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# Superior Ignition and Combustion Performance of TiB<sub>2</sub> Integrated Al/CuO Nanothermites

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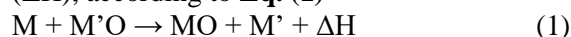
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**Abstract:** Nanothermites, composed of a fuel and an oxidizer, belong to a class of energetic materials that release energy as a result of a redox reaction. Reactive multilayer films, also referred to as nanolaminates, have been widely utilized as a prevalent technology in this field. Al stands out as a prominent fuel choice due to its cost-effectiveness, abundance and high energy density. Constrained by its high ignition point, there has been a strong interest in modifying Al-based thermites through chemical alterations. This work explored the influence of nano-TiB<sub>2</sub> addition to CuO/Al and examined the effects on the overall energetic properties.

## I. INTRODUCTION

Thermite reactions have long been explored and applied to high temperature/high heat applications owing to the release of a large amount of energy upon a simultaneous oxidation-reduction reaction. Composed of a metal (or metalloid, M) and an oxidizer (metal oxide, M'O), the chemical reaction is highly dependent on oxygen transport from the latter to the former resulting in high exothermic output ( $\Delta H$ ), according to **Eq. (1)**



Several technologies have been applied at nano-scale to enhance the energy output and alter the reactivity of the thermite. One such common structure is reactive multilayer films (RMF), where layer-by-layer structures are prepared primarily using physical vapor deposition in an alternating manner according to a specific stoichiometry and equivalence ratio.

Aluminum has gained its place as one of the most used fuel in nanoscale energetic composites over the past few decades of research. This comes as a result of its advantages such as being cheap, abundant, stable and having high specific energy density. However, since it suffers from high ignition point, several research efforts including pre-treatment, modification of native oxide shell and use of alternative oxides<sup>1-3</sup>, have been directed towards improving its ignition and combustion performance. Binary fuels have been gaining momentum in such area over the past years. For example, Al-Zr binary fuel reportedly possesses much lower ignition thresholds than their single fuel counterpart<sup>4</sup>.

In this work, TiB<sub>2</sub>, a material possessing a high oxygen affinity and low sinter ability is

used alongside Al, together with a strong oxidizer such as CuO, to improve its ignition and combustion performance. It was found that TiB<sub>2</sub> integrated CuO/Al nanothermites exhibit superior ignition performance demonstrating a ~100% shorter ignition delay compared to CuO/Al<sup>5</sup>. We additionally show a two-fold improvement in the burn rate in CuO/Al-TiB<sub>2</sub> compared to CuO/Al.

## II. MATERIALS AND METHODS

### A. Fabrication of nanolaminates

*Table 1: Summary of samples*

Sample name	Loading (%)	Thickness (nm)	
		Al	TiB <sub>2</sub>
CuO/Al	0	200	-
CuO/Al-TiB <sub>2</sub> 25%	25	159	25
CuO/Al-TiB <sub>2</sub> 50%	50	106	49
CuO/Al-TiB <sub>2</sub> 62.5%	62.5	80	62
CuO/Al-TiB <sub>2</sub> 75%	75	53	74
CuO/TiB <sub>2</sub>	100	-	100

CuO/Al-TiB<sub>2</sub> RMF structures are deposited using D.C. magnetron sputtering in an equipment from Thin Film Equipment, Italy. The sputtering targets (Al, Cu, TiB<sub>2</sub>) are purchased from Neyco, France and used as is. Further details about the manufacturing process can be found in our previous works<sup>5,6</sup>. A 10-bilayers (BL) film deposition begins with CuO, followed by Al and TiB<sub>2</sub>. Various Al-TiB<sub>2</sub> concentration distribution, represented by TiB<sub>2</sub> loading, resulting in the preparation of several configurations of CuO/Al-TiB<sub>2</sub> are compared

against the reference CuO/Al sample. **Table 1** summarizes the corresponding thicknesses of the films for each sample. CuO thickness is set to 200 nm. The deposition is carried out on 4-inch standard glass wafers patterned for contact pads and well as the Ti resistive element using optical photolithography. Free-standing RMF were also prepared using a lift-off process.

### B. Material Characterization

The morphology and chemical composition of the RMF as well as their interfaces were analyzed using scanning electron microscopy (SEM) and energy dispersive X-Ray spectroscopy (EDX) using FEI Helios NanoLab DualBeam FIB-SEM. Thermal analysis was carried out using differential scanning calorimetry (DSC) utilizing a NETZSCH DSC 404 F3 Pegasus system. The DSC trace was normalized to the foil mass, typically 5 mg, and noted from room temperature to 950 °C under a constant flow of Ar.

