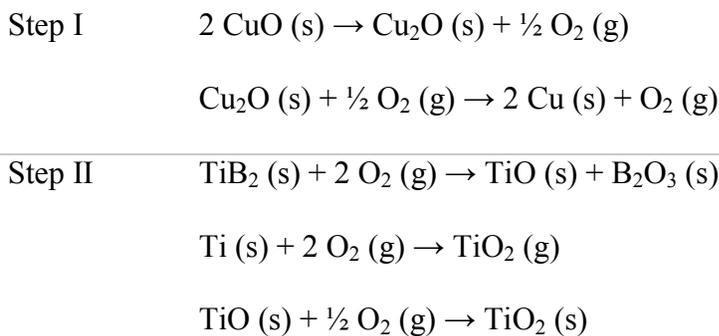
TiB₂ follows a similar regime except in the binary fuels, in addition, it facilitates CuO/Al main reaction to begin earlier as well.

3.4 Discussions and reaction scenario

STEM-EELS for the different temperature stages coupled with DSC, XRD and EDX revealed:

- i. *Strong affinity of TiB₂ to oxygen that catalyzes CuO decomposition:* TiB₂ in direct contact with CuO boosted the latter's decomposition at temperatures as low as 380 °C.
- ii. *TiB₂ dissociation and further Ti and B oxidation:* Owing to the oxygen release from CuO, Ti-B bonds break, enabling Ti and B to oxidize to TiO_x and B₂O₃ at ~ 300 °C and 410 °C respectively. Note that the Ti-B bond dissociation energy is 272 kJ.mol⁻¹ against 820 kJ.mol⁻¹ and 670 kJ.mol⁻¹ for B-O and Ti-O bonds respectively. This additionally explains the low auto-ignition point of CuO/TiB₂ thermite.
- iii. *Reduction of liquid B₂O₃ in contact with Al:* Some elemental boron is detected at temperatures >550 °C (post region R₂, **Figure 2**) likely caused by the reduction of liquid B₂O₃ (melting point of 450 °C) in contact with Al.
- iv. *Oxidation of Al post melting:* The ultimate reaction stage is the oxidation of metallic aluminum with the remaining oxygen (R₃, **Figure 2**).

The reaction steps are thus tabulated below:



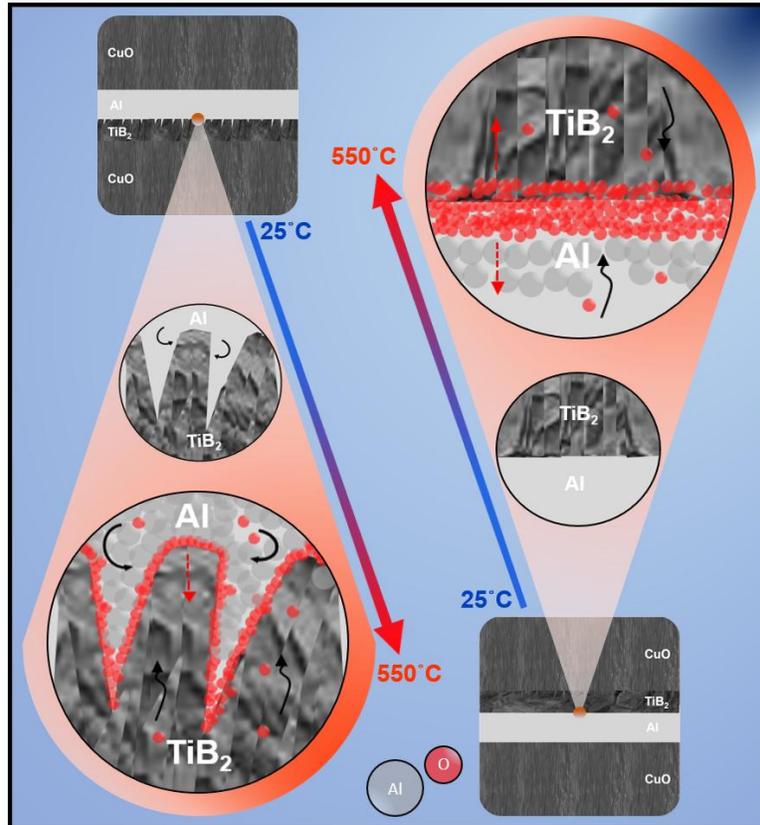
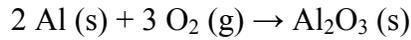
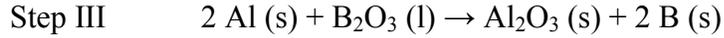
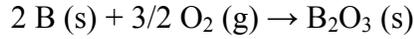


