Influence of Triphenylphosphine-Coated Aluminum Nanoparticles on the Combustion Dynamics of Al/CuO Nanothermites Mesh in Confined Spaces

Xin-Rong Lu[a], Ming-Hsun Wu[a,*], Ying-Shou Cheng[b] and Chao-Wei Huang[b]
[a]National Cheng Kung University, Department of Mechanical Engineering, Tainan, Taiwan
[b]National Cheng Kung University, Department of Engineering Science, Tainan, Taiwan

1 Introduction

Aluminum-based nanothermites are often enhanced with a passivation layer on aluminum nanoparticles (Al NPs) to mitigate premature oxidation. Although such coatings stabilize the aluminum core against atmospheric oxygen, they also modify combustion behavior by altering ignition thresholds, burn rates, and energy release profiles. Moreover, the decomposition of the passivation layer and its interactions with other nanothermite constituents introduce additional complexity into the combustion process. Thus, a detailed understanding of how these passivation layers affect nanothermite combustion is essential for optimizing energetic performance.

Triphenylphosphine (PPh_3) has been explored as a protective coating for Al NPs due to its high stability and hydrophobicity, which are advantageous for long-term storage. Cui et al. [1] demonstrated a "one pot" wet-chemical method for synthesizing Al NPs coated with PPh_3 (Al@PPh_3), forming a thin protective layer that enhances storage stability and minimizes oxidation. However, this coating may also alter combustion dynamics, necessitating further investigation. In previous work, Lu et al. [2] reported distinctive burning behaviors in powder-form Al/CuO nanothermites containing Al@PPh_3. Strand burner tests revealed that at low Al@PPh3 proportions, the coating enhances the burn rate,achieving reaction front propagation velocities of ~ 400 m/s. However, higher proportions of Al@PPh_3 inhibited the thermite reaction between Al and CuO, ultimately suppressing combustion ("No Go").

The purpose of this study is to further evaluate the effect of incorporating Al@PPh_3 into mesh-form Al/CuO nanothermites in confined spaces. The nanothermite are asssembled via electrophoretic deposition (EPD) method on the copper mesh. The method enables uniform and scalable deposition of energetic materials onto a structured substrate. Previous work demonstrated the successful fabrication of Al/CuO nanothermite wires using EPD, with maximum combustion speeds of 43.8 cm/s in open space [3]. To improve scalability and practicality, CuO nanowires were instead grown on a copper mesh, providing a larger reactive surface area for enhanced combustion performance. The EPD method was then employed to assemble Al/CuO nanothermites onto this structured copper mesh.

Variation in thermite composition affect gas generation, temperatures, and reaction propagation speeds, which in turn influences their suitability for different applications [4]. Owing to their relatively high gas generation, Al/CuO nanothermites have been considered for propulsion systems. In confined

Correspondence to: minghwu@ncku.edu.tw

spaces, rapid combustion produces pressure waves that may be harnessed for propulsion. Hence, understanding the pressure evolution during combustion is critical for assessing the feasibility of these formulations.

This work aims to elucidate the influence of triphenylphosphine-coated aluminum on the combustion performance of mesh-form Al/CuO nanothermites. In particular, the effects of the PPh_3 passivation layer on burn rates and pressure dynamics in structured nanothermite meshes are examined.

2 Experimental Setup

The fabrication of the nanothermite mesh began with growing CuO nanowires (NWs) on a copper mesh via thermal oxidation. The copper mesh was cut to dimensions of 1 cm × 8 cm and cleaned by immesrions in a 35 wt% HCl solution for one minute to remove surface containinants. After a deionized water rinse and two minutes of sonication, the cleaned copper mesh was thermally oxidized in a high-temperature furnace (F-11-28, Tender) at 550°C for two hours under continuous air purge, resulting in the uniform formation CuO nanowires on the mesh wire surface as shown in Fig. 1(a).