### C. Characterization of energetic properties

The ignition and combustion tests are carried out using Joule's resistive heating in a D.C. electrical setup. A constant power of 6.125 W is used to perform each test to maintain the consistency. Ten tests are done and a mathematical average is reported. The microscopic and macroscopic videos of combustion are collected and processed to determine the propagation rate.

## III. RESULTS AND DISCUSSIONS

### A. Energetic behavior

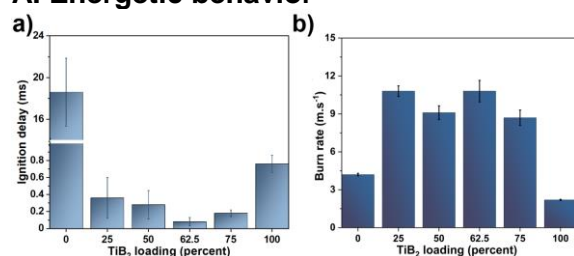


FIG. 1. a) Ignition delay b) Propagation rate as a function of TiB<sub>2</sub> loading

**Figure 1a** shows the variation in ignition delay as a function of TiB<sub>2</sub> loading. Compared to CuO/Al igniting at  $18.6 \pm 3.26$  ms, all configurations of CuO/Al-TiB<sub>2</sub> demonstrated a reduction in the ignition delay by over 95%. 25% shows a massive drop to  $0.36 \pm 0.240$  ms, while 50%, 62.5% and 75% recorded  $0.28 \pm 0.166$  ms,  $0.08 \pm 0.05$  and  $0.18 \pm 0.039$  ms ignition delays respectively. Specifically, CuO/Al-TiB<sub>2</sub> 62.5%

exhibited a ~100% better ignition time against the reference CuO/Al sample. It is worth noting that CuO/Al-TiB<sub>2</sub> system noted a ~50% improvement in the ignition delays against CuO/TiB<sub>2</sub> sample. **Figure 1b** illustrates the change in the burn rates with loading. Whereas CuO/Al burns at  $4.2 \pm 0.1$  m.s<sup>-1</sup>, CuO/Al-TiB<sub>2</sub> 25% propagated at  $10.8 \pm 0.42$  m.s<sup>-1</sup>, 50% at  $9.1 \pm 0.54$  m.s<sup>-1</sup>, 62.5% at  $10.8 \pm 0.85$  m.s<sup>-1</sup> and 75% at  $8.7 \pm 0.61$  m.s<sup>-1</sup>. These burn rate values are ~4 times better than CuO/TiB<sub>2</sub>, which propagated at a mere  $2.2 \pm 0.04$  m.s<sup>-1</sup>. While each CuO/Al-TiB<sub>2</sub> shows an improvement in the propagation rates by a factor of 2, they exhibit comparable burn rates among themselves.

### B. Thermal behavior

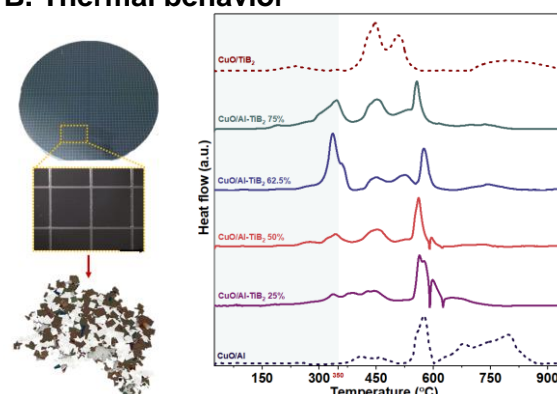


FIG. 2. Thermite multilayer foils and DSC scans of CuO/Al, CuO/TiB<sub>2</sub> and CuO/Al-TiB<sub>2</sub>

Ignition behavior can be understood to some extent from the low temperature oxidation of the thermites. **Figure 2** shows the DSC traces obtained from CuO/Al, CuO/TiB<sub>2</sub> and each configuration of CuO/Al-TiB<sub>2</sub>. One of the most striking features is the early oxidation onset in CuO/Al-TiB<sub>2</sub>, around ~300 °C, against CuO/Al, which does not show any significant exothermic event before ~370 °C. It must be noted that CuO oxygen release temperature is nearly 350 °C. Furthermore, while each concentration of CuO/Al-TiB<sub>2</sub> undergoes similar scheme of reaction, they distinctively differ in the amount of heat released in the first exothermic event. Rapider is the redox reaction, shorter is the time leading up to ignition as shown in Section 3A.