Figure 5: Schematic of an outlook on the oxidation and potential microstructural changes of $\text{TiB}_2\text{-Al}$ and Al-TiB_2 interfaces. While the oxide layer (in red) can grow bidirectionally in $\text{CuO-Al-TiB}_2\text{-CuO}$, $\text{CuO-TiB}_2\text{-Al-CuO}$ features a unidirectional oxide growth which is inhibited by Al due to lower probability of Al-O bond formation than that of Ti-O

Importantly, STEM-EELS also allowed to depict the differences in the performances of $\text{CuO/TiB}_2\text{-Al}$ versus CuO/Al-TiB_2 systems. In the former, i.e., when Al is sputtered onto TiB_2 , Al is seen to migrate into the perpendicular columns of TiB_2 which penalizes its reactivity. We observed that TiB_2 possesses a very small grain size compared to Al and is characterized by less

dense columnar morphology. When Al is deposited over TiB_2 , it tends to fill into any crevices (**Figure 3a** and **Figure 3e**). Then upon annealing, when oxidation begins as a result of oxygen ion diffusion, the alumina layer formed at the boundaries prevent oxygen movement through the underneath TiO_x inhibiting oxidation as the temperature increases⁵². The schematic of the mechanism taking place at sufficiently high temperatures ($> 550\text{ }^\circ\text{C}$) is shown in **Figure 5**. Moreover, the delamination behavior as well as nano-structural losses in $\text{CuO/TiB}_2\text{-Al}$ at temperatures as low as $\sim 475\text{ }^\circ\text{C}$ may hinder and/or delay chemical exchanges/reactions provides another potential explanation for its lower performance in comparison to CuO/Al-TiB_2 . This severity of the damage in the nanostructure simply comes from the direct CuO-TiB_2 contact that then results in rapid oxidizer consumption. As a premise of this phenomenon, a 2 BL CuO/TiB_2 was annealed to $550\text{ }^\circ\text{C}$ and the resulting TEM micrographs (**Figure S11, Supplementary Information**) exhibited similar destroyed nanolaminate.

4. Conclusion

The effect of TiB_2 as an additive thin film on the initiation and combustion properties of CuO/Al multilayers was studied. The $\text{CuO/TiB}_2\text{-Al}$ and CuO/Al-TiB_2 multilayers demonstrated much higher burn rates of $8.3\text{ m}\cdot\text{s}^{-1}$ and $10.8\text{ m}\cdot\text{s}^{-1}$ respectively, compared to the CuO/Al and CuO/TiB_2 , which burn at $4.3\text{ m}\cdot\text{s}^{-1}$ and $2.2\text{ m}\cdot\text{s}^{-1}$, respectively. The additive TiB_2 not only enhances the burn rate by $\sim 50\%$ compared to the CuO/Al reference sample but also exhibited $\sim 100\%$ lower ignition energy of 1.3 mJ ($\text{CuO/TiB}_2\text{-Al}$) and 0.033 mJ (CuO/Al-TiB_2) in comparison to unary fuel-based multilayers. Overall, this study shines light upon the utility of TiB_2 as an additive thin film to realize the ultimate goal of enhancing the ignitability and burn rate of CuO/Al thermites. The results demonstrated (i) a strong affinity of TiB_2 to oxygen that enhances CuO decomposition at temperature as low as $380\text{ }^\circ\text{C}$; (ii) a concomitant TiB_2 oxidation, to TiO , and B_2O_3 ; (iii)

continuation of Ti oxidation into TiO_2 depending upon the availability of the oxidizer; (iv) Al oxidation at high temperatures via liquid B_2O_3 as well as remaining gaseous oxygen. This study also highlights the criticality of the order of stacking of metallic layer in nanothermites. The reaction in CuO/Al-TiB₂ system was found to evolve rapider than CuO/TiB₂-Al (auto-ignition point is 380 °C against 445 °C for CuO/Al-TiB₂) but propagate less aggressively (slower flame propagation) due to the presence of Al in the TiB₂ grain boundaries which degrades the reactivity.