To assess the influence of PPh_3 on reaction propagation in the nanothermite mesh, three Al NP formulations were prepared: (1) a 0% Al@PPh_3 mixture containing only commercial aluminum powder (50 nm with a native oxide layer, Bojun), (2) a 50% Al@PPh_3 mixture containing a 1:1 ratio of commercial aluminum powder and Al@PPh_3 NPs, and (3) a 100% Al@PPh_3 mixture consisting solely of Al@PPh_3 NPs. The Al@PPh_3 NPs were synthesized in-house using a precursor reduction method [2], yielding particles with a nominal size of 58 nm and a PPh_3 layer thickness of approximately 2.5 nm.

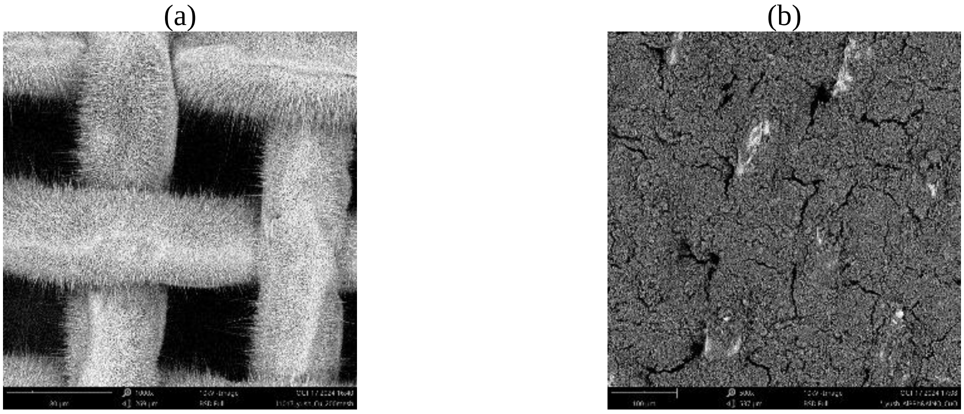

Figure 1 SEM image of the 200 mesh CuO grid (a) before and (b) after EPD of 50% Al@PPh_3 aluminum nanoparticles.

The deposition of Al NP mixture onto the CuO-coated copper mesh was performed using the EPD method. The prepared aluminum powders were dispersed in an ethanol solution at a concentration of 3 mg/mL and ultrasonically agitated to ensure uniform dispersion. The CuO nanowire blanketed copper mesh was immersed in the suspension. Al NPs, possessing a positive surface charge when dispersed in the ethanol solution, migrated towards mesh wires as a 60 V electric field was applied across the medium, where the copper core served as the negative electrode Fig. 1(b) showed the microscopic images of the copper grid before and after EPD.

A specialized combustion fixture was designed to evaluate combustion performance in confined spaces. The fixture consisted of two polycarbonate (PC) plates and a copper gasket that together formed an enclosed chamber to house the structured nanothermite (Fig. 2(a)). The mesh was positioned within a groove in the copper gasket, and the assembly was secured using flanges to ensure a sealed environment. An igniter and the 4 pressure taps, spaced at 2 cm intervals as shown in Figure 2(b), allowed detailed monitoring of pressure evolution during the reaction. Ignition was achieved using an electric match.

