Reaction Propagations of Al/CuO Nanothermite Layers Assembled on Copper Grids

Wan-Lien Hsu and Ming-Hsun Wu
Department of Mechanical Engineering, National Cheng Kung University
Tainan, Taiwan

1 Introduction

Nanothermites are metastable inter-molecular composites (MIC) composed of a reactive metal as the fuel and a less reactive metal oxide as the oxidant. Compared with micro-size aluminium powder, the specific surface-to-volume ratio of nano-size powder is largely increased, and the diffusion distance between fuel and oxidant is reduced, thereby decreasing the ignition delay and enhancing the reaction propagation rate [1,2]. Weismiller et al. [3] showed the influences of particle sizes on the ignition delay time and burning velocity of thermites. The reduction of particle size will enhance the combustion rate and shorten the ignition delay time. However, as the particle size is reduced to a certain size, heat release from the active content in the particle becomes insufficient, leading to slower reaction. The fast burning energetic materials featuring high gas generation rate can be utilized for propulsion, actuation, explosives, and pyrotechnics. Aluminum and copper oxide are one of the common combinations for these purposes.

Nanothermite is typically prepared by physically mixing of fuel and oxidant nanoparticles dispersed in a solution using ultrasonication [4]. It can also be assembled with various methods including arrested reactive milling [5], self-assembly [6], electrophoretic deposition [7], and vapor deposition [8]. A novel method based on electrophoretic deposition for assembling Al/CuO nanothermite on copper wire grown on a copper wire was successfully developed in our previous study [9]. Copper oxide nanowires was first grown on a copper wire through thermal oxidation, and then the wire was submerged in the dispersion containing aluminium nano powder. Since aluminium nanoparticles carries positive surface charge in the ethanol/water solution, they will be driven into the CuO nanowire cluster and form an interweaved Al/CuO thermite layer as electric field is applied across the wall and the copper wire in the middle of the container. Yin et al. [10] found faster and more violent burning with copper oxide nanorods as the oxidizer in the Al/CuO nanothermite prepared by the electrophoretic deposition method. It is interesting to note that the nanorod is geometrically similar to the copper oxide nanowires in our previous work.

Compared with the original electrophoretic deposition method, which deposit both fuel and oxidizer nanoparticles dispersed in the solution through electrophoresis at the same time, our method has more flexibility on tuning thermite properties such as stoichiometry and packing density, which are key factors determining the burning characteristics. It has been proven that the burning rate can be adjusted by changing the electrophoresis voltage, deposition time, and aluminum powder particle size [11]. Very

Correspondence to: author@email.address.here

thin copper wire, typically with diameter on the order of tens of microns, is preferred for the method to minimize the remaining copper core after thermal oxidation. The copper core is not combustible and reduce the reaction propagation speed of the outer thermite layer due to the extra heat loss and thermal capacity. Its existence is nonetheless necessary because it serves as negative electrode during electrophoretic deposition. It was also very difficult to handle a copper wire less than 50 μm in the fabrication process since the wire after oxidation is too fragile. To address the dilemma, we replace the wire with copper mesh as the starting substrate in the present work. With the interlaced wires, the working substrate is much stronger and easier to handle; thinner wire with less remaining copper core can also possibly be used.

Therefore, the purpose of this paper is to validate the feasibility of using copper mesh as the substrate for growing copper oxide nanowires on the mesh wire surface, and subsequently for nanothermite assembly through electrophoretic deposition. Burn rate measurements in ambient atmosphere were also carried out using high-speed camera to validate the feasibility of nanothermite assembly using the substrate. Commercial copper grids with sizes of 100, 150, 200 and 250-mesh were tested to study the influence of mesh size of the copper substrate on combustion characteristics. Overall equivalence ratio of the thermite layer was controlled at near stoichiometric.

2 Nanothermite Assembly on Copper Grid

The preparation of nanothermites on a copper mesh is similar to the approach documented in Ref. [9]. The process began with the growth of copper oxide nanowires on copper meshes, and then deposition of nano aluminum particles on the copper mesh through electrophoretic deposition was carried out. Commercial copper meshes were utilized in the present work. Measurements using SEM were carried out to obtain actual wire diameters and spacings between wires. Actual dimensions for the 100, 150, 200 and 250-mesh copper nets are outlined in Table 1. The measured spacing values were within 5 μm of the mesh designation values. The commercial copper mesh roll (1 m wide) was cut into strips of 1 cm wide and 8 cm long for subsequent processes and burn test.