Funding Sources

C.R. received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grand agreement No. 832889 - PyroSafe). M.R. Z. was supported by Air Force Office of Scientific Research (AFOSR) and Army Research Office (ARO).

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors grateful acknowledge support from the European Research Council (H2020 Excellent Science) Researcher Award (grant 832889 – PyroSafe). This work was also supported by LAAS-CNRS technology platform, a member of Renatech network. The authors also acknowledge the help from Teresa Hungria and Claudie Josse for TEM lamina preparations and observations.

Appendix A. Supplementary data

Supplementary data to this article can be found online

References:

- (1) Dreizin, E. L.; Schoenitz, M. Mechanochemically Prepared Reactive and Energetic Materials: A Review. *J Mater Sci* **2017**, *52* (20), 11789–11809. <https://doi.org/10.1007/s10853-017-0912-1>.
- (2) Yetter, R. A.; Risha, G. A.; Son, S. F. Metal Particle Combustion and Nanotechnology. *Proceedings of the Combustion Institute* **2009**, *32* (2), 1819–1838. <https://doi.org/10.1016/j.proci.2008.08.013>.
- (3) Liang, D.; Liu, J.; Xiao, J.; Xi, J.; Wang, Y.; Zhou, J. Effect of Metal Additives on the Composition and Combustion Characteristics of Primary Combustion Products of B-Based Propellants. *J Therm Anal Calorim* **2015**, *122* (1), 497–508. <https://doi.org/10.1007/s10973-015-4750-6>.
- (4) Zhu, C.-G.; Wang, H.-Z.; Min, L. Ignition Temperature of Magnesium Powder and Pyrotechnic Composition. *Journal of Energetic Materials* **2014**, *32*. <https://doi.org/10.1080/07370652.2013.812162>.
- (5) Levashov, E.; Mukasyan, A.; Rogachev, A.; Shtansky, D. Self-Propagating High-Temperature Synthesis of Advanced Materials and Coatings. *International Materials Reviews* **2016**, *62*, 1–37. <https://doi.org/10.1080/09506608.2016.1243291>.
- (6) Wang, L. L.; Munir, Z. A.; Maximov, Y. M. Thermite Reactions: Their Utilization in the Synthesis and Processing of Materials. *JOURNAL OF MATERIALS SCIENCE* **1993**, *28* (14), 3693–3708. <https://doi.org/10.1007/BF00353167>.
- (7) Troianello, T. Precision Foil Resistors Used as Electro-Pyrotechnic Initiators. In *2001 Proceedings. 51st Electronic Components and Technology Conference (Cat. No.01CH37220)*; 2001; pp 1413–1417. <https://doi.org/10.1109/ECTC.2001.928019>.
- (8) Jr, T. W. B.; Simpson, R. L.; Gash, A. E.; Jr, J. H. S. Nano-Laminate-Based Ignitors. US7951247B2, May 31, 2011. <https://patents.google.com/patent/US7951247B2/en> (accessed 2022-11-13).
- (9) Kang, X.; Zhang, J.; Zhang, Q.; Du, K.; Tang, Y. Studies on Ignition and Afterburning Processes of KClO₄/Mg Pyrotechnics Heated in Air. *J Therm Anal Calorim* **2012**, *109* (3), 1333–1340. <https://doi.org/10.1007/s10973-011-1991-x>.
- (10) Fu, S.; Shen, R.; Zhu, P.; Ye, Y. Metal–Interlayer–Metal Structured Initiator Containing Al/CuO Reactive Multilayer Films That Exhibits Improved Ignition Properties. *Sensors and Actuators A: Physical* **2019**, *292*, 198–204. <https://doi.org/10.1016/j.sna.2019.04.019>.
- (11) Ahn, J. Y.; Kim, S. B.; Kim, J. H.; Jang, N. S.; Kim, D. H.; Lee, H. W.; Kim, J. M.; Kim, S. H. A Micro-Chip Initiator with Controlled Combustion Reactivity Realized by Integrating Al/CuO Nanothermite Composites on a Microhotplate Platform. *J. Micromech. Microeng.* **2015**, *26* (1), 015002. <https://doi.org/10.1088/0960-1317/26/1/015002>.
- (12) Pouchaïret, J.-L.; Rossi, C. PyroMEMS as Future Technological Building Blocks for Advanced Microenergetic Systems. *Micromachines* **2021**, *12* (2), 118. <https://doi.org/10.3390/mi12020118>.
- (13) Nicollet, A.; Lahiner, G.; Belisario, A.; Souleille, S.; Djafari-Rouhani, M.; Estève, A.; Rossi, C. Investigation of Al/CuO Multilayered Thermite Ignition. *Journal of Applied Physics* **2017**, *121* (3), 034503. <https://doi.org/10.1063/1.4974288>.

