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Superior Ignition and Combustion Performance of TiB₂ Integrated Al/CuO Nanothermites

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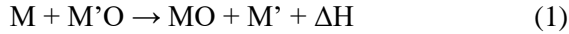
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Abstract: Nanothermites, composed of a fuel and an oxidizer, belong to a class of energetic materials that release energy as a result of a redox reaction. Reactive multilayer films, also referred to as nanolaminates, have been widely utilized as a 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-TiB₂ 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 (ΔH), 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 oxides¹⁻³, 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 counterpart⁴.

In this work, TiB₂, 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 TiB₂ integrated CuO/Al nanothermites exhibit superior ignition performance demonstrating a ~100% shorter ignition delay compared to CuO/Al⁵. We additionally show a two-fold improvement in the burn rate in CuO/Al-TiB₂ compared to CuO/Al.

II. MATERIALS AND METHODS

A. Fabrication of nanolaminates

Table 1: Summary of samples

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

CuO/Al-TiB₂ RMF structures are deposited using D.C. magnetron sputtering in an equipment from Thin Film Equipment, Italy. The sputtering targets (Al, Cu, TiB₂) are purchased from Neyco, France and used as is. Further details about the manufacturing process can be found in our previous works^{5,6}. A 10-bilayers (BL) film deposition begins with CuO, followed by Al and TiB₂. Various Al-TiB₂ concentration distribution, represented by TiB₂ loading, resulting in the preparation of several configurations of CuO/Al-TiB₂ 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

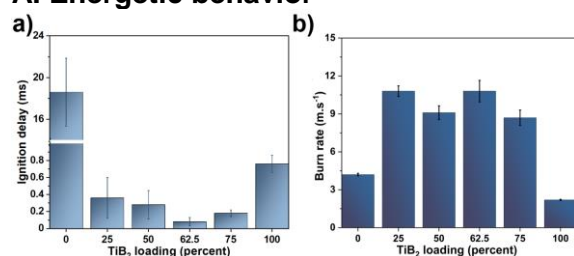


FIG. 1. a) Ignition delay b) Propagation rate as a function of TiB₂ loading

Figure 1a shows the variation in ignition delay as a function of TiB₂ loading. Compared to CuO/Al igniting at 18.6 ± 3.26 ms, all configurations of CuO/Al-TiB₂ demonstrated a reduction in the ignition delay by over 95%. 25% shows a massive drop to 0.36 ± 0.240 ms, while 50%, 62.5% and 75% recorded 0.28 ± 0.166 ms, 0.08 ± 0.05 and 0.18 ± 0.039 ms ignition delays respectively. Specifically, CuO/Al-TiB₂ 62.5%

exhibited a ~100% better ignition time against the reference CuO/Al sample. It is worth noting that CuO/Al-TiB₂ system noted a ~50% improvement in the ignition delays against CuO/TiB₂ sample. **Figure 1b** illustrates the change in the burn rates with loading. Whereas CuO/Al burns at 4.2 ± 0.1 m.s⁻¹, CuO/Al-TiB₂ 25% propagated at 10.8 ± 0.42 m.s⁻¹, 50% at 9.1 ± 0.54 m.s⁻¹, 62.5% at 10.8 ± 0.85 m.s⁻¹ and 75% at 8.7 ± 0.61 m.s⁻¹. These burn rate values are ~4 times better than CuO/TiB₂, which propagated at a mere 2.2 ± 0.04 m.s⁻¹. While each CuO/Al-TiB₂ shows an improvement in the propagation rates by a factor of 2, they exhibit comparable burn rates among themselves.

B. Thermal behavior

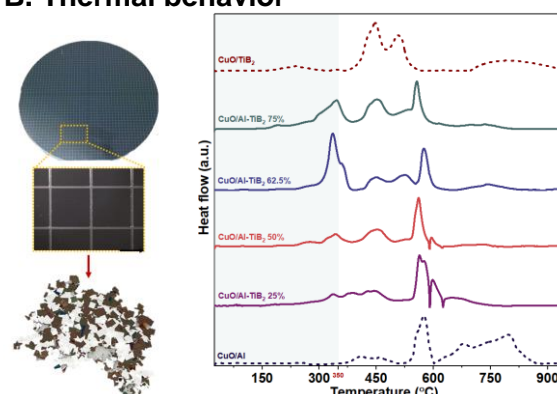


FIG. 2. Thermite multilayer foils and DSC scans of CuO/Al, CuO/TiB₂ and CuO/Al-TiB₂

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/TiB₂ and each configuration of CuO/Al-TiB₂. One of the most striking features is the early oxidation onset in CuO/Al-TiB₂, 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-TiB₂ 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-TiB₂ and the role of TiB₂, combustion product residues were subjected to SEM-EDX. **Figure 3** shows the SEM micrographs obtained from CuO/Al, CuO/TiB₂ and different CuO/Al-TiB₂ samples. As can be seen in **Figure 3a**, large alumina agglomerates are found on the surface.

As TiB_2 is integrated into CuO/Al system, the size of the agglomerates decreases significantly. Furthermore, each CuO/Al- TiB_2 sample is characterized by the formation of oxides of B and Ti. It must be noted that B_2O_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 TiB_2 concentration goes up. These come up as a result of rapid reduction of CuO to Cu via TiB_2 . It should be noted that TiB_2 oxidation on CuO surface is reportedly aggressive⁵.

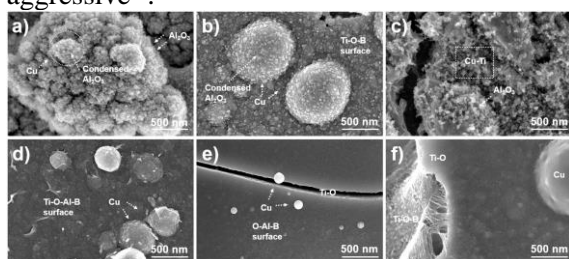


FIG. 3. SEM images of the combustion product collected from a) CuO/Al; CuO/Al- TiB_2 at loadings b) 25% c) 50% d) 62.5% e) 75%; f) CuO/ TiB_2

D. Combustion mechanism

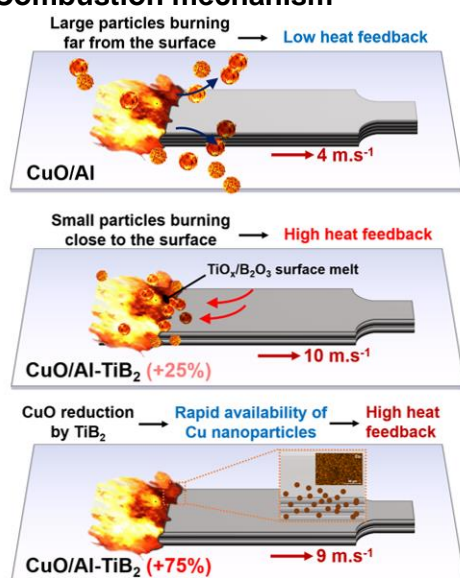


FIG. 4. Schematics comparing the combustion mechanism in CuO/Al, CuO/Al- TiB_2 25% (Al-rich) and 75% (TiB_2 -rich) nanothermites

Figure 4 displays a simple schematic to explain the scheme of the reaction driving the self-sustained propagation in CuO/Al and CuO/Al- 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 TiB_2 loading is

increased to 25%, the oxidation leads to the formation of a surface melt composed of amorphous B_2O_3 and highly porous TiO_x . This melt effectively traps burning Al particles ensuring better heat feedback. Furthermore, CuO reduction to Cu via 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- 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- 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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