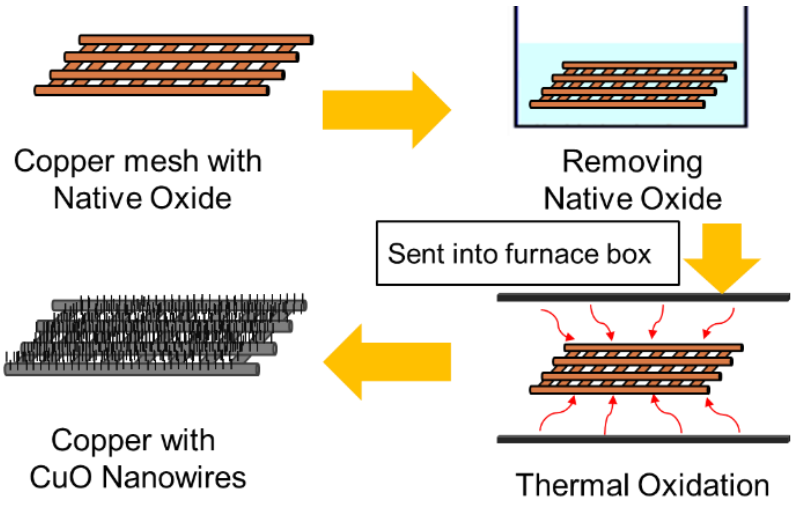

Figure 1: The thermal oxidation process for fabricating CuO nanowires on a copper mesh.

Figure 1 shows the procedure of CuO nanowire growth on a copper mesh through thermal oxidation. First, soak the mesh in 35 wt.% HCl for 1 minute to remove native oxide layer and surface impurities,

then rinse with deionized water and clean in an ultrasonicator for 2 minutes. After completing the pre-cleaning, the copper mesh is placed in a high-temperature box furnace (F-11-28, Tender) for thermal oxidation. It is worth noting that fresh air should be continuously introduced into the furnace during the thermal oxidation process, otherwise, uniform nanowire cluster cannot be obtained. The temperature was raised from room temperature to 550 ℃ at a rate of 25 ℃/min and maintained constant temperature for 2 hours. Finally, the mesh was left in the furnace to be naturally cooled to room temperature. The thermal oxidation results are shown in Fig. 2. Nanowires uniformly blanket the surface of the mesh wires in all four copper grids. Cross-sectional view of SEM images and EDS results confirmed that similar to oxidation of a single copper wire, each oxidized mesh wire consists of a copper core, thick cupric oxide shell layer, thin copper oxide shell layer, and copper oxide nanowires on top.

Table 1: Dimensions of the copper meshes in the present study.

Mesh Size	Line Width (μm)	Line Spacing (μm)
100	95.9	147.5
150	59.6	103.2
200	51.5	74.6
250	31.2	54.5

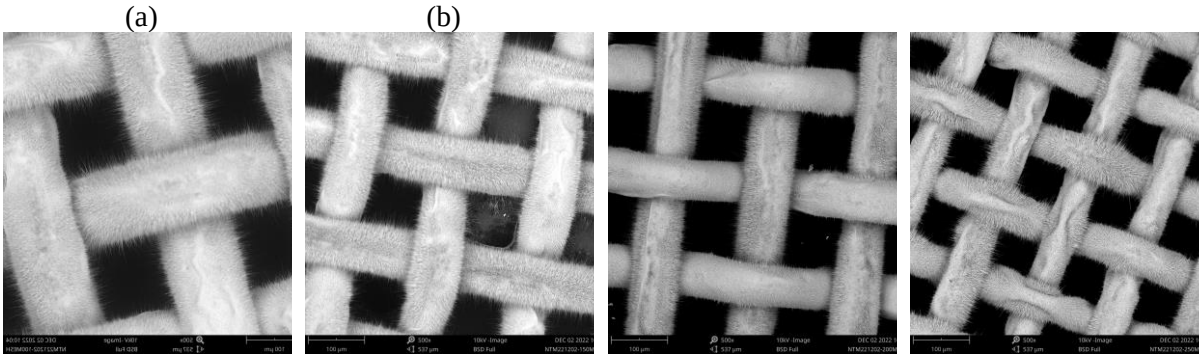

Figure 2: SEM images of (a) 100, (b) 150, (c) 200, and (d) 250-mesh copper grid after thermal oxidation.