- (14) Bockmon, B.; Pantoya, M.; Son, S.; Asay, B. Burn Rate Measurements of Nanocomposite Thermites. In *41st Aerospace Sciences Meeting and Exhibit*; American Institute of Aeronautics and Astronautics. <https://doi.org/10.2514/6.2003-241>.
- (15) Li, S.; Guo, T.; Yao, M.; Song, J.; Ding, W.; Mao, Y.; Chen, J. Effect of Bismuth Oxide Particles Size on the Thermal Excitation and Combustion Properties of Thermite Systems. *ChemistryOpen* **2021**, *10* (4), 464–470. <https://doi.org/10.1002/open.202000358>.
- (16) Weir, C.; Pantoya, M. L.; Daniels, M. A. The Role of Aluminum Particle Size in Electrostatic Ignition Sensitivity of Composite Energetic Materials. *Combustion and Flame* **2013**, *160* (10), 2279–2281. <https://doi.org/10.1016/j.combustflame.2013.05.005>.
- (17) Rossi, C. Engineering of Al/CuO Reactive Multilayer Thin Films for Tunable Initiation and Actuation. *Prop., Explos., Pyrotech.* **2019**, *44* (1), 94–108. <https://doi.org/10.1002/prop.201800045>.
- (18) Wu, T. Unexpected Enhanced Reactivity of Aluminized Nanothermites by Accelerated Aging. *Chemical Engineering Journal* **2021**, *9*.
- (19) Wang, H.; Julien, B.; Kline, D. J.; Alibay, Z.; Rehwoldt, M. C.; Rossi, C.; Zachariah, M. R. Probing the Reaction Zone of Nanolaminates at $\sim\mu\text{s}$ Time and $\sim\mu\text{m}$ Spatial Resolution. *J. Phys. Chem. C* **2020**, *124* (25), 13679–13687. <https://doi.org/10.1021/acs.jpcc.0c01647>.
- (20) Meda, L.; Marra, G.; Galfetti, L.; Severini, F.; De Luca, L. Nano-Aluminum as Energetic Material for Rocket Propellants. *Materials Science and Engineering: C* **2007**, *27* (5), 1393–1396. <https://doi.org/10.1016/j.msec.2006.09.030>.
- (21) Richard A. Yetter. Progress towards Nanoengineered Energetic Materials. *Proceedings of the Combustion Institute* **2021**, *38* (1), 57–81.
- (22) Aly, Y.; Schoenitz, M.; Dreizin, E. L. Aluminum-Metal Reactive Composites. *Combustion Science and Technology* **2011**, *183* (10), 1107–1132. <https://doi.org/10.1080/00102202.2011.584090>.
- (23) DeLuca, L. T. Overview of Al-Based Nanoenergetic Ingredients for Solid Rocket Propulsion. *Defence Technology* **2018**, *14* (5), 357–365. <https://doi.org/10.1016/j.dt.2018.06.005>.
- (24) Ma, X.; Li, Y.; Hussain, I.; Shen, R.; Yang, G.; Zhang, K. Core–Shell Structured Nanoenergetic Materials: Preparation and Fundamental Properties. *Advanced Materials* **2020**, *32* (30), 2001291. <https://doi.org/10.1002/adma.202001291>.
- (25) Sambamurthi, J. K.; Price, E. W.; Sigman, R. K. Aluminum Agglomeration in Solid-Propellant Combustion. *AIAA Journal* **1984**, *22* (8), 1132–1138. <https://doi.org/10.2514/3.48552>.
- (26) Cohen, N. S. A Pocket Model for Aluminum Agglomeration in Composite Propellants. *AIAA Journal* **1983**, *21* (5), 720–725. <https://doi.org/10.2514/3.8139>.
- (27) Wang, H.; Kline, D. J.; Zachariah, M. R. In-Operando High-Speed Microscopy and Thermometry of Reaction Propagation and Sintering in a Nanocomposite. *Nat Commun* **2019**, *10* (1), 3032. <https://doi.org/10.1038/s41467-019-10843-4>.
- (28) Sullivan, K. T.; Piekielek, N. W.; Wu, C.; Chowdhury, S.; Kelly, S. T.; Hufnagel, T. C.; Fezzaa, K.; Zachariah, M. R. Reactive Sintering: An Important Component in the Combustion of Nanocomposite Thermites. *Combustion and Flame* **2012**, *159* (1), 2–15. <https://doi.org/10.1016/j.combustflame.2011.07.015>.
- (29) Chakraborty, P.; Zachariah, M. R. Do Nanoenergetic Particles Remain Nano-Sized during Combustion? *Combustion and Flame* **2014**, *161* (5), 1408–1416. <https://doi.org/10.1016/j.combustflame.2013.10.017>.
- (30) Aly, Y.; Dreizin, E. L. Ignition and Combustion of Al-Mg Alloy Powders Prepared by Different Techniques. *Combustion and Flame* **2015**, *162* (4), 1440–1447. <https://doi.org/10.1016/j.combustflame.2014.11.010>.
- (31) Aly, Y.; Schoenitz, M.; Dreizin, E. L. Ignition and Combustion of Mechanically Alloyed Al-Mg Powders with Customized Particle Sizes. *Combustion and Flame* **2013**, *160* (4), 835–842. <https://doi.org/10.1016/j.combustflame.2012.12.011>.