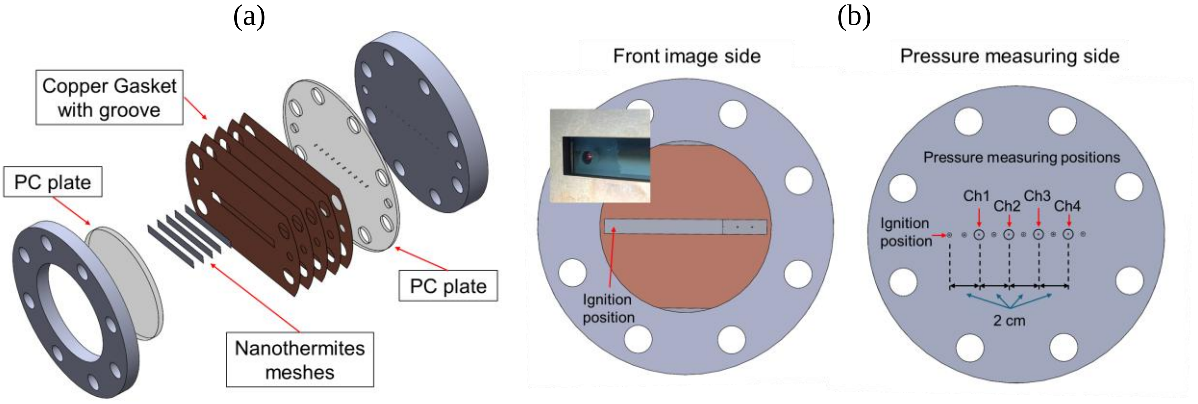

Figure 2: Confined space nanothermites meshes combustion fixture (a) Machinery exploded figure. (b) Schematic diagram of ignition position and pressure measuring position.

For burn rate tests, a digital delay signal generator (DG535, Stanford Research Systems) synchronized ignition with high-speed camera imaging and pressure data collection. Dynamic pressure transducers (113B series, PCB Piezotronics) connected via a pressure transducer signal conditioner (482, PCB Piezotronics) to a high-speed oscilloscope (DSO3024, Keysight) enabled precise recording of pressure variations. Pressure transducers were installed at 4, 6, and 8 cm downstream from the ignition position (Channels 2, 3, and 4, respectively). A color high-speed camera (MiroLab 310, Vision Research) simultaneously captured the reaction propagation, permitting accurate determination of burn rates and insights into combustion behavior.

3 Results and Discussion

Table 1 summarizes the combustion outcomes for various compositions and mesh layer configurations, indicating whether the reaction was self-sustaining ("Go") or failed to propagate ("No Go"). These results underscore the combined effects of Al@PPh_3 proportion and the surface-to-volume ratio on reaction sustainability in confined spaces. Notably, only the 0% and the 5-layer 50% Al@PPh_3 configurations produced self-sustaining combustion, allowing further analysis of burn rates and pressure dynamics. In contrast, the nanothermite composed entirely of 100% Al@PPh_3 NPs failed to propagate, even when stacked in five layers within the confined space, although open-environent tests confirmed its ignitability with a direct torch flame. These observations suggests that the protective PPh_3 layer significantly hinders reaction propagation in confined environments, likely due to its influence on heat transfer and reaction kinetics.

Table 1: Self-sustainability of reaction in nanothermites mesh.

Sample	1 layer	5 layer
0% Al@PPh_3	Go	Go
50% Al@PPh_3	No go	Go
100% Al@PPh_3	No go	No go

Additionally, while a single-layer 50% Al@PPh_3 nanothermite mesh did not sustain combustion, a five-layer configuration did. This indicates a crucial interplay between heat generation and heat loss rates affecting reaction propagation in the confined setup. As the number of layers increases, the reduced surface-to-volume ratio minimizes heat loss to the surroundings, thereby facilitating sustained combustion. Similar influence on the reaction propagation in powder-form nanothermites have been found in Ref. [5]. Conversely, a higher proportion of Al@PPh_3 NPs reduces the overall heat generation rate, making sustained reaction propagation more difficult.