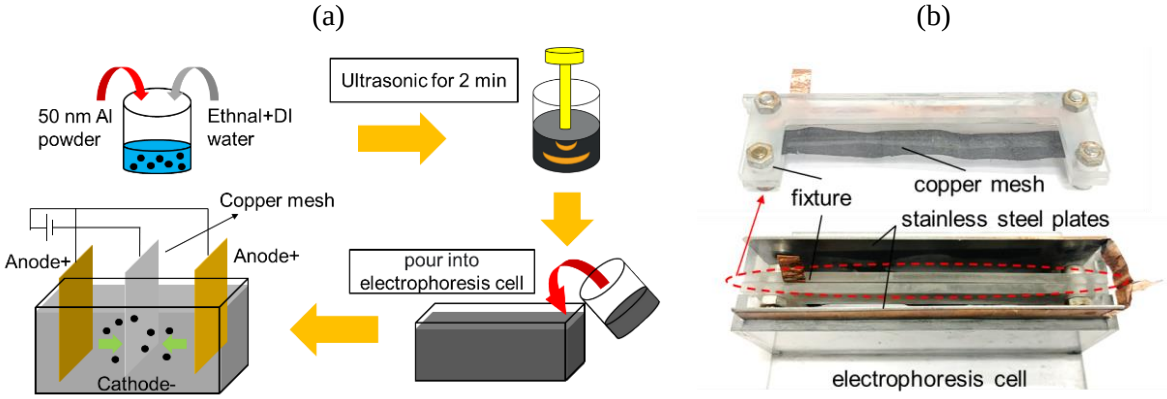

Figure 3: (a) Process of electrophoretic deposition of aluminium nano particles on copper mesh with CuO nanowires on the mehs wires, (b) Apparatus for electrophoretic deposition of aluminium nanoparticles onto copper mesh.

The process of depositing aluminium nano particles on a copper grids by electrophoresis is illustrated in Fig. 3(a). Aluminum powder with nominal diameter of 50 nm (99.9%, Bojun Co., Ltd.) was dispersed in ethanol aqueous solution at a concentration of 3 mg/mL. The mixture was ultrasonicated to enhance uniform dispersion of nanoparticles in the solution. Finally, the colloid was poured into the electrophoresis cell, in which electrophoretic deposition of aluminium nanoparticles were carried out. Aaluminum particles at nanoscale can react with oxygen in ambient environment easily, and form native oxide layer of 2-5 nm on the surface. So, the powder was stored in a nitrogen purged glove box to prevent oxidation before being used. The apparatus for electrophoretic deposition is shown in Fig. 3(b). There was a detachable fixture holding the 8 cm × 1 cm copper mesh. The fixture was clung to the walls of the short ends of the rectangular cell. Negative pole of the power supply was connected to the copper grid, while positive pole was connected to the opposing stainless-steel plates, on longitudinal side walls, which were the positive electrodes during electrophoresis. Electrophoretic deposition duration can be precisely controlled at 1/100 sec increment by a timer relay regulating the output of the power supply. The voltage applied for electrophoretic deposition was 60 V.

3 Influence of Mesh Size on Reaction Propagation

Deposited weight of the aluminium nanoparticles was an essential parameter for estimating the stoichiometry of the thermite layer. Consequently, experiments were carried out to determine the relationship between deposition weight and electrophoresis duration for the four meshes. More particles were deposited on a denser mesh within the same duration due to the large surface area. Deposited weight increases with the duration of the applied voltage. The correlations between deposition mass and duration are linear with shorter deposition duration (< 3 min), but the increase rate gradually slows down as the electrophoresis time increases. The trend can be explained by the reduction of aluminium particles concentration in the colloid as time goes on.