- (32) Hastings, D.; Rodriguez, N.; McCann, H.; Schoenitz, M.; Dreizin, E. L. Titanium-Boron Reactive Composite Powders with Variable Morphology Prepared by Arrested Reactive Milling. *Fuel* **2022**, *310*, 122313. <https://doi.org/10.1016/j.fuel.2021.122313>.
- (33) Chiu, L. H.; Nagle, D. C.; Bonney, L. A. Thermal Analysis of Self-Propagating High-Temperature Reactions in Titanium, Boron, and Aluminum Powder Compacts. *METALLURGICAL AND MATERIALS TRANSACTIONS A* **8**.
- (34) Vummidi Lakshman, S.; Gibbins, J. D.; Wainwright, E. R.; Weihs, T. P. The Effect of Chemical Composition and Milling Conditions on Composite Microstructure and Ignition Thresholds of AlZr Ball Milled Powders. *Powder Technology* **2019**, *343*, 87–94. <https://doi.org/10.1016/j.powtec.2018.11.012>.
- (35) Wainwright, E. R.; Weihs, T. P. Microstructure and Ignition Mechanisms of Reactive Aluminum–Zirconium Ball Milled Composite Metal Powders as a Function of Particle Size. *J Mater Sci* **2020**, *55* (29), 14243–14263. <https://doi.org/10.1007/s10853-020-05031-5>.
- (36) Shoshin, Y. L.; Dreizin, E. L. Particle Combustion Rates for Mechanically Alloyed Al–Ti and Aluminum Powders Burning in Air. *Combustion and Flame* **2006**, *145* (4), 714–722. <https://doi.org/10.1016/j.combustflame.2005.11.006>.
- (37) Wu, T.; Singh, V.; Julien, B.; Tenailleau, C.; Estève, A.; Rossi, C. Pioneering Insights into the Superior Performance of Titanium as a Fuel in Energetic Materials. *Chemical Engineering Journal* **2023**, *453*, 139922. <https://doi.org/10.1016/j.cej.2022.139922>.
- (38) Gany, A.; Netzer, D. W. Combustion Studies of Metallized Fuels for Solid-Fuel Ramjets. *Journal of Propulsion and Power* **1986**, *2* (5), 423–427. <https://doi.org/10.2514/3.22924>.
- (39) MACEK, A.; SEMPLE, J. Combustion of Boron Particles at Atmospheric Pressure. In *5th Propulsion Joint Specialist*; American Institute of Aeronautics and Astronautics. <https://doi.org/10.2514/6.1969-562>.
- (40) Guo, W.; Chang, S.; Cao, J.; Wu, L.; Shen, R.; Ye, Y. Precisely Controlled Reactive Multilayer Films with Excellent Energy Release Property for Laser-Induced Ignition. *Nanoscale Res Lett* **2019**, *14* (1), 301. <https://doi.org/10.1186/s11671-019-3124-6>.
- (41) Zapata, J.; Nicollet, A.; Julien, B.; Lahiner, G.; Esteve, A.; Rossi, C. Self-Propagating Combustion of Sputter-Deposited Al/CuO Nanolaminates. *Combustion and Flame* **2019**, *205*, 389–396. <https://doi.org/10.1016/j.combustflame.2019.04.031>.
- (42) Adams, D. P. Reactive Multilayers Fabricated by Vapor Deposition: A Critical Review. *Thin Solid Films* **2015**, *576*, 98–128. <https://doi.org/10.1016/j.tsf.2014.09.042>.
- (43) Salvagnac, L.; Assie-Souleille, S.; Rossi, C. Layered Al/CuO Thin Films for Tunable Ignition and Actuators. *Nanomaterials* **2020**, *10* (10), 2009. <https://doi.org/10.3390/nano10102009>.
- (44) Julien, B.; Dubreuil, P.; Josse, C.; Salvagnac, L.; Pelloquin, S.; Esteve, A.; Rossi, C. Effect of Substrate-Induced Localized Stress on the Combustion Properties of Al/CuO Reactive Multilayer Films. *Thin Solid Films* **2021**, *740*, 139000. <https://doi.org/10.1016/j.tsf.2021.139000>.
- (45) T. P. Weihs. Self-Propagating Reactions in Multilayer Materials. In *Handbook of Thin Film Process Technology*; D.A. Glocker, S.I. Shah, Eds.; IOP Publishing, 1998.
- (46) Singh, V. and J., Baptiste and Salvagnac, Ludovic and Pelloquin, Sylvain and Hungria, Teresa and Josse, Claudie and Belhaj, Mohamed and Rossi, Carole. Influence of Process Parameters on Energetic Properties of Sputter-Deposited Al/CuO Reactive Multilayers. *Nanotechnology* **2022**.
- (47) Biswas, P.; Xu, F.; Ghildiyal, P.; Zachariah, M. R. In-Situ Thermochemical Shock-Induced Stress at the Metal/Oxide Interface Enhances Reactivity of Aluminum Nanoparticles. *ACS Appl. Mater. Interfaces* **2022**, *14* (23), 26782–26790. <https://doi.org/10.1021/acsami.2c05412>.
- (48) Marín, L.; Nanayakkara, C. E.; Veyan, J.-F.; Warot-Fonrose, B.; Joulie, S.; Estève, A.; Tenailleau, C.; Chabal, Y. J.; Rossi, C. Enhancing the Reactivity of Al/CuO Nanolaminates by Cu Incorporation at the