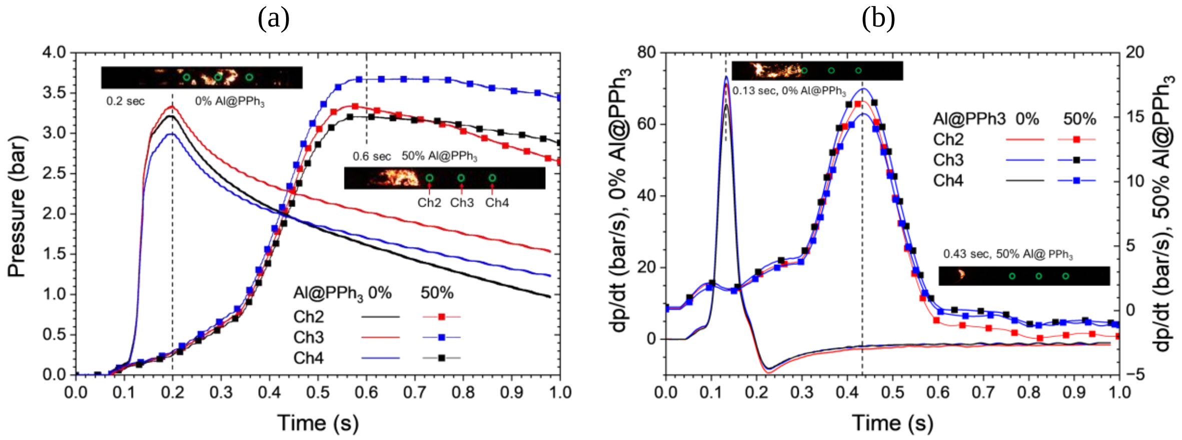

Figure 3: The pressure-time relationship of three measured pressure points during the confined space combustion of (a) 5 layers Al@PPh_3 50% nanothermites meshes (b) 5 layers Al@PPh_3 0% nanothermites meshes.

Figure 3(a) shows pressure-time profiles measured at 4, 6, and 8 cm downstream from the ignition point for five-layer samples of both 0% and 50% Al@PPh_3 nanothermites. The corresponding pressure derivatives are depicted in Fig. 3(b). Time zero in the charts represents the moment the triggering voltage was sent to the electric match. A consistent, minor pressure increase of 0.035 bar was observed at 0.07 seconds, corresponding to the ignition of the electric match, even though it is barely visible on the figure. For self-sustaining reactions, the pressure continued to rise. In the 0% Al@PPh_3 sample, a sharp pressure surge began at around 0.1 seconds and peaked near 0.2 seconds. In contrast, the pressure rise for the 50% Al@PPh_3 thermite was significantly slower, with a delayed major pressure surge occurring at around 0.3 seconds and peaking at approximately 0.58 seconds.

High-speed visualization revealed that in both formulations, the visible reaction front had not reached the first operating pressure tap (Ch 2) at the time of peak pressure rise. In the 50% Al@PPh_3 sample, the visible reaction front had traveled only 3 cm downstream from the ignition point when the peak pressure was recorded. The pressure signals from the three channels exhibited only slight time differences. Analysis of the time lag between Ch3 and Ch4 determined that the pressure wave traveled at 12.5 m/s in the 0% Al@PPh_3 sample, an order of magnitude faster than the 1.3 m/s observed in the 50% Al@PPh_3 meshes. These results highlight the inhibitory effects of PPh_3 on reaction propagation. Interestingly, despite this inhibition, the peak pressure in the 50% Al@PPh_3 case was slightly higher than that in the PPh_3-free meshes. This pressure enhancement is attributed to additional gas generation from PPh_3 decomposition. The increased gas production also contributes to a prolonged pressure plateau near the peak for the 50% Al@PPh_3 nanothermite.

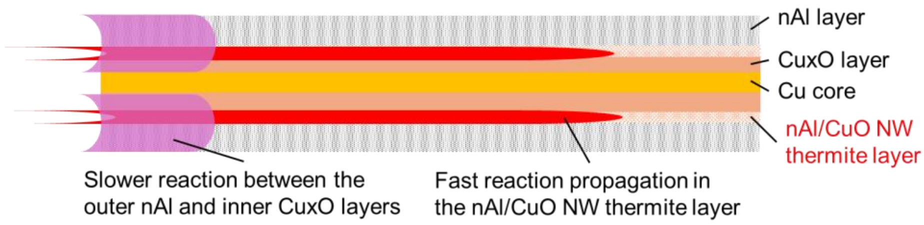

Figure 4: The combustion mechanism of nanothermites meshes in confined space.