Due to the existence of native oxide layer on the surface of an aluminium nanoparticle, not all weight deposited on the wire is able to contribute to the thermite reaction. The thickness of native oxide layer does not strongly depend on the particles size, so the proportion of reactive aluminum in a nanoparticle decreases with particle diameter. The percentage of active content (C_{act}) of aluminum powder was experimentally determined by thermogravimetric analysis (TGA) in the present study to estimate the weight of aluminum in the thermite layer. The aluminium powder was heated from room temperature to 1400 ℃ at a rate of 10 ℃/min in air purged at 100 cc/min throughout the process. The thermogravimetric curve of the 50 nm aluminum powder shows that most of the weight gain occurred at around 600 ℃, which is lower than the melting point (660 ℃) of bulk aluminum. In order to calculate C_{act} of aluminum powder, it is assumed that the weight gain results from complete oxidation of aluminum into aluminum oxide (Al_2O_3). It was estimated that the active content in the aluminium particles was 76.5 % based on the experimental data.

Specimens with overall equivalence ratio around 1 were fabricated on the copper grids to reveal the influence of mesh size on the burn rate of thermite mesh. The amount of copper oxides formed on the copper wire was derived by weighting the wire before and after thermal oxidation. Overall stoichiometry of the thermite layer was controlled by adjusting the electrophoretic deposition duration using the empirical correlation along with the estimated value of active content. Oxides shells underlying the interweaved layer of copper oxide nanowire and aluminium nanoparticle were also taking into consideration in the stoichiometry assessment since the oxides can participate in the redox reaction.

For the burn test, the thermite mesh strip was suspended on a holder at top end, and ignited using an electric arc at the bottom end. The reaction propagation was recorded by a color high-speed camera (MiroLab 310, Vision Research) with the exposure set at 10 μs and the frame rate at 10,000 fps. The burn rate is derived by measuring the distance traveled by the reaction front along the strip in a fixed amount of time. Propagations of combustion waves along 100, 150, 200, and 250-mesh thermite strips were shown in Figs. 4. The combustion wave propagating along the 250-mesh thermite strip was the the

most intense. The reaction wave observed on the 100-mesh copper grid was relatively weak, and the grid structure remained almost intact after combustion. In contrast, no grid structure was left for the 250-mesh strip, only tiny condensed spheres were found after the test.

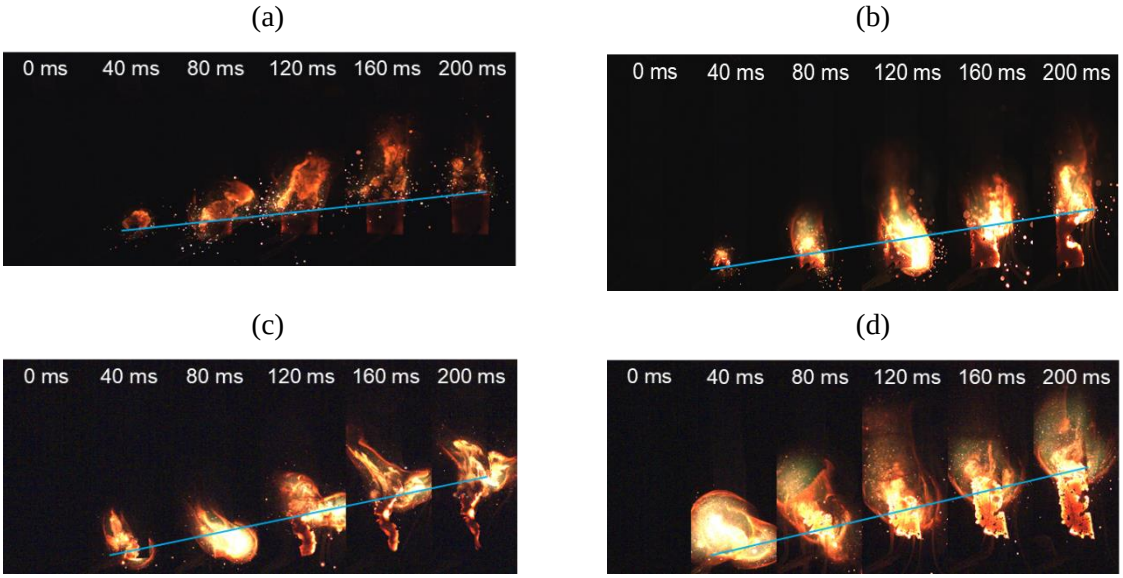

Figure 4: Combustion wave propagation along (a) 100, (b) 150, (c) 200, and (d) 250 -mesh thermite strip.