- Interfaces. *ACS Appl. Mater. Interfaces* **2015**, 7 (22), 11713–11718.
<https://doi.org/10.1021/acsami.5b02653>.
- (49) Julien, B.; Cure, J.; Salvagnac, L.; Josse, C.; Esteve, A.; Rossi, C. Integration of Gold Nanoparticles to Modulate the Ignitability of Nanothermite Films. *ACS Appl. Nano Mater.* **2020**, 3 (3), 2562–2572.
<https://doi.org/10.1021/acsanm.9b02619>.
- (50) Mitterbauer, C.; Kothleitner, G.; Hofer, F. Comparative Electron Energy-Loss Near-Edge Fine Structure Investigations Of Titanium Oxides. *Microsc Microanal* **2003**, 9 (S02), 834–835.
<https://doi.org/10.1017/S1431927603444176>.
- (51) Zhao, W.; Wang, H.; Kline, D. J.; Wang, X.; Wu, T.; Xu, J.; Ren, H.; Zachariah, M. R. Influence of Titanium Addition on Performance of Boron-Based Thermites. *Chemical Engineering Journal* **2022**, 134837. <https://doi.org/10.1016/j.cej.2022.134837>.
- (52) Bakhit, B.; Palisaitis, J.; Thörnberg, J.; Rosen, J.; Persson, P. O. Å.; Hultman, L.; Petrov, I.; Greene, J. E.; Greczynski, G. Improving the High-Temperature Oxidation Resistance of TiB₂ Thin Films by Alloying with Al. *Acta Materialia* **2020**, 196, 677–689.
<https://doi.org/10.1016/j.actamat.2020.07.025>.