It is also worth noting that the pressure traces in Fig. 3(b) revealed three distinct stages of pressure rise for the 50% Al@PPh$_3$ nanothermite, compared to only two stages in the 0% Al@PPh$_3$ samples. This behavior stems from the multi-layered structure of the nanothermite mesh wires, as illustrated in Fig. 4. The nanothermite mesh wire comprises a copper core, copper oxides shells, a nanothermite layer where Al NPs and CuO nanowires are intimately interwoven, and an outer layer of deposited Al NPs. The combustion process mirrors this structural hierarchy in sequential stages. Ininitially, a rapid redox reaction occurs within the nanothermite layer, where the short diffusion distance between the Al NPs and CuO nanowires (on the order of tens of nanometers) lead to high temperature and intense gas generation, which in turn drives a convective combustion wave through the confined space. Subsequently, this high-speed combustion front ignites reactions between the outer nano-aluminum powder layer and the underlying copper oxide layers. In this secondary stage, the reaction rate is limited by the larger diffusion length and slower inter-diffusion of reactants. This results in a more gradual yet sustained burn. The PPh$_3$ coating on the Al NPs introduces further complexity. Its endothermic decomposition absorbs heat, delaying the thermite redox reaction, while the resulting hydrocarbon byproducts may consume oxygen. This additional effect introduces an extra temporal offset in the reaction sequence, thereby contributing to the intermediate stage observed in the 50% AlPPh$_3$ pressure trace.

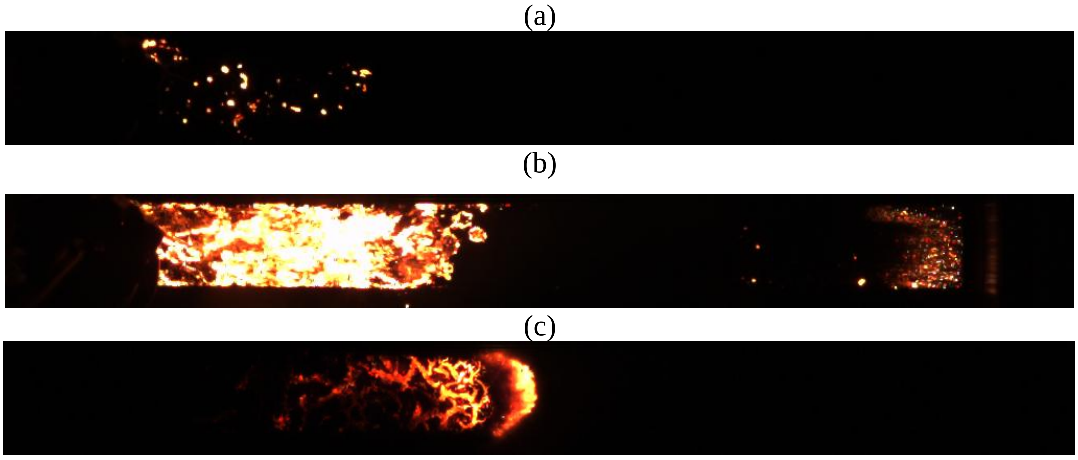

Figure 5: Visible reaction zone structure in 5 layers of 0% Al@PPh$_3$ nanothermite meshes at (a) 0.115 sec, (b) 0.14 sec, and (c) in 50% Al@PPh$_3$ meshes at 1 sec after trigger.