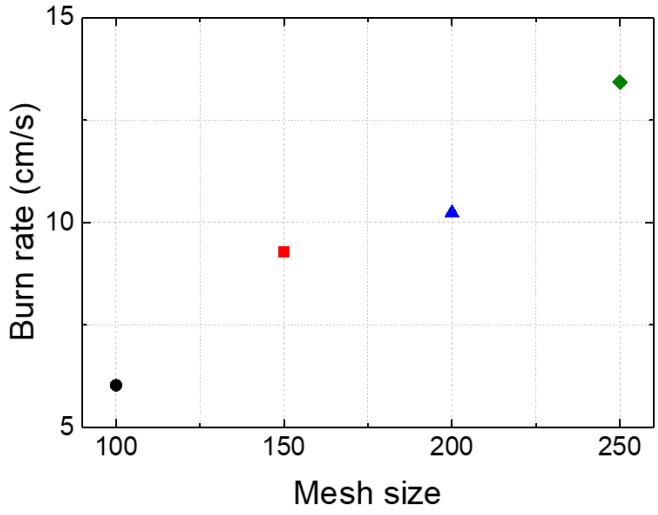

Figure 5: Dependence of burn rate on mesh size of the thermite strip

Figure 5 shows that the burn rate linearly increases with mesh size. The burn rate along the 250-mesh thermite strip was 13.4 cm/s, and the propagation velocity of the reaction wave was half at 6 cm/s for 100-mesh grid. A denser mesh carries larger amount of thermite per unit area, which results in stronger reaction wave. The thinner wire in a denser mesh further reduce the inactive copper core to enhance the reaction propagation speed.

4 Conclusions

Al/CuO nanothermite was assembled on copper grids of 100, 150, 200 and 250 -mesh by depositing aluminium nanoparticles into CuO nanowire cluster on the mesh wire surface. Self-sustained reaction propagation along the thermite mesh strip was achieved for all four mesh sizes, demonstrating the feasibility of the approach. Through the burn tests, it was found that with larger copper mesh number, reaction propagation rate along the mesh strip became fater, and the combustion wave was more violent. The results were due to the increase of reactive Al/CuO nanothermite per unit area and the reduction of unreative copper core in a denser mesh. Analysis on the high-speed images shows that the burn rate increases linearly with mesh size.

4 Acknowledgements

Financial supports from Ministry of Science and Technology, Taiwan under grants MOST 110-2221-E-006-091-MY2 are gratefully acknowledged.

References

[1] E.L. Dreizin, Prog. Energy Combust. Sci. 35 (2) (2009) 141-167.

[2] D.G. Piercey, T.M. Klapotke, Central European Journal of Energetic Materials 7 (2) (2010) 115-129.

[3] M.R. Weismiller, J.Y. Malchi, J.G. Lee, R.A. Yetter, T.J. Foley, Proc. Combust. Inst. 33 (2011) 1989–1996.

[4] S. Son, T. Foley, R. Yetter, M. Wu, G. Risha, J. Propul. Power 23 (4) (2007) 715-721.

[5] A. Ermoline, D. Stamatis, E. Dreizin, Thermochimica Acta 527 (2012) 52-58.

[6] K. Zhang, C. Rossi, M. Petrantoni, N. Mauran, J. Microelectromechanical Sys. 17 (4) (2008) 832-836.

[7] K. Sullivan, J. Kuntz, A. Gash, J. Applied Physics 112 (2012) 024316.

[8] K. Zhang, C. Rossi, M. Petrantoni, N. Mauran, J. Microelectromechanical Sys. 17 (4) (2008) 832-836.

[9] Y.-C. Chiang, M.-H Wu, Proc. Combust. Inst. 36 (3) (2017) 4201-4208.

[10] Y. Yin, X. Li, Vacuum 163 (2019) 216-223.

[11] Y.-C. Chiang, M.Sc. Thesis, National Cheng Kung University, Taiwan, 2017.