### C. Imaging of the combustion product

To fully understand the reasons for the improvement in the propagation rate of CuO/Al-TiB<sub>2</sub> and the role of TiB<sub>2</sub>, combustion product residues were subjected to SEM-EDX. **Figure 3** shows the SEM micrographs obtained from CuO/Al, CuO/TiB<sub>2</sub> and different CuO/Al-TiB<sub>2</sub> samples. As can be seen in **Figure 3a**, large alumina agglomerates are found on the surface.

As  $\text{TiB}_2$  is integrated into CuO/Al system, the size of the agglomerates decreases significantly. Furthermore, each CuO/Al- $\text{TiB}_2$  sample is characterized by the formation of oxides of B and Ti. It must be noted that  $\text{B}_2\text{O}_3$  is liquid above  $\sim 450^\circ\text{C}$ . This results in the formation of a surface matrix composed of  $\text{TiO}_x\text{-B}_2\text{O}_3$ . Another striking feature is the growing presence of oval shaped Cu particles as  $\text{TiB}_2$  concentration goes up. These come up as a result of rapid reduction of CuO to Cu via  $\text{TiB}_2$ . It should be noted that  $\text{TiB}_2$  oxidation on CuO surface is reportedly aggressive<sup>5</sup>.

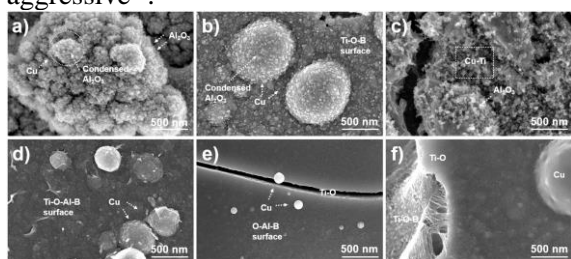


FIG. 3. SEM images of the combustion product collected from a) CuO/Al; CuO/Al- $\text{TiB}_2$  at loadings b) 25% c) 50% d) 62.5% e) 75%; f) CuO/ $\text{TiB}_2$

#### D. Combustion mechanism

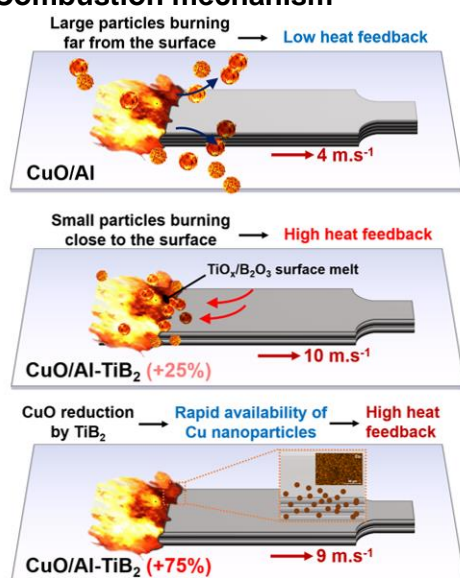


FIG. 4. Schematics comparing the combustion mechanism in CuO/Al, CuO/Al- $\text{TiB}_2$  25% (Al-rich) and 75% ( $\text{TiB}_2$ -rich) nanothermites

**Figure 4** displays a simple schematic to explain the scheme of the reaction driving the self-sustained propagation in CuO/Al and CuO/Al- $\text{TiB}_2$ . Since Al burns in vapor phase, a significant amount of heat is lost to the environment because of Al droplets' low surface proximity. This leads to a minimal heat transfer to the unburnt thermite. When  $\text{TiB}_2$  loading is

increased to 25%, the oxidation leads to the formation of a surface melt composed of amorphous  $\text{B}_2\text{O}_3$  and highly porous  $\text{TiO}_x$ . This melt effectively traps burning Al particles ensuring better heat feedback. Furthermore, CuO reduction to Cu via  $\text{TiB}_2$  serves as an additional heat source, attributed to its higher thermal conductivity compared to CuO. This results in much higher propagation rates in CuO/Al- $\text{TiB}_2$ .

#### IV. CONCLUSION

Reactive multilayer films were fabricated through sputter deposition, and their energetic characteristics were examined. The low-temperature exothermic events were observed to impact the ignition behavior exhibited by each sample. An innovative ternary system, CuO/Al- $\text{TiB}_2$  62.5%, exhibited superior ignition performance with an approximately 100% reduction in the ignition delay. The combustion behavior was governed by heterogeneous gas-condensed phase reactions. Findings demonstrated a twofold improvement in burn rates compared to the CuO/Al reference sample. This study underscores the potential of ternary systems in enhancing ignition performance in reactive multilayer films.

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