High-speed visualization supports this interpretation. Sporadic, sparkling particles ejected far downstream from the primary reaction front (Figs. 5(a) and 5(b)) coincide with the onset of the initial pressure rise. In the 0% Al@PPh$_3$ sample, the initial convective wave rapidly initiated subsequent thermite reactions throughout the entire mesh. In contrast, the presence of PPh$_3$ resulted in an intermediate stage associated with its decomposition. The typical reaction front structures for the 0% and 50% Al@PPh$_3$ cases are shown in Figs. 5(b) and (c), respectively. The detachment of a parabolic reaction front from the upstream, web-like reaction zone for the samples with PPh$_3$ (Fig. 5(c)) may indicate the combustion of hydrocarbons generated by PPh$_3$ decomposition

Reaction front propagation velocities during the later thermite reaction stages were determined using high-speed visualization images. The results indicate that the reaction propagated at 298 mm/s in the five-layer 0% Al@PPh$_3$ nanothermite, while its single-layer counterpart burned at 188 mm/s, highlighting the impact of surface-to-volume ratio for reaction propagation in the confined space. On the other hand, the five-layer 50% Al@PPh$_3$ nanothermite displayed a significantly lower burn rate of 45 mm/s. Notably, these later-stage propagation velocities are considerably slower than the initial convective burning velocities inferred from the pressure traces. The results also confirmed that the incorporation of Al@PPh$_3$ decelerates the combustion process at both stages.

4 Conclusion

This study examined the combustion dynamics of Al/CuO nanothermite meshes containing triphenylphosphine-coated aluminum nanoparticles (Al@PPh$_3$) in confined spaces. The presence of Al@PPh$_3$ significantly delayed ignition due to the protective layer, which had to be decomposed before aluminum could react with copper oxide. The combustion process unfolded in multiple stages, beginning with an initial rapid convective burn within the nanothermite layer. For the PPh$_3$-free samples, the initial wave immediately triggered a subsequent thermite reaction characterized by a more intense yet slower propagation phase, attributed to reactions between the outer aluminum and the underlying copper oxide layers. In contrast, in samples containing PPh$_3$, an intermediate combustion phase emerged prior to the main thermite reaction, involving the decomposition of PPh$_3$, and its associated reactions.

Burn rate measurements revealed that incorporating Al@PPh$_3$ significantly reduced combustion speed for both initial convective burning and later diffusive-controlled thermite combustion. For the main thermite combustion stage, a five-layer 50% Al@PPh$_3$ mesh burned at 45 mm/s, compared to 298 mm/s for its uncoated counterpart. Reaction sustainability was influenced by layering and Al@PPh$_3$ content, as single-layer 50% Al@PPh$_3$ nanothermite failed to sustain combustion, while the five-layer version successfully propagated due to the larger heat generation. At 100% Al@PPh$_3$, combustion was entirely suppressed. Notably, the peak pressure generated by the reacting nanothermite meshes in the confined channel was higher with the presence of PPh$_3$. These findings underscore the trade-off between improved aluminum nanoparticle stability and reduced reactivity, highlighting the need for further optimization to balance thermal management and energetic performance in practical applications.

Acknowledgements

This work is financially supported by National Chung-Shan Institute of Science and Technology and National Science and Technology Council, Taiwan.

References

[1] Cui Y, Zhao S, Tao D, Liang Z, Huang D, Xu Z. (2014). Synthesis of size-controlled and discrete core–shell aluminum nanoparticles with a wet chemical process. Materials Letters 121: 54.

[2] Lu XR, Cheng YS, Huang CW, Wu MH. (2025). Influence of triphenylphosphine-coated aluminum nanoparticles on the reactions of Al/CuO nanothermites. 15th Asia-Pacific Conference on Combustion. 18-22 May 2025, Singapore.

[3] Chiang YC, Wu MH. (2017). Assembly and reaction characterization of a novel thermite consisting aluminum nanoparticles and CuO nanowires. Proceedings of the Combustion Institute 36: 4201.

[4] Kabra S, Gharde S, Gore PM, Jain S, Khire VH, Kandasubramanian B (2020), Recent trends in nanothermites: fabrication, characteristics, and applications, Nano Express 1, 032001.

[5] Son SF, Asay BW, Foley TJ, Yetter RA, Wu MH, Risha GA. (2007). Combustion of nanoscale Al/MoO3 thermite in microchannels, Journal of Propulsion and Power 23